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The Photo-Conductivity of Lead Chromate

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The variation of the photo-conductivity of lead chromate with wave-length of the exciting radiation is described. The conductivity referred to unit intensity of the incident radiation is a maximum in the blue corresponding to a value of 5×10^{-3} amp./watt at saturation. Subsidiary maxima occur in the red and the near ultraviolet. These results are in conflict with that of previous investigations. Data on the spectral scattering of lead chromate are also presented. The dependence of photo-conductivity on time, electric field, and previous history of the specimen are illustrated. On the basis of unit quantum efficiency, the mean displacement distance of photoelectrons in lead chromate is found to be 3×10^{-3} cm. Various alternative explanations of the observed behavior are discussed.

INTRODUCTION

MANY crystalline substances are affected by radiation lying in the visible or near ultraviolet portion of the spectrum. Thus, copper oxide, selenium, and properly prepared specimens of zinc sulphide become conducting when exposed to radiations of suitable wave-lengths, whereas the silver and thalium halides darken under similar exposure. Undoubtedly the most extensive experimental investigations of the sensitivity of solids to light are those conducted by Pohl[1] and his collaborators on the alkali halides containing a stoichiometric excess of alkali metal atoms, and those conducted by various investigators[2] on the blackening of silver bromide. The development of the theory of solids during the last decade has brought with it a fairly complete interpretation of the photosensitivity of these materials and suggests that similar interpretive work may be possible in many other cases that are of practical as well as scientific interest.

One of the most interesting cases of this type centers about the darkening of lead chromate, which forms the basis of the chrome yellow pigments. Depending upon the manner of preparation, this material exhibits varying degrees of darkening when exposed to ordinary sunlight. Since this substance appears to offer a number of interesting complexities not found in the materials studied hitherto, it was decided that it should be made the subject of extensive investigations designed to reveal the source of the light sensitivity.

The present paper deals with the light absorption and the photo-conductivity of lead chromate in the visible and very near ultraviolet region of the spectrum. Subsequent papers will deal with both thermal and optical darkening of the material and with the factors that influence its conductivity when not exposed to light. As will be seen in these subsequent papers, this work permits a reasonable and unambiguous interpretation of the mechanism of darkening by light.

METHOD

Difficulty in obtaining large single crystals of lead chromate necessitates the use of the powdered pigment. The commercial preparation is found to be a relatively poor photo-conductor. It is consequently necessary to study specially purified lead chromate. The samples are composed of fine needles about 0.45 micron in diameter. The preparation of satisfactory specimens is complicated by the fact that lead chromate is insoluble in all the usual solvents except metal hydroxides and cannot be melted without suffering marked structural changes. The obvious solution of this difficulty would seem to be, at first thought, to obtain specimens in the form of pressed pellets. This type of specimen, however, does not prove satisfactory because of the difficulty of preparing pressed pellets which are sufficiently dry. In such

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[1] See the survey article by R. W. Pohl, Physik. Zeits. **39**, 36 (1938).

[2] A short résumé of this work appears in Chapter XVII of *Modern Theory of Solids* by F. Seitz (McGraw-Hill, New York, 1940); see also a survey article by J. H. Webb, J. App. Phys. **11**, 19 (1940); Mott and Gurney, *Electronic Processes in Ionic Crystals* (Oxford, London, 1940).

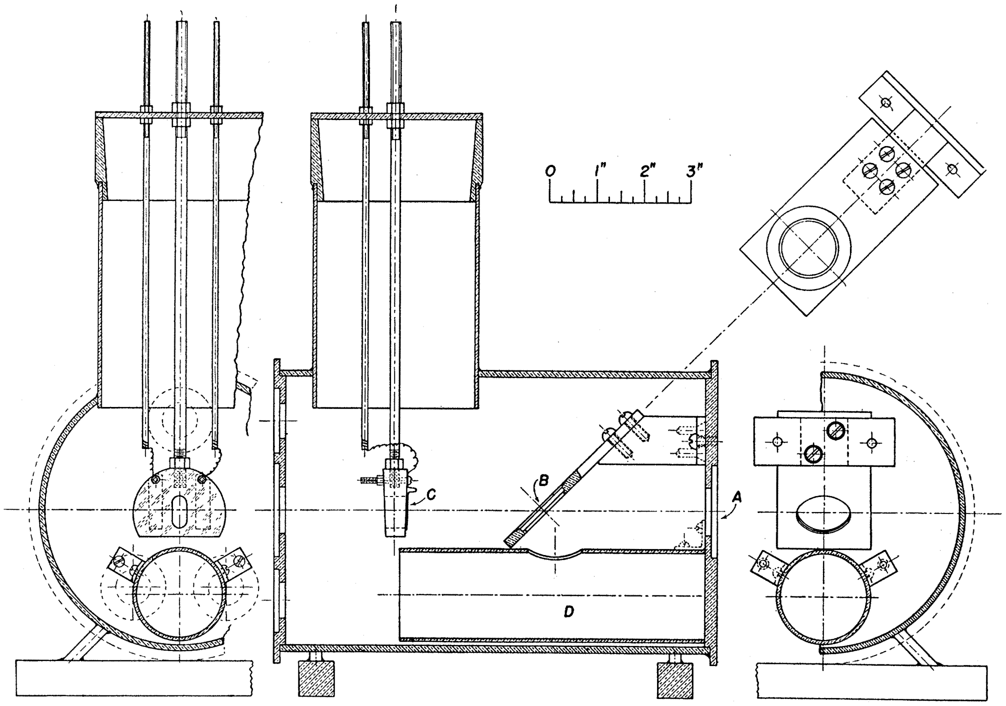

FIG. 1. Vacuum mount for specimen and photo-cell. In the center is shown a side view of the chamber. The beam of light enters through the quartz window *A*. Most of it is transmitted through the inclined quartz plate *B* and falls upon the specimen mounted on the leucite block *C*. The remaining light is reflected by the plate onto the photo-cell at *D*.

pellets, the dark currents arising from the moisture absorbed during pressing are sufficient to mask the smaller photo-currents. It is found necessary, therefore, to prepare specimens in such a way that the initially dried powder is not subsequently exposed to the slightest trace of water vapor. This is accomplished by drying the powder in a cell constructed from microscope slides. One slide contains a hole $\frac{3}{4}''$ in diameter and rests on top of another, thus forming a shallow disk-like container into which the loose powder is tamped. The cell and pigment are then baked in a furnace at 100°C for 24 hours. While the cell is still hot, a third slide is placed on the other two and the combined cell is sealed tightly with ceresin wax. The cover slide is of Corex D glass on which are evaporated suitable aluminum electrodes. The cell is supported against a leucite block by means of phosphor bronze clips which also serve to make electrical contact with the electrodes. The leucite block is then suspended in a vacuum chamber in such a manner that the specimen intercepts a beam of light admitted to the chamber by a quartz window. The aluminum electrodes are arranged to expose to the light a rectangular aperture 2 cm × 2 mm.

The light source consists of a water-cooled, high pressure mercury arc designated by the General Electric Company as type H-6. The luminous flux of the lamp is focused by a quartz lens onto a slit placed in front of a concave metal grating conjugate to the plane of the specimen. This grating has a one-meter focal length and the 15,000 lines per inch are ruled to give maximum intensity in the second order. The grating and specimen are on a standard Rowland mounting except that the position of the light source and the specimen are interchanged. This is done in order that the specimen may be illuminated by various wave-lengths with a minimum of electrical disturbance.

The photo-currents are measured by means of a three-stage d.c. amplifier described by Harnwell and Ridenour.[3] The first stage is an electrometer

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[3] G. P. Harnwell and L. N. Ridenour, Rev. Sci. Inst. **11**, 346 (1940).

tube mounted in an evacuated chamber to reduce the humidity about the input resistance. The vacuum chamber is made of steel ½″ thick to serve as a magnetic and electric shield. The overall sensitivity is 2×10^{-17} amp./mm. A PJ-22 vacuum photo-cell and amplifier circuit is used to monitor the intensity of the incident light. The photo-cell is directly beneath a quartz plate inclined at 45 degrees to the incident beam as shown in Fig. 1. The incident light is split into two beams so that 95 percent is transmitted through the window and allowed to fall upon the specimen, and the remaining 5 percent is reflected down to the photo-cell. The amplified photo-cell current and the photo-currents in the specimen are determined simultaneously.

The spectral sensitivity of the photo-cell is determined by comparing the output of the cell with that of a thermopile calibrated in terms of a standard lamp. The calibration of the photo-cell is accomplished by placing the thermopile in the specimen mount in the place normally occupied by the specimen. Thus, the same fraction of light that falls on the specimen in an actual experiment is now incident on the thermopile. The output of the thermopile is determined by a low resistance galvanometer. An optical path of 8 meters is used with the galvanometer to assure an accuracy of 1 percent in the thermopile readings. This calibration is necessary since the spectral sensitivity of the photo-cell may deviate appreciably from the industrial calibration curve furnished by the manufacturer because of aging and temperature effects.

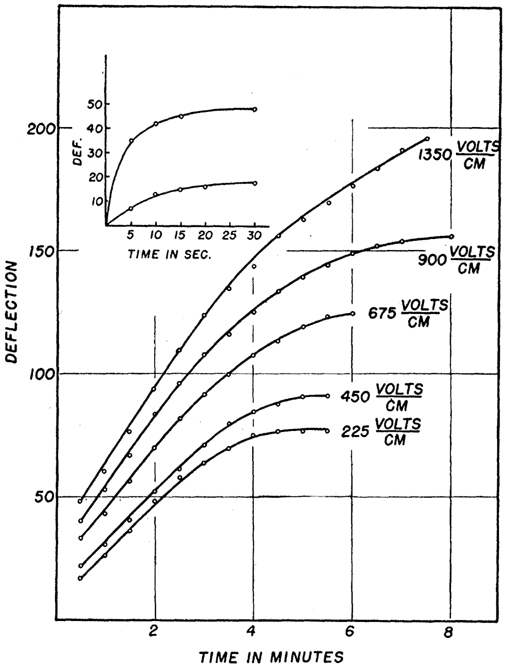

FIG. 3. Dependence of the photo-conductivity upon time in pure powdered lead chromate for various applied fields. The inset gives the first 30-second interval in greater detail for the lowest and highest voltage. 50 scale divisions correspond to a current of 1×10^{-7} amp.

Batteries supply any desired voltage up to 360 volts to the specimen. This corresponds to a field of 1350 volts/cm for the slit width used in these experiments. A potentiometer is used to balance out the dark currents which are of the same order of magnitude as the photo-currents. All batteries are contained in a drying box and shielded. A circuit diagram of the apparatus appears in Fig. 2.

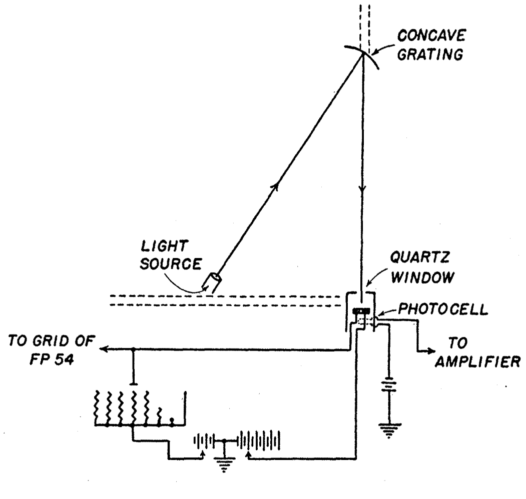

FIG. 2. Circuit diagram of the apparatus for the spectral photo-conductivity measurements.

RESULTS

Preliminary to an investigation of the spectral sensitivity of the photo-conductivity, it is necessary to examine the dependence of photo-conductivity on time of exposure and applied field. This is accomplished by impressing fields ranging from 225 to 1350 volts/cm upon the specimen and noting the resulting photo-conductivity for specified times of illumination. Figure 3 shows the results of this preliminary investigation. The inset shows the first 30-second interval of the

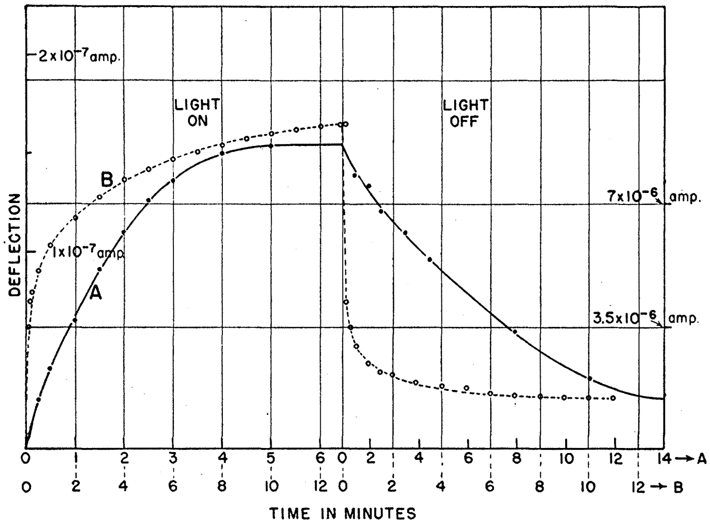

FIG. 4. (A) The rise and decay with time of the photo-currents in pure powdered lead chromate. The magnitude of the photo-current is indicated on the left axis. (B) Onset and decay of the photo-currents in a sintered pellet as a function of time. Current values are here indicated on the axis to the right. Note that the currents in the sintered pellet are a factor of 40 greater than the currents in the powdered sample.

225- and 1350-volt curves in greater detail with the intermediate plots omitted. It should be noted that there is a definite tendency toward saturation after the first 20 seconds of illumination. At the end of this relatively short period, the curve suddenly starts to rise with a sharper slope. The saturation time of this phenomena results from a consideration of the three types of observed photo-currents.[4] The electrons which are freed by the light quanta and make their way unhindered to the anode form what is known as the primary current. Not all the freed electrons, however, reach the anode. A great many of them may be trapped in various types of trapping centers from which they may be reexcited either thermally or optically into the conduction band. Electrons thus excited form a secondary current which is both time and voltage dependent. The curves in the inset of Fig. 3 represent the secondary currents superimposed upon the primary currents. The primary current is instantaneous and independent of the time of illumination. Owing to the finite time constants of the input circuit of the amplifier and the relative sizes of the primary and secondary currents, it is impossible to separate the former from the latter in the case of lead chromate.

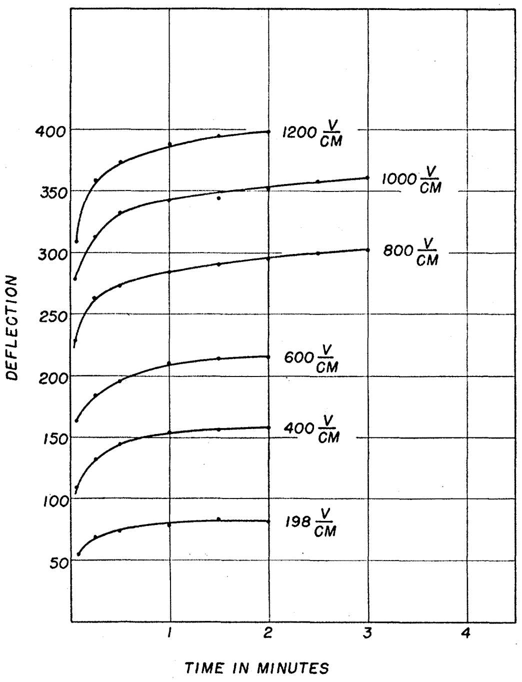

FIG. 5. Time dependence of photo-current for various fields in a sintered pellet. 100 scale divisions correspond to a current of 7×10^{-6} amp. This curve should be compared with the similar curve for powdered samples illustrated in Fig. 3.

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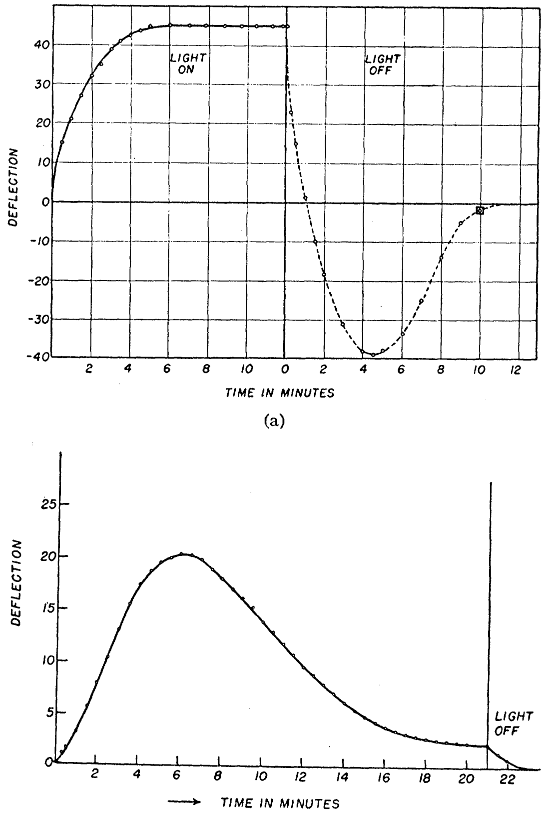
[4] See F. Seitz, *Modern Theory of Solids* (McGraw-Hill, New York, 1940), Chapter XV.

The additional photo-current which rises sharply after the first 30 seconds of illumination may be due to additional electrons which enter the specimen from the cathode and move through it to the anode. This flow is induced by the space charge fields set up in the specimen by the migration of the primary and secondary electrons to the anode.[5] It should be expected that this current, too, would be time and voltage dependent, since the space charge fields are altered in virtue of the secondary photo-current. This explanation is further bolstered by an examination of the build-up and decay of the photo-currents as a function of time for a specified voltage. This dependence is illustrated by curve *A* in Fig. 4.



(a)

(b)

FIG. 6. Time dependence of the photoconductivity of impure lead chromate powders. (a) Shows the onset and decay for a powder which has been internally treated with impurities. It is seen that as the light is turned off there is a surge of current in the opposite direction tending to reduce the net dark current. (b) The same curve for material whose particle surfaces have been coated with impurities. In this case, polarization and grain boundary resistance tends to reduce the photo-current while the light is still on. Scale units are arbitrary.

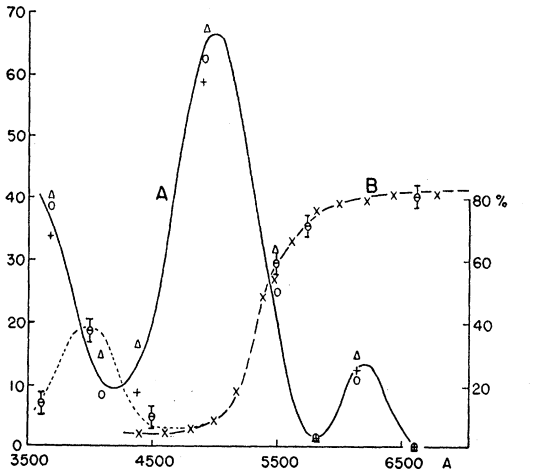


FIG. 7. (A) The spectral dependence of the photo-conductivity of lead chromate. The maximum at 5000A corresponds to a current of 5×10^{-3} amp/watt. (B) The spectral scattering lead chromate. The crosses are points obtained by Luckeish. The barred circles represent the results obtained in this laboratory. The ordinates on the right are the percent of scattered light.

In order to investigate the effect of grain density on the behavior of the photo-conductivity, a similar set of experiments were conducted on pressed pellets of $PbCrO_4$ sintered at 400°C. The density of such a sintered pellet closely approximates that of a single crystal and results from the union of the particles at the grain boundaries. In the case of a crystal the flow of electrons is unimpeded by grain boundaries and is limited only by thermal scattering and trapping. We may expect, therefore, that the current-time dependence of photo-conductivity in the powder will vary somewhat from that in the pellet. To investigate this effect, the photo-currents in the pill were studied as a function of time and voltage, the same as for the powder. The results are shown in Curve *B* of Fig. 4 and in Fig. 5. It is evident from these curves that there is no major difference between the behavior of a sintered pill and the pure powder. In both cases the secondary currents saturate due to the effects of trapping and space charge. The current rise, however, is much more rapid in the case of the sintered pellet. The time required to reach complete saturation varies from specimen and is presumably due to poor contact at the grain boundaries which may cause the flow of electrons

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[5] Reference 4, p. 569.

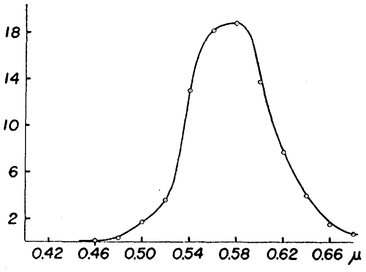

FIG. 8. The spectral reflectivity of lead chromate as viewed by the human eye. The scattering by the powder is multiplied by the spectral eye sensitivity to yield the illustrated curve. Ordinate units are arbitrary.

to cease before all the secondary electrons have been excited. That the resistance between grains is important is demonstrated by comparing the curves in Fig. 4 with similar curves, shown in Fig. 6, for lead chromate whose grains are coated with surface impurities. The most striking effect of the surface coating is the reduction of the photo-currents by a factor of approximately five. Furthermore, the onset and decay of the photo-conductivity varies considerably with the impurity. Both curves exhibit a behavior which can be explained by assuming that the space charge and resulting polarization in these specimens are greater than in the case of the pure material. Thus, for the material illustrated in Fig. 6A, the space charge causes a negative current to flow when the illumination is cut off. In the case illustrated in Fig. 6B, the polarization becomes so great that the secondary currents actually decrease upon continued illumination. Because of the increased resistance at the grain boundaries, the larger space charges in the case of the coated material are not unexpected.

The measurements of the spectral sensitivity of the photo-conductivity of lead chromate were made in much the same manner as the calibration previously described. The results are plotted as Curve *A* in Fig. 7 where the abscissa represents the wave-length of the incident light in angstrom units and the ordinates are the photo-currents referred to unit incident energy by means of corrected photo-cell readings. The peaks in the ultraviolet and the blue correspond to absorption bands observed in solutions of potassium chromate. Since the position of these bands would not be appreciably altered by the lattice, this may be considered as evidence that these bands are associated with the chromate ion. The corresponding photo-conductivity peaks may be interpreted as resulting from the excitation of electrons from the chromate ion from its fundamental bands into the conduction band or again as due to electrons excited from impurity centers by excitation waves produced by the interaction of the light with the chromate ions. It is doubtful, however, whether the peak in the red is also due to fundamental chromate ion absorption. It may possibly be due to absorption centers associated with interstitially placed positive ions or to foreign impurities. Evidence for this is discussed below.

The relative size of the various maxima is of considerable interest. To understand this more fully, it would be necessary to examine the ratio of photo-current to light absorbed rather than incident light. It will be seen that this is of considerable importance in interpreting the added peak in the red. In order, therefore, to obtain a qualitative indication of the shape of the absorption curve and to compare these results with the photo-conductivity data, experiments on the spectral scattering of the material were carried out. A carefully pressed $PbCrO_4$ surface was placed in the specimen mount in the position normally occupied by the inclined quartz plate. Thus the beam of the monochromatic light entering the chamber would be incident upon the

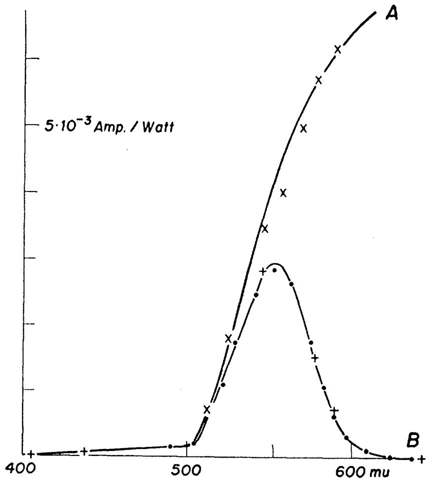

FIG. 9. Kapp's work on the spectral photo-conductivity of lead chromate. *A* represents the photo-conductivity referred to unit absorbed light whereas *B* is referred to unit incident light.

chromate surface at an angle of 45 degrees. The photo-cell then measures the light that is scattered down to it by the inclined surface. The data are referred to the same beam of light scattered from a perfectly white surface placed in an identical position. The curve resulting appears in *B*, Fig. 7 and is compared to a curve obtained by Luckiesh[6] in similar investigations on chrome yellow. It should be noted that there is a well-defined maximum in the neighborhood of 4000A. This maximum in scattering corresponds to the observed minimum of photo-conductivity in that region. The relatively high scattering in the red is probably associated with the fact that in this region the particle size approaches the order of magnitude of the wave-length of the incident light.

The scattering curve shows that the maximum scattering by lead chromate occurs in the red region of the spectrum. The yellow appearance of $PbCrO_4$ results from the spectral sensitivity of the eye. Thus the product of the scattering and the eye sensitivity is plotted in Fig. 8. This curve has a minimum in the yellow as expected.

On comparing the spectral photo-conductivity with the spectral scattering, it becomes evident that if we refer the relative photo-conductivity to the absorbed rather than the incident light, the height of the maximum in the red will be increased relative to the respective peaks in the blue and the ultraviolet. When the efficiency is calculated on this basis, the maxima in the red and the blue are more nearly equal. Assuming a 100 percent quantum conversion efficiency for the blue line, one may now calculate the mean displacement distance of the electrons. If I is the intensity of the absorbed radiation per unit distance between electrodes, the measured current i should be

$$i = \eta I e \omega / h\nu,$$

where $h\nu$ is the energy of the absorbed light quanta and ω is the mean displacement distance. η is the fraction of absorbed light quanta that free electrons, i.e., quantum efficiency.[7] The value of I is determined experimentally by comparing the thermopile deflection due to the blue line to that of a standard luminous source. It turns out to be of the order of 1.45 ergs/cm/sec. The mean path calculated on this basis turns out to be approximately 3×10^{-3} cm.

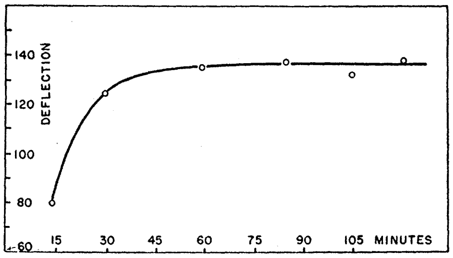

FIG. 10. Photo-conductivity in the red plotted as a function of time of illumination with ultraviolet light.

It is interesting to compare this datum with the only other available datum on the photo-conductivity of lead chromate. The spectral photo-conductivity of single crystals of $PbCrO_4$ found by Kapp[8] is reproduced in Fig. 9. Referring conductivity to incident light intensity, Kapp finds a sharp maximum of photo-conductivity in the yellow which tapers off at greater wave-lengths until it finally approaches zero. This is in apparent contradiction to the results obtained in this laboratory. Although Kapp finds only one maximum, the authors find three. Moreover, Kapp finds the photo-conductivity rising sharply in precisely the same region that the writers find the curve approaching a minimum. The fact that Kapp worked with natural single crystals would seem to offer a possible explanation of this apparent contradiction. It is quite possible that natural single crystals contain sufficient impurities to mask the natural photo-conductivity of pure lead chromate.

The results of one further experiment indicate the possible explanation of the photo-conductivity in the red. A sample was alternately illuminated with ultraviolet light from a Hanovia lamp and with red light. The photo-conductivity in the red as a function of time of illumination with ultraviolet light was studied. These results appear in Fig. 10. It is seen that the red photo-current increases with time of illumination with ultraviolet. This experiment may be explained as follows. The illumination with ultraviolet light may free electrons from bound levels. Many of these freed electrons can now be trapped in higher empty levels presumably arising from impurities. These

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[6] M. Luckiesh, J. Frank. Inst. **184**, 73 (1917).

[7] A detailed discussion appears in Seitz, reference 4, p. 565.

[8] G. Kapp, Ann. d. Physik **22**, 257 (1935).

trapped electrons can now be nearer the conduction band and may be excited to it by light of lower energy. As the exposure to ultraviolet light in increased, more electrons will be trapped in the higher impurity levels, and the photoconductivity in the red will increase. This increase will finally saturate when equilibrium is achieved between the number of electrons excited from the impurity levels into the conduction band and the number of electrons being retrapped.

It is the hope of the authors that the results of this investigation will be of material assistance in interpreting the spectral darkening of lead chromate which is now being studied by us in collaboration with A. H. Smith. The results of the latter investigation will be available shortly. A theoretical interpretation of the results of both these experiments will be presented by Dr. Frederick Seitz who initiated this program of research and whose active interest throughout the investigation was largely responsible for its completion.

In conclusion, the authors desire to express their indebtedness to the Krebs Pigments Department of the E. I. duPont de Nemours and Company for financial assistance in the form of a fellowship for one of us (J. E. G.) and for a plentiful supply of carefully prepared lead chromate, and to M. L. E. Chwalow who took an active part in the initial phases of the investigation.

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Intensity Anomalies and Perturbations in the CN Bands

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The rotational structures of the 0,0 violet and the 9,4 red CN bands, developed by $CHCl_3$ in active nitrogen, are measured on plates from the first and second orders of a 30-ft. grating. The rotational constants of the $b^2\Sigma, v=0$ and the $a^2\Sigma, v=4$ states are in good agreement with the previously published values; those for the $v=9^2\Pi$ state are $B'_9=1.5312\pm0.0008$ cm^{-1}, $D'_9=7.408\pm0.002\times10^{-6}$ cm^{-1}. The Λ-doubling in this state, except for four perturbations, can be represented by use of the constants $p_0=+0.01597$ and $q_0=-0.00080$. The value $\gamma'=+0.021$ is determined for the spin doubling in the $b^2\Sigma, v=0$ state. Four perturbations are found at $K=4$, 7, 11, and 15 for $b^2\Sigma$; extra P and R lines separated from the main lines by $\Delta\nu=-0.352$ cm^{-1}, $+0.938$ cm^{-1}, $+1.177$ cm^{-1}, and $+1.212$ cm^{-1}, respectively, appear in both the 0,0 and 0,1 bands of the violet system. In the red system, shifts of the right amount and direction in the lines $Q_1[3\frac{1}{2}]$, $R_1[7\frac{1}{2}]$, $P_1[7\frac{1}{2}]$, $R_2[10\frac{1}{2}]$, $P_2[10\frac{1}{2}]$, and $Q_2[15\frac{1}{2}]$ confirm the assumption that rotational levels of $^2\Pi, v=9$, perturb those of $b^2\Sigma, v=0$, and that the perturbations occur for the K and J values indicated. (Brackets denote upper state J.) The values of the perturbation matrix elements are obtained for the various levels. Some anomalies of the R branch band lines in the range 23–29 of K' values in the 0,0 violet band are mentioned.

The mechanism responsible for the enhancements of the main and extra lines of the 0,0 violet band is discussed. Collisions involving interstate transfer ($^2\Pi\rightarrow a^2\Sigma$) evidently occur, or are enhanced, at each perturbed level; and rapid redistribution of molecules among rotational levels by collisions must also occur. Where spin doublets are resolvable in the violet bands, rotational redistribution occurs without change of spin direction.

INTRODUCTION

Historical

IN 1928, G. Herzberg[1] reported that certain lines are enhanced in the emission of bands of the violet cyanogen system coming from the level $b^2\Sigma$, $v=0$, when excited by active nitrogen. The photographs were taken with a low dispersion instrument. Herzberg proposed fluorescence or collisions of the second kind as a tentative explanation. H. T. Byck,[2] in 1929, confirmed the experimental results; however, he found no evidence for a mechanism related to fluorescence, and therefore restricted the explanation to collisions of the second kind.

M. Fred, in 1932, photographed the above bands in the first order of a 21-ft. grating in this

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* Now at Birmingham-Southern College, Birmingham, Alabama.

[1] G. Herzberg, Zeits. f. Physik **49**, 512 (1928).

[2] H. T. Byck, Phys. Rev. **34**, 453 (1929).