SPECTRO-PHOTOELECTRICAL EFFECTS IN ARGENTITE THE PRODUCTION OF AN ELECTROMOTIVE FORCE BY ILLUMINATION

By Paul H. Geiger

Abstract

Electromotive force produced by illumination of argentite.—If argentite (Ag_2S) is connected in a closed circuit with a galvanometer and one surface of contact is illuminated, an e.m.f. is produced which increases with the intensity, reaching a limit of about .013 volt for 600 candle-meters and over. On continued exposure, marked fatigue is shown, the e.m.f. decreasing in a few minutes to half value. By use of a monochromatic illuminator and a suitable intensity control, the e.m.f. was found to show a sharp maximum for about 1μ. The results were found independent of the contacts used whether Cu, Al, Fe, Sn, Ag or water. The effect is clearly not thermoelectric. Various samples showed similar results. No transmitted light effect was observed. *Six other minerals* showed the effect to a greater or less extent, including molybdenite (MoS_2) and acanthite (Ag_2S).

Resistance of argentite.—(1) *Variation with voltage.* The resistance, measured instantaneously was only half as great for 20 as for 4 volts. The resistance is about 4/5 as great in the light as in the dark, the ratio being independent of voltage. (2) *Variation with time of current flow.* The resistance increased with time, the crystal finally reaching a state when it was no longer light sensitive. Recovery was slow.

Introduction

BROWN, Sieg, Pfund, Coblentz and many others have studied the change of resistance of various substances, notably selenium, with change of illumination. T. W. Case[1] has discovered some twenty different crystalline substances which show an increase in conductivity with illumination. Kennard and Dieterich[2] found that the contact potential (measured on open circuit) varied with the intensity of illumination.

This investigation was undertaken with the purpose of studying the electrical and photoelectrical properties of argentite, a natural mineral whose chemical composition is given by the formula Ag_2S. After the work was well under way, a new and unexpected property was discovered.[3] This was the production of an electromotive force in a closed circuit consisting only of a galvanometer and a piece of argentite, when light fell upon one of the contacts on the crystal. This phenomenon was studied in detail; the effects were recorded for different

[1] T. W. Case, Phys. Rev. **9**, 305, 1917
[2] E. H. Kennard and E. O. Dieterich, Phys. Rev. **9**, 58, 1917
[3] H. H. Sheldon and P. H. Geiger, Phys. Rev. **19**, 389, 1922

intensities, for different wave-lengths, and for different metals and water as contact materials.

Some twenty different pieces of argentite were secured. These were not isolated crystals but were crystal conglomerates, so no effort was made to study the various properties along different crystal axes. The specimens varied in length from 5 to 20 mm, and in width from 3 to 8 mm. Samples were secured from the following localities: Batopilas, Mexico; Arispe, Sonora, Mexico; Freiberg, Saxony, Germany; and Schneeberg, Saxony, Germany. The crystals were kept in a desiccator in order that moisture would not affect the results. All of the results given in this paper have been checked with crystals differing greatly in appearance and coming from different regions, so it is assured that the results recorded hold true for argentite in general, not merely for individual specimens.

Production of an E.M.F. in a Closed Circuit by Illumination

To study the circumstances of the appearance of a current when a crystal was illuminated, a d'Arsonval galvanometer (Leeds and Northrup, high sensitivity) was connected directly to two knife edge contacts on the crystal. It was found that illuminating one contact gave a deflection in one direction and illuminating the other contact gave a deflection in the opposite direction. Illuminating the center of the crystal gave no deflection if the two contacts were shaded or equally illuminated. A number of tests were made which showed conclusively that the e. m. f. produced was not a thermoelectric force.

Tests on other minerals. All the available pieces of argentite were tested and found to produce an electromotive force upon illumination. Specimens of the following kinds of minerals also gave a deflection on illumination, although, in almost every case, smaller than that obtained with argentite: proustite (Ag_3AsS_3) ; pyrargyrite (Ag_3SbS_3); bournonite [$3(Cu_2,PbS)\ Sb_2S_3$]; molybdenite (MoS_2); stephanite (Ag_5SbS_4); acanthite (Ag_2S).

Specimens of the following, although listed by Case[1] as among those showing a change of resistance with light, failed to give a deflection large enough to be detected: galenite (PbS); stibnite (Sb_2S_3); polybasite (Ag_4SbS_6). One sample of cuprite (Cu_2O) showed the effect to a remarkable extent, while two others failed to give a perceptible deflection.

Crystal Fatigue as a Result of Constant Illumination

The deflection of a galvanometer connected to two contacts on an illuminated argentite crystal does not remain constant during the time the light is on, but gradually decreases. When the light is turned off the galvanometer will usually swing back past the original zero nearly as far as the deflection made when the light was first turned on. Under some conditions, when the crystal was illuminated for a short time, the galvanometer would start to swing in one direction, then would reverse, the first swing reaching a value about one fourth of the total final swing. On turning the light off, the procedure was reversed, i. e., the galvanometer gave an increased reading before going back to zero.

Fig. 1 shows graphically the behavior when the light is supplied for a long period of time. Here the deflection, after a maximum at the start, gradually decreased to a point below zero. After about 8 minutes the light was turned off, resulting in a deflection in the same sense as

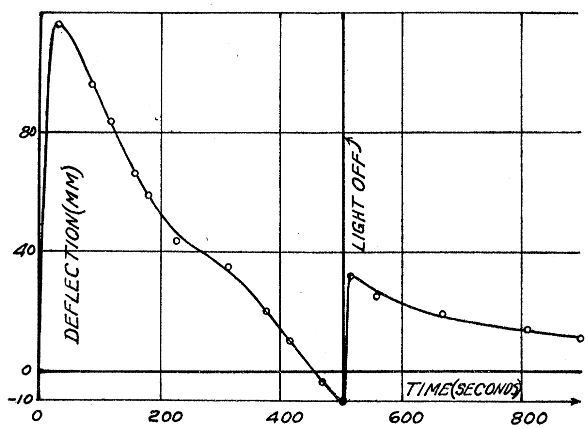

Fig. 1. Galvanometer deflection with continued exposure

when the light was turned on. Since the galvanometer was critically damped and since its ballistic period was 13 seconds, the actual rise of the current immediately after the illumination ceased was probably greater and faster than is indicated by the curve. A short time after this 8 minute exposure, the crystal was found to be greatly fatigued; only a quarter of the usual effect could be secured by turning on the light. A study of Fig. 1 makes it evident that there can be no continuous transformation of light energy into electrical energy by this means.

Variation in Electromotive Force with Varying Intensities of Illumination

Fig. 2 shows how the e.m.f. produced by light varies with the light intensity. One contact on the crystal was carefully shielded from the light, the other was illuminated by a 16 candle power automobile headlight. The intensity was varied by changing the distance between the lamp and the crystal. The filament area was so small that it could be considered a point source, so the relative intensities of illumination on the crystal could be calculated from the inverse square law. An ammeter was used to keep the filament current constant. Especially for high intensities, the resistance of the crystal would not remain constant and variable thermoelectric forces would be introduced which would affect the results so that the galvanometer deflections would not be proportional to the electromotive forces produced by light. For this reason, measurements of the e.m.f. generated were made by a potentiometer method; a measured current flowing through a known resistance placed in the galvanometer circuit, being adjusted until the galvanometer gave zero deflection. By balancing out the thermoelectric

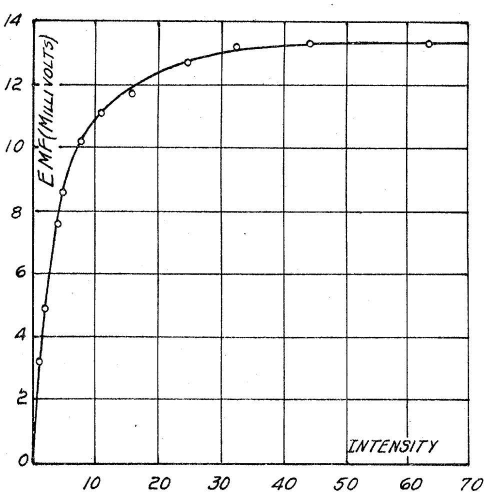

Fig. 2. E.m.f. as function of intensity

forces while the crystal was unilluminated and subtracting algebraically the value thus obtained from the value found with the crystal illuminated, the actual e.m.f. was determined. The unit of intensity used in Fig. 2 is arbitrary, being the intensity produced by the lamp at a distance of one meter. It is seen that only for the smaller intensities does the proportionality between the e.m.f. and the intensity hold true. This curve also shows that a limiting e.m.f. of 0.013 volt was produced.

Wave-Length Sensibility Curves

In order to find the comparative effect of radiations of different wave-lengths upon the production of the electromotive force, apparatus to give light of different wave-lengths, each with the same energy content, was constructed. Fig. 3 represents diagrammatically the equipment used. The light source was a 110 volt 400 watt stereopticon lamp with a plane filament. The lamp was so oriented that the image on the slit B made by the convex lens A was nearly linear. The filament current was furnished by a 130 volt storage battery; this voltage being used because more than normal brilliancy was required at times. A 60 degree, 8 cm carbon disulphide prism with glass sides was used to obtain the desired dispersion. The monochromatic light selected by slit D fell on the concave spherical silvered mirror M which could be rotated so that the monochromatic light would be focused on either the crystal or a thermopile. The crystal was connected as before to the high resistance galvanometer. A low resistance d'Arsonval galvanometer was connected to the thermopile as shown. In order to obtain sufficient energy to give suitable deflections, the slits were made over a millimeter in width.

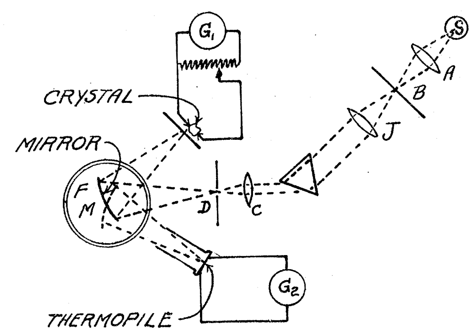

Fig. 3. Monochromatic illuminator

The calibration was accomplished by calculation, using the values for the index of refraction of carbon disulphide found in the Tables of Landolt, Börnstein und Meyerhoff. This calibration was checked experimentally by using fused salts which gave strong isolated spectral lines.

In order that equal light energies should fall on the crystal for each setting of the spectrometer, the current flowing through the lamp was regulated to the value which would give, for each spectrometer setting, equal amounts of energy as measured by the thermopile. The lamp was recalibrated several times as the work proceeded in order to avoid changes due to the aging of the filament. It was found however that no appreciable change occurred.

To obtain the first spectral sensibility curves a crystal was clamped between two copper clamps with knife edges. The values of the galvanometer deflections with differing wave-lengths are shown in Fig. 4. Similar curves were taken using samples of argentite from different regions of the world. In every case the results showed a maximum effect to be produced by radiation of wave-length 1μ.

It was thought that perhaps the metal used as a contact material had an influence on the spectral selective effect, so contact jaws of aluminum, iron, tin and silver were made and used. It was found that in every case, the maximum of the sensibility curve was at the same place.

Water was also used as a contact material. For this part of the investigation a crystal was partially immersed in distilled water contained in a glass rectangular cross section. The water acted as one of the contacts, a copper plate immersed in it being connected to the galvanometer. The other contact was made by winding a fine wire tightly

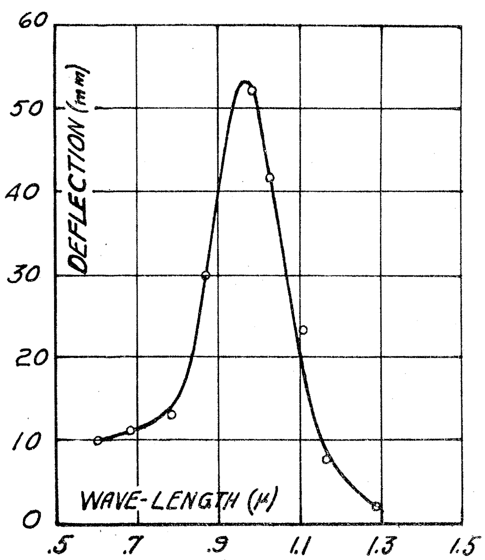

Fig. 4. Wave-length sensibility curve of argentite

about the crystal. The light passed through one side of the glass dish and through about 3 mm of water before reaching the crystal. Since radiations of different wave-lengths are reflected and absorbed by glass and water to different extents, the values of the filament current for each spectrometer setting had to be redetermined. A water cell 3 mm thick was placed in front of the thermopile and the filament currents which gave equal light energies as then measured by the thermopile were recorded. Since it was necessary that the path of the light reaching the crystal be equivalent to the path traversed in going to the thermopile, the dish in which the crystal was to be immersed was made with the front face composed of two pieces of glass each of the same thickness as the sides of the compensating cell.

Each time the galvanometer was first connected to an immersed unilluminated crystal, a very large deflection resulted. Wave-length sensibility curves taken under this condition showed a maximum effect in the visible spectrum. The crystal was extremely sensitive to light at these times. After the crystal had been connected in a closed circuit for eight or ten days the counter e.m.f. decreased to a small value and the maximum effect was found to be at 1μ as before. When water was used as a contact material much larger deflections were obtained than when any of the metals were used. This was probably due to the better contact and the larger area illuminated.

The sensitivity of argentite to radiations in the near infra-red suggests that a cell for use in some infra-red research might be constructed which would offer several advantages.[4]

Increase of Resistance with the Time of Flow of Current

When the properties of argentite were first being studied, it was found that when a crystal was placed in one arm of a Wheatstone bridge a balance could not be secured. If the galvanometer circuit was kept closed the galvanometer made erratic movements. The usual steps were taken to render the galvanometer steady; such as shielding, carefully insulating the wiring, thoroughly drying the crystal, etc. It was thought that perhaps the heating effect of the bridge current caused the irregular deflections, so the battery was connected continuously for several days. Measurements made then showed that the resistance had become extremely great. After a number of tests it was found that the resistance of any piece of argentite would increase with the time of flow of current through it.

Measurements of the resistance of the crystal at different known times after the bridge current was turned on, were made almost instantaneously by inserting the galvanometer in the bridge circuit for a definite short period by means of a Helmholtz pendulum. By substituting a known variable resistance for the crystal and adjusting it until the same deflection was obtained as when the crystal was in circuit, all other factors remaining the same, the desired resistance determination was made.

This study showed that the resistance increased with the time of flow of current; that the time taken for a crystal to reach the final condition

[4] Since the above results were obtained, there has appeared in the Bulletin of the Bureau of Standards, (Scientific Paper No. 446) an article by W. W. Coblentz entitled, "Spectrophotoelectrical Sensitivity of Argentite, (Ag_2S)." In this article the change of resistance with illumination is discussed at length. It was found that the maximum change in resistance per unit radiant energy was due to radiation of wave-length 1.35μ at ordinary temperatures, and 1.1μ at very low temperatures.

depended on its previous electrical history; that the time for recovery was long; that the increase in resistance was confined to portions carrying the greater share of the current; that the crystal was not light sensitive after a current had flowed through it for some time.

Variation of Resistance with Potential

Brown,[5] Pfund[6] and others have shown that some light-sensitive substances exhibit a change in resistance with a change in applied potential, and therefore tests for this effect were made on argentite. The work was complicated somewhat because the current necessary to make the observations would increase the resistance if allowed to flow for an appreciable time. The usual Wheatstone bridge arrangement was used with the exception that the galvanometer was connected permanently in the circuit and the battery current turned on for a definite short interval by means of the Helmholtz pendulum. The circuit was found to be non-inductive by a preliminary test, so no error was introduced by connecting the galvanometer before the battery was connected. A rheostat in the battery circuit was adjusted to give the desired voltage over the crystal, the pendulum was released and the resulting galvanometer deflection recorded. The value of the resistance was determined by substitution as before. The process was repeated, working from 1 volt upwards to 20 volts.

Since current was flowing through the crystal for only about 1/10 second for each determination and since the potential was raised for each succeeding measurement, it seemed unlikely that the results would be vitiated to any appreciable extent by the flow of current through the crystal; but to make certain, the curve was repeated, this time allowing at least 24 hours between each reading. The curve thus obtained was identical with the first. If any error of this sort did appear, it would mean that a higher value for the resistance would be obtained for the greater voltages, so it is sure that there is a decrease in the resistance with an increase in potential difference.

The upper curve in Fig. 5 shows how the resistance changes with potential difference when the crystal is protected from light. The lower curve is the same except that the crystal was illuminated by a 25 watt tungsten lamp through a 2 cm water cell. In obtaining the data for this curve the contact jaws were shielded from the light, so that the resistance measurements would not be affected by the e.m.f. produced by light. The current was turned on the lamp by a contact on the

[5] F. C. Brown, Phys. Rev. **4**, 85, 1914
[6] A. H. Pfund, Phys. Rev. **7**, 295, 1916

Helmholtz pendulum. From the data from which these two curves were plotted, the change in resistance (due to light) per unit resistance was calculated for different values of the potential difference. It was found that this ratio was a constant, within experimental error, over the range of voltages covered, i. e., from 1 to 20 volts.

THE TRANSMISSION OF THE LIGHT EFFECT

In 1913 Brown and Sieg,[7] working with isolated crystals of selenium, found that when light fell upon a portion of a crystal, the resistance of a remote portion of that crystal was reduced. No evidence of such a transmitted light action was found in argentite, although it was looked

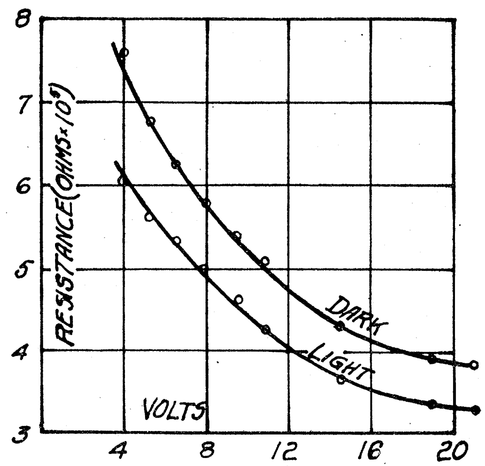

Fig. 5. Variation of resistance with potential

for and could have been detected by the methods used even if it had existed only to a much smaller extent than had been found for selenium. Perhaps if a sufficiently large isolated crystal could be secured the effect would be found. Pfund[8] found that there was no transmission of the light effect in cuprous oxide; and Coblentz[9] found none in molybdenite.

In conclusion, the writer wishes to express his thanks to Dr. H. H. Sheldon who suggested the interesting possibilities in the study of crystal conduction and who gave aid during the time the work was being done.

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ANN ARBOR, MICHIGAN,
January 27, 1923.

[7] F. C. Brown and L. P. Sieg, Phil. Mag. **28**, 497, 1914; Phys. Rev. **4**, 85, 1914
[8] A. H. Pfund, Phys. Rev. **7**, 298, 1916
[9] W. W. Coblentz, Bull. Bur. of Stds. **15**, 121, 1919