NOTES ON THE CHANGE OF RESISTANCE OF CERTAIN SUBSTANCES IN LIGHT.[1]

By T. W. Case.

THE author has been making a systematic search for substances which show a change of resistance when exposed to light. The results of this search may prove interesting to those who are working in the same field, as several new light-active substances have been found.

Considerable work has already been done upon substances which change their resistance under the influence of light. The best known examples of this effect are selenium, stibnite and cuprous oxide, of which the latter has recently been announced by Professor A. H. Pfund, at Johns Hopkins, Physical Review, 7 (1916), 298.

As Professor Brown, of Iowa University, obtained much better results with a large crystal of selenium than had been obtained originally with the finely divided form, crystallized mineral specimens were used in this investigation where possible.

It may not be out of place here to give a description of the apparatus used, as it was simple and highly effective. It consisted essentially of an arc lamp and a variable speed water motor mounted upon a concrete base. The water motor drove a disk which had 15 sectorial openings; and so served to rapidly interrupt the beam of light produced by the arc, and brought to focus upon the substance under observation. Lead wires ran from this substance to an Ayrton shunt, which was connected to a three-step De Forrest Audion Amplifier. (The third step of this instrument was capable of increasing the energy of the original impulse 12,000 per cent.) High resistance receivers could be inserted in any one of these steps; and if any photoelectric action was produced by the interrupted beam of light, a distinct note would be heard in the receivers. The pitch of this note varied directly with the number of light interruptions per unit of time.

The crystal specimen under examination was held in a small clamp in the path of the interrupted beam of light. Contact was made at the ends of the crystal through the agency of thin platinum foil, which was pressed firmly against the crystal by a spring of variable tension in the

[1] The conditions of this experiment do not cover the minerals in all possible structures. Hence the negative actions are not necessarily conclusive.

Mineral.	Composition.[1]	Conductivity.	Action.
Sulphur		N.C.[2]	None
Selenium	Se	G.C.[3]	Fair, easily audible
Tellurium		G.C.	None
Antimony	Contains sometimes silver, iron or arsenic	G.C.	None
Bismuth		G.C.	None
Realgar	AsS	N.C.	None
Orpiment	As_2S_3	N.C.	None
Stibnite	Sb_2S_3	P.C.[4]	Small
Bismuthinite	Bi_2S_3	P.C.	Very good
Tetradymite	$Bi_2(TeS)_3$	N.C.	None
Molybdenite	MoS_2	G.C.	Fair
Domeykite	Cu_3As	G.C.	None
Algodonite	Cu_6As	G.C.	None
Whitneyite	Cu_9As	G.C.	None
Argentite	Ag_2S	G.C.	Good, large fatigue
Hessite	Ag_2Te	G.C.	None
Galenite	PbS	G.C.	Fair
Altaite	PbTe		None
Clausthalite	PbSe	G.C.	None
Berzelianite	Cu_2Se	N.C.	None
Crookesite	$(Cu, Tl, Ag)_2Se$	N.C.	None
Chalcocite	Cu_2S	N.C.	None
Stromeyerite	$(Ag, Cu)_2S$	N.C.	None
Sternbergite	Ag, Fe_2S_3	G.C.	None
Acanthite	Ag_2S	G.C.	Good, large fatigue
Sphalerite	ZnS	N.C.	None
Metacinnabarite	HgS	G.C.	None
Guadalcazarite	Found near above, contains a little zinc	N.C.	None
Cinnabar	HgS	N.C.	None
Covellite	CuS	P.C.	None
Greenockite	CdS	N.C.	None
Millerite	NiS	P.C.	None
Niccolite	NiAs	N.C.	None
Breithauptite	NiSb	P.C.	None
Pyrrhotite	$Fe_{11}S_{12}$	G.C.	None
Polydymite	Ni_4S_5	G.C.	None
Bornite	Cu_3FeS_3	G.C.	None
Linnaeite	Co_3S_4	G.C.	None
Chalcopyrite	$CuFeS_2$	G.C.	None
Stannite	$Cu_2.S.FeS.SnS_2$	G.C.	None

[1] The formulæ given for the minerals are those obtained from the mineral dealers; the order is that of Dana's System of Mineralogy.

[2] N.C. is used in this work as meaning that the substance is practically a non-conductor in the dark.

[3] G.C. indicates that a crystal of the substance one mm. on a side, in the holder used, at an applied potential of 110 volts has a resistance of less than 1 megohm.

[4] P.C. indicates that a crystal of the substance one mm. on a side, in the holder used, at an applied potential of 110 volts has a resistance greater than 1 megohm.

Mineral.	Composition.	Conductivity.	Action.
Hauerite.........	MnS_2	G.C.	None
Cobaltite.........	CoS_2CoAs_2	N.C.	None
Gersdorffite.......	NiAsS	G.C.	None
Corynite.........	Ni(AsSb)S	N.C.	None
Ullmannite.......	NiSbS	G.C.	None
Marcasite........	FeS_2	G.C.	None
Arsenopyrite......	FeAsS	G.C.	None
Pearceite.........	Ag_9AsS_6	G.C.	Fair
Sylvannite.......	(Au, Ag)Te_2	N.C.	None
Calaverite........	(Au, Ag)Te_2	N.C.	None
Kermesite........	Sb_2S_2O	N.C.	None
Zinkenite.........	$PbSb_2S_4$	G.C.	None
Sartorite.........	$PbAs_2S_4$	N.C.	None
Rathite..........	$3PbS_2As_2S_3$	P.C.	None
Emplectite.......	$CuBiS_2$		None
Chalcostibite.....	$CuSbS_2$	P.C.	None
Galenobismutite ..	$PbBi_2S_4$	G.C.	None
Miargyrite.......	$AgSbS_2$	G.C.	Fair
Plagionite........	$5PbS.4Sb_2S_3$	N.C.	None
Schirmerite.......	$3(Ag_2Pb)S.2B_{12}S_3$	N.C.	None
Cosalite..........	$Pb_2B_{12}S_5$	G.C.	None
Jamesonite.......	$Pb_2Sb_2S_5$	P.C.	Fair
Kobellite.........	$Pb_2(BiSb)_2S_5$	P.C.	None
Semseyite........	$Pb_7Sb_6S_{16}$		None
Freieslebenite.....	$(Pb, Ag_2)_5Sb_4S_{11}$	P.C.	None
Bournonite.......	$3(Cu_2, Pb)S.Sb_2S_3$	P.C.	Good
Boulangerite......	$Pb_3Sb_2S_6$	N.C.	Good
Fizelyite.........	$Ag_2Pb_5Sb_8S_{18}$	N.C.	None
Guitermanite.....	$10PbS.3As_2S_3$	N.C.	None
Pyrargyrite.......	Ag_3SbS_3	P.C.	Fair
Proustite.........	Ag_3AsS_3	G.C.	Good
Tetrahedrite......	$Cu_8Sb_2S_7$	G.C.	None
Stephannite......	Ag_5SbS_4	G.C.	Fair
Polybasite........	Ag_9SbS_6	G.C.	Fair
Enargite.........	$3Cu_2S.As_2S_5$	N.C.	None
Epiboulangerite...	$Pb_3Sb_2S_8$	N.C.	None
Cerargyrite.......	Silver Chloride	N.C.	None
Iodyrite..........	AgI	P.C.	Fair
Fluorite..........	CaF_2	N.C.	None
Laurionite........	$PbCl_2.Pb(OH)_2$	N.C.	None
Cumengeite.......	$PbCuCl_2(OH)_2$	N.C.	None
Quartz (tiger eye) .	SiO_2	N.C.	None
Valentinite.......	Sb_2O_3	N.C.	None
Bismite..........	Bi_2O_3	N.C.	None
Molybdite........	MoO_3	N.C.	None
Cervantite........	Sb_2O_4	N.C.	None
Cuprite[1].........	Cu_2O	P.C.	Fair
Chalcotrichite.....	Cu_2O	N.C.	None

[1] Cuprite was predicted to show this action by Professor A. H. Pfund (Phys. Rev., 7 (1916), 298).

Mineral.	Composition.	Conductivity.	Action.
Silver oxide	Ag_2O (pastiles freshly prepared)	P.C.	Fair
Periclasite	MgO	N.C.	None
Manganosite	MnO	P.C.	None
Zincite	ZnO	N.C.	None
Massicot	PbO	N.C.	None
Tenorite	CuO	P.C.	None
Corundum	Al_2O_3	N.C.	None
Hematite	Fe_2O_3	G.C.	None
Ruby spinel	$MgAl_2O_4$	N.C.	None
Magnetite	$FeO.Fe_2O_3$	G.C.	None
Franklinite	$(FeZnMn)O(FeMn)_2O_3$	P.C.	None
Chromite	$FeCr_2O_4$	P.C.	None
Chrysoberyl	$BeAl_2O_4$	N.C.	None
Hausmannite	Mn_3O_4	N.C.	None
Minium	Pb_3O_4	N.C.	None
Cassiterite	SnO_2	G.C.	None
Rutile	TiO_2	N.C.	None
Brookite	TiO_2	N.C.	None
Pyrolusite	MnO_2	G.C.	None
Turgite	$Fe_4H_2O_7$	G.C.	None
Diaspore	$Al_2O_3.H_2O$	N.C.	None
Göthite	$FeO(OH)$	N.C.	None
Limonite	$2Fe_2O_3.3H_2O$	N.C.	None
Brucite	$MgO.H_2O$	N.C.	None
Gibbsite	$Al(OH)_3$	N.C.	None
Chalcophanite	$(Mn, Zn)O.2MnO_2.2H_2O$	N.C.	None
Psilomelane	H_4MnO_5	N.C.	None
Lampadite	MnO_2	P.C.	None
Calcite	$CaCO_3$	N.C.	None
Siderite	$FeCO_3$	N.C.	None
Smithsonite	$ZnCO_3$	N.C.	None
Phosgenite	$PbCO_3.PbCl_2$	N.C.	None
Malachite	$CuCO_3$ $Cu(OH)_2$	N.C.	None
Azurite	$2CuCO_3$ $Cu(OH)_2$	N.C.	None
Aurichalcite	$2(Zn, Cu)Co_3.3(Zn, (Cu)(OH)_2$	N.C.	None
Microcline	$KAlSi_3O_8$	N.C.	None
Albite (soda felsspar	$NaAlSi_3O_8$	N.C.	None
Actinolite	$(CaMgFe)SiO_3$	N.C.	None
Beryl	$Be_3Al_2Si_6O_{18}$	N.C.	None
Garnet	$Ca_3Al_2Si_3O_{12}$	N.C.	None
Dioptase	H_2CuSiO_4	N.C.	None
Zircon	$ZrSiO_4$	N.C.	None
Cyrtolite	(Altered zircon)	N.C.	None
Gadolinite	$Be_2FeY_2Si_2O_{10}$	N.C.	None
Zoisite	$Ca_2(AlOH)Al_2(SiO_4)_5$	N.C.	None
Epidote	$HCa_2(Al, Fe)_3Si_3O_{13}$	N.C.	None
Prehnite	$H_2Ca_2Al_2Si_3O_{12}$	N.C.	None
Chrondrodite	$H_2Mg_{19}Si_8O_{34}F_4$	N.C.	None
Tourmaline	R_6SiO_5	N.C.	None

Mineral.	Composition.	Conductivity.	Action.
Staurolite........	$H_4(FeMg)_6(AlFe)_{24}Si_{11}O_{66}$	N.C.	None
Apophyllite......	$H_7KCa_4(SiO_3)_8$ and $4\frac{1}{2}H_2O$	N.C.	None
Stilbite..........	$H_4(Na_2.Ca)Al_2Si_6O_{18}$ and $4H_2O$	N.C.	None
Laumontite......	$H_4CaAl_2Si_4O_{14}$ and $2H_2O$	N.C.	None
Penninite........	$Hg(Mg, Fe)_5Al_2Si_3O_{18}$	N.C.	None
Talc.............	$H_2Mg_3Si_4O_{12}$	N.C.	None
Sepiolite.........	$H_4Mg_2Si_3O_{10}$	N.C.	None
Pyrophyllite......	$Al_2Si_3O_9$ and H_2O	N.C.	None
Thaumasite......	$CaSiO_3.CaCO_3.CaSO_4.15\ H_2O$	N.C.	None
Perovskite........	$CaTiO_3$	N.C.	None
Columbite........	$FeCb_2(Ta)_2O_6$	N.C.	None
Samarskite.......	$R_3R_2(Nb, Ta)_6O_2$	P.C.	None
Euxenite (columbate yttria).....	$R(NbO_3)_3\ R_2(TiO_3)_3$ and $3/2\ H_2O$	N.C.	None
Vanadinite.......	$Pb_3V\ 1/3\ PbCl$	N.C.	None
Olivenite.........	$Cu_3As_2O_8{:}Cu(OH)_2$	N.C.	None
Descloizite.......	$Pb_2O_2VO_3$	N.C.	None
Vivianite.........	$Fe_3P_2O_8$ and $8H_2O$	N.C.	None
Torbernite........	$Cu(UO)_2P_2O_8$ and $8H_2O$	N.C.	None
Barite...........	$BaSO_4$	N.C.	None
Crocoite.........	$PbCrO_4$	P.C.	None
Wulfenite........	$PbMoO_4$	N.C.	None
Aguilarite........	$AgSAg_2Se$	N.C.	None
Chalcedony.......	SiO_2	N.C.	None
Copalite.........	(Fossil Copal)	P.C.	None
Lorandite........	$TlAsS_2$	N.C.	None
Smoky quartz.....	SiO_2	N.C.	None

clamp. An E.M.F. of 110 volts was placed in series circuit with the crystal, the audion apparatus and a protective resistance. In the work with very fragile crystals the clamp was replaced by a mounting of the crystal upon a small cork, current being sent through the specimen through the agency of gold leaf contacts at the ends of the crystal.

In some instances, the resistance of the crystal under examination was such that the impressed voltage allowed either too much or too little current to flow through the apparatus. With low resistance crystals this was taken care of by the shunt. With crystals of very high resistance the voltage and size of the crystal were adjusted until the desired current was obtained. A list of the minerals examined, an indication of their photo activity as determined by the note on the receivers, and their relative conductivity in the dark as shown on pages 305–309.

The active substances are being further studied in regard to their resistance changes, fatigue, deduction and induction periods. Two specimens which show remarkable action are acicular crystals of bismuth sulphide (bismuthinite), and a granular lead antimony sulphide. It suffices to say here that the resistance of a piece of the latter 1 mm. by 10 mm., reduces about 5,000 per cent. from the value in the dark in dull sunlight at an applied potential of 110 volts. If the substance be actually heated up, either by exposure to heat or passing a current which slowly heats the substance, then the resistance is gradually lowered, but this is a slow process. All of the photo active sulphides show the quick light reaction in the red part of the spectrum. Both the bismuthinite and the lead antimony sulphide give fine results when used as a transmitter in a photo phone system, using a manometric flame for transforming the voice variations into light variations. The voice reproduction is very clear and loud. Specimens of lead antimony sulphide at present show no evidence of an induction period or fatigue, outside of the slow heating effect due to the current which reaches an equilibrium after several hours, after which the light reaction then becomes constant. This, as well as its large change of resistance with small variations of light intensity allow it to be used as a very delicate actinometer.

Summary.

1. An apparatus has been described for the detection of certain photo electric phenomena.

2. The change of resistance of certain substances in light are being studied; and a number of new compounds have been found which show a change of conductivity in light.

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