ACTINO-ELECTRIC EFFECTS IN ARGENTITE

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Abstract

Actino-electric effects are observed in argentite and it is shown that the *seat of conversion of light into electronic energy* occurs both at the contacts as well as at certain spots on the crystal. The effect is found to be absent if the crystal structure is destroyed. The actino-electric current-intensity curves show a peculiar secondary effect at certain intensities. On investigation of the actino-electric e.m.f.'s with reference to varying times of exposure and constant times of recovery it is found that an exponential relation exists between them which can be represented by $i=Ae^{-at}$. The a, however, is not a constant but increases with time of recovery and is the determining factor in the dark current and photoelectric hysteresis of the crystal. It may be very intimately connected with the positive part of the primary photoelectric current as described by Gudden and Pohl.

IN STUDYING the mechanism of photoelectric action in crystals it has been necessary in most cases to apply large potential differences to the ends of the crystal in order to make the photoelectric currents large enough to be measurable. This has, in many cases, introduced spurious and secondary effects which were difficult to measure or even to recognize. Since, however, molybdenite,[1] cuprite, argentite[2] and a few other crystals give measurable photoelectric currents, even when no potential difference is applied, it seemed worthwhile, in virtue of the fact that there would be one less spurious and unwanted effect present, to attempt a few investigations into the mechanism of photoelectric action in crystals by making use of this actino-electric effect.

Before it becomes possible to explain the mechanism of the production of photo-e.m.f.'s in crystals, it is necessary to determine exactly where the conversion of light energy into electronic energy occurs. There are two contradictory opinions as to the source or origin of the photo-electrons. Coblentz[1] working mainly with molybdenite shows that the seat of actino-electric action is at certain points or loci along the crystal surfaces, separated by as little as 0.1 mm, and not at the contacts of crystal with conductor. Geiger[3] finds just the opposite to be true in the case of argentite, no effect being observable when the contacts are shielded from light, and only when one contact is illuminated are the currents large enough to be measurable.

The procedure reported here, as applied to argentite, was similar to that used by Coblentz and consisted in moving an illuminated slit before the crystal. The galvanometer used was an ordinary high sensitivity L. & N. galvanometer which had a sensitivity of about 10,000 megohms. The crystals

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[1] W. W. Coblentz, Scientific Papers of Bur. of Stds. No. 486, April 1924.

[2] H. H. Sheldon and P. Geiger, National Acad. Sc. Proc. **8**, 161 (1922).

[3] P. H. Geiger, Phys. Rev. **22**, 461 (1923).

exposed to the light were chosen largely from samples obtained from Saxony and Mexico, since it was found that these crystals gave larger deflections of the galvanometer. The samples were about 1 or 2 cm long and of varying thicknesses. Since argentite when found naturally does not form very large crystals, these samples were all in the form of aggregates of very small crystals. Contacts with the crystal were made by winding very thin and carefully cleaned copper wire around the crystal as near to the ends as possible, and then the two free ends of the copper were connected in series with a galvanometer. The word crystal as used here applies not to a single crystal but to the whole aggregate sample.

The usual precautions were taken to eliminate spurious deflections of the galvanometer and the light passed through a continuous-flow water-cell. A gas-filled, 400-watt, tungsten lamp was used for a light source.

Many different samples were tried. The results with two such crystals of argentite are shown in Figs. 1, 2, 3. In Fig. 1 are presented two curves obtained when a crystal (Sample K) was illuminated in regions of width 2 mm and 0.25 mm respectively all along one face of the crystal. The two curves are similar except for height. Diminishing the slit width and consequently the total amount of light falling on the crystal decreases the effect. It is evident from these two curves that around the contacts, which were located at crystal settings of 3 and 13.5 mm approximately, the effects in this sample are extremely large. The contacts were not covered so that they could be illuminated the same as the remainder of the crystal. These effects are not the ordinary thermo-electric effects which act slowly giving continuously increasing deflections as the temperature of the junction

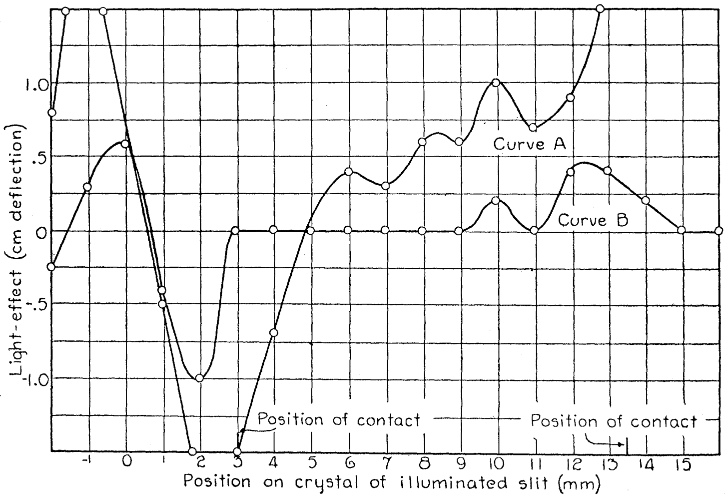

Fig. 1. Actino-electric response curves when an illuminated slit is moved along the crystal. Curve A is for a slit width of 2 mm. Curve B for 0.25 mm. slit width. The contacts were not covered and could be illuminated.

increases. The deflections produced are instantaneous (i.e., within the period of the galvanometer) and remain constant over fairly long periods. In practice it is actually quite easy to distinguish the thermal from the actino-electric effect. In Fig. 1 it will be seen that at the left contact the actino-electric e.m.f. actually reverses itself for slight displacement of the region of illumination. Contact actino-electric effects are therefore present as well as slight body effects around a crystal setting of 10. These body effects are more certainly verified by the curves represented in Fig. 2 and Fig. 3. In both cases the contacts were covered and shielded so that no light could

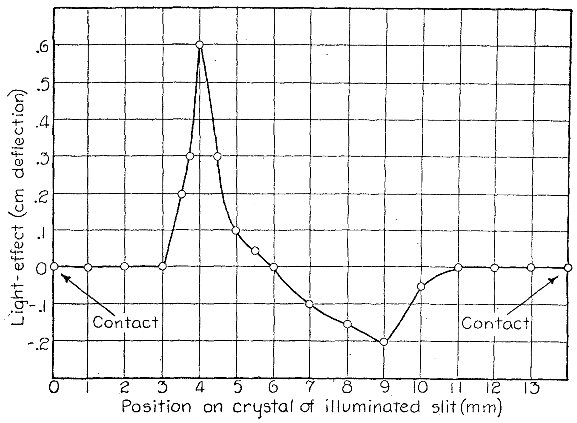

Fig. 2. Response curve when another face of the same crystal as was used to obtain Fig. 1 (sample K) is exposed. In this case both contacts were covered so that no light could strike the contacts.

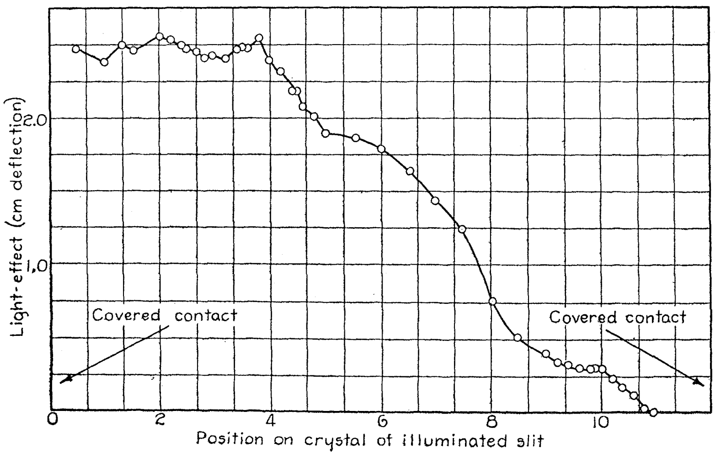

Fig. 3. Actino-electric effects observed in Sample L (argentite) when both contacts are carefully shielded from light.

reach them. Any deflections must now be due to the body effect at certain regions between the contacts similar to those observed by Coblentz in the case of molybdenite.[1]

The conclusion to be arrived at is that both contact and body effects occur in most crystals. In some the body effects are small whereas contact effects are large and vice versa. When different metals such as aluminum, nickel, copper, iron, etc., were used for contacts it was found that the contact-effects did not change appreciably. The effects along the surface at points or loci are certainly present and it seems highly probable (although this point cannot yet be definitely settled) that the so-called contact effects are due to actino-electrically active spots near or at the contacts and within the zone of illumination. As for the spots or loci of light action, Röntgen[4] has shown that in blue-colored, naturally occurring, NaCl crystals the seats of action are the small colloidal Na (metallic) particles and hence he supposes that the source of electrons is in places where the molecular lattice of NaCl has been distorted by the Na lattice, giving rise to electrons which may be loosely bound. Something of a similar nature may occur on the surface of the argentite (Ag_2S) crystals where the distortion may be due to minute impurities (which certainly are present) or else to discontinuities where one crystal cleaves to another. This is partially borne out by the experimental fact that when the crystal structure is destroyed (by hammering or filing) the loci become insensitive to light. It would seem then the effect of the light is not only to produce loosely-bound electrons with a consequent change in resistance as is the case for selenium, but to create in addition e.m.f.'s in these regions which together with the change in resistance produce measurable currents.

Intensity investigations. Tests were carried out in an attempt to find a relation between the intensity of the light and the actino-electric e.m.f. in which particular attention was directed to securing accuracy and the elimination of spurious effects. The crystal was illuminated in a region which showed large actino-electric sensitivity, this region not necessarily being at the contact. Another important consideration was the necessity of obtaining a region in which consecutive exposures gave the same deflections or, in other words, the polarization was negligible for all but the largest intensity.

We can therefore assume that polarization was negligible for small intensities whereas for the large intensities the deflections were corrected by carrying out separate measurements on the magnitude of polarization. The units for intensity are arbitrary and the deflections (in cm) are really a measure of the total photoelectric current which in this case can also be taken as actino-electric e.m.f. since polarization and change in resistance are negligible as evidenced by constant galvanometer deflections at a certain intensity. The final result is given (for a particular sample) in Fig. 4.

There is, therefore, no simple proportionality between the actino-electric current (or e.m.f.) and the intensity. Although all the crystals tested gave results similar to those shown in Fig. 4 and none gave evidence of any simple

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[4] W. C. Röntgen, Ann. d. Physik. **64**, 1 (1921).

relation existing between the actino-electric effect and the intensity of illumination, all the crystals gave a sharp bend in the curve at a certain intensity. This result has already been found by Sheldon and Geiger.[2] It was found that this intensity at which the bend occurs varies for different crystals and even for different regions on the same crystal. The curve (Fig. 4) shows that beyond a certain intensity (in this case about 7 units) the deflection increases more rapidly, hence a secondary effect comes into play producing the additional increase in slope.

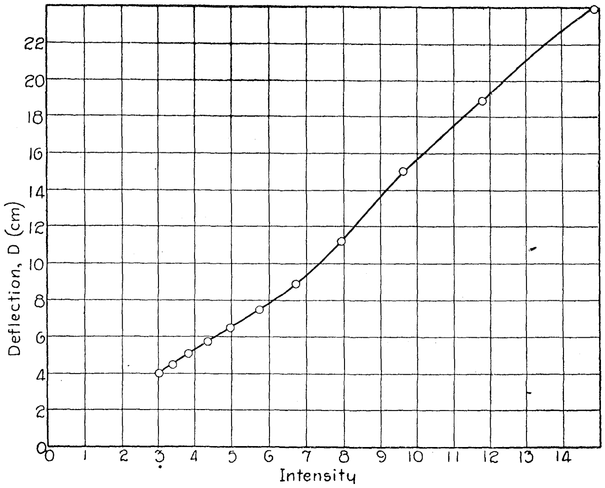

Fig. 4. Relation between actino-electric current (or e.m.f.) and intensity of illumination.

These curves seem to be of a similar nature to those obtained by Gudden and Pohl[5] in diamond, ZnS, etc., where secondary effects occur on application of high potential differences. In the case of argentite, however, the different results on the several crystals do not seem to obey the same laws.

A STUDY OF THE ACTINO-ELECTRIC FATIGUE EFFECT IN CRYSTALS OF ARGENTITE

The following effects have been shown by previous workers to take place. On exposure a decrease in resistance occurs which, after a very short time, however, becomes zero. Furthermore, on account of a flow in current (not dependent on light illumination) an increase in resistance takes place. Lastly, actino-electric e.m.f.'s are produced in spots or regions or at the contacts. Since all these variations take place simultaneously it is difficult to distinguish one from the other. Other factors which also enter into the observed photoelectric current are changes in dark current and the previous electrical history of the crystal, such as time of exposure, recovery, etc. The difficulty involved in studies of fatigue effects is that they vary enormously and quite

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[5] B. Cudden and R. Pohl Zeits. f. Physik. **16,** 3 (1923).

unexpectedly for different sections and parts of the same aggregate of crystals and even for the same crystals under different treatment. The only way any progress can be made is to eliminate as many of these factors as possible, then to keep the remainder constant while investigating one at a time.

In the first part of this paper we are dealing with only two of these several effects. This was because of the nature of the conditions specified and the precautions taken which made it possible to obtain constant deflections on repeated exposure to light. In this way any effects, which required measurable and fairly long periods of time for them to become effective, were eliminated. The observed currents were consequently due to an actino-electric e.m.f. and a change in resistance, which change, however, occurs instantaneously (or very nearly so) and does not vary any more by the time the deflections were measured.

The tests to be described were of a slightly different nature. The crystals and conditions worked with were those which did not give constant deflections on repeated exposure. The deflections became less showing that a time-factor was now involved, ordinarily known as photoelectric fatigue. The slit used for illuminating the crystal was made fairly wide so that the area of photoelectric sensitivity was fairly large thus increasing the deflections. The crystal was now illuminated for a fixed period of time, then left in darkness for another specified period of time, then exposed again and this procedure repeated. The deflections on repeated exposure were measured and found to become less and less.

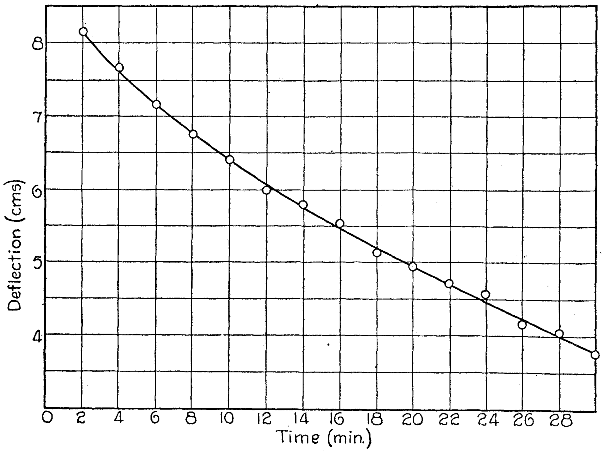

Fig. 5. Curve showing fatigue when exposed for 2 min. and allowed to recover 2 min. between readings. (See curve B, Fig. 6.)

The data and curves recorded here were taken with a view to studying the effect of time exposure and recovery on the actino-electric sensitivity of the crystal.

Since the same region was always exposed to the same intensity for repeated exposures we may assume as a first approximation that the spontaneous change in resistance mentioned before is the same every time the crystal is exposed. Consequently the observed decrease must be due to the change in actino-electric sensitivity which occurs in argentite when current flows through the crystal. This change must of course depend upon the time of exposure and the time for which the crystal is allowed to recover between exposures because argentite crystals will regain their original sensitivity if left in darkness long enough.

A crystal was chosen which showed fairly large actino-electric current as well as fatigue. The crystal was simply connected in series with a galvanometer, the light placed at such a distance that thermal e.m.f.'s were negligible, an additional precaution being a continuous-flow water-cell about 5 cm thick. Readings were taken for an exposure of 2 min. and times of recovery which were arranged to be either 1, 2, or 3 minutes. Fig. 5 shows the result. When current was plotted logarithmically against total time of exposure, a straight line resulted (within experimental error) thus showing that the decrease in sensitivity follows an exponential law. The same was true when the times of recovery were changed to 2 and 3 minutes as will be seen in the logarithmic curves in Fig. 6 in which the various readings seem to give the straight line relations indicated.

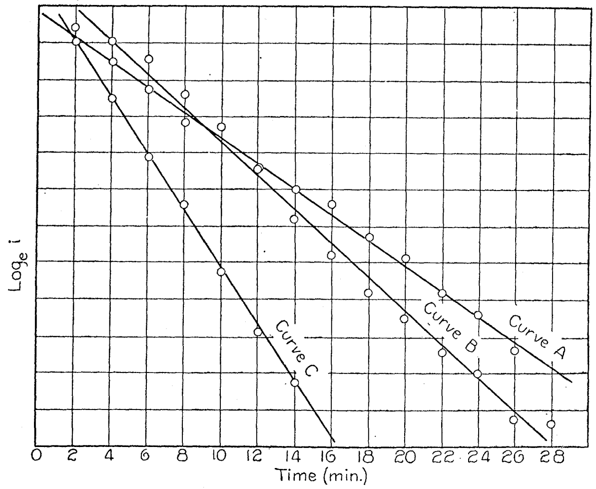

Fig. 6. Logarithm of the actino-electric current plotted against total time of exposure for various times of recovery (see Table I).

We can therefore represent our results by an equation of the form $i = Ae^{-at}$ where t is the total time of exposure and a is a constant depending upon the time of recovery. Just what this a is and the factors which effect it will be determined by the causes of the photoelectric fatigue. In Table I are shown the results obtained for a when the time of recovery is varied.

From this table it will be seen that a increases as the time of recovery increases and is not a constant as, for example, is the time constant factor L/R in the exponential decay of current of an inductive circuit. The a

varies and depends for one of its variations on the time of recovery. We therefore write the expression for current as $i = Ae^{-f(t_r)t}$ where t is the total time of exposure and t_r the time of recovery.

TABLE I

Experimental values found for a.

Time of exposure	Time of recovery	a
2 min.	1 min. (curve *A*)	0.068
2 min.	2 min. (curve *B*)	.087
2 min.	3 min. (curve *C*)	.152

In conclusion, the writer wishes to express his thanks to Prof. H. H. Sheldon for suggesting this topic and for valuable help rendered during these investigations, as well as to Prof. J. C. Hubbard for his helpful advice in the interpretation of some of the above results.

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