

A STUDY OF THE PROPERTIES OF
CRYSTAL DETECTORS

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TABLE OF CONTENTS

	Page
Introduction	1
Apparatus	3
Table I	7
Mineral description	12
Galena	12
Pyrite	14
Silicon	16
Molybdenite	17
Carborundum	18
Psilomelane	19
Zincite	19
Bornite	20
Mercury	20
Deductions	22

PREFACE

Since the discovery of wireless telegraphy, a great many types of devices have been invented for the purpose of detecting oscillating waves of electricity. One of the most simple, though relatively efficient devices, is the use of a crystal of suitable substance, placed in the phone circuit. The function of the crystal is to permit the oscillations to pass in one direction only. This rectifying property is shared by several natural and artificial crystal substances. The exact nature of the properties, which enable a crystal to detect, has never been worked out.

This paper is the result of experiments of various kinds, directed so as to link up crystal structure and composition with the electrical phenomena as detectors.

In writing this paper, the author has made use of the abundant supply of information found in the standard works on mineralogy and crystallography. A list of the publications used, will be found at the end of this paper.

The author wishes to express his appreciation of the hearty support given by Professor Henry Landes. He also wishes to acknowledge the assistance received from Professor George E. Goodspeed Jr., under whose direction the experiments were carried out. The author wishes to thank Mr. Sheldon L. Glover, who first suggested the problem of this paper, and whose experiments in radio work have been of great assistance.

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INTRODUCTION

A study of electromagnetic waves seems to show, without doubt, that light is due to waves of the same nature. The waves of light differ from these electromagnetic waves, by their very much shorter wave length. It is therefore logical, in the study of the electrical phenomena of a crystal, to make use of analogies with known optical properties.

Crystals are divided, optically, into two groups,

1. Isotropic, or those which permit light to travel through them with equal velocity in every direction.
2. Anisotropic, or crystals which allow the light to travel with greater ease through some directions than through others.

Crystals are isotropic and anisotropic also, with respect to electromagnetic waves. This fact should be kept in view, in the study of the ability of a crystal to detect or rectify electromagnetic oscillations.

In general, most mineral, excepting those having a metallic lustre among the sulphides and oxides, are non-conductors of electricity. It is chiefly from these two groups of minerals, that possible detectors might be found. The artificial furnace products also offer a field of considerable possibility for one in search of a reliable

crystal detector.

The crystal that is used as a detector, is placed in series with the phone circuit. It is usually clamped in a cup-shaped metal conductor, which serves as a terminal for the wire connection. (Figure 1). The other connection is made by a metal point, capable of adjustment for pressure.

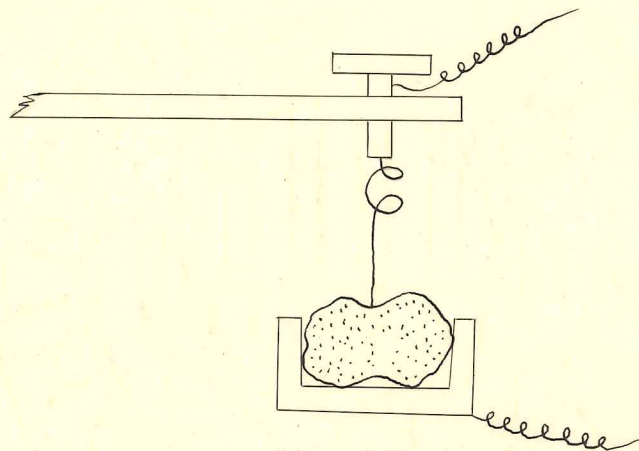


Figure 1.

The electrical oscillations are allowed to pass in one direction through the crystal, but in the other direction they are cut off. In this manner a potential is built up, which destroys the equilibrium of the circuit. The phones remain silent as long as equilibrium is established, but the slightest potential, on one side or the other, causes the diaphragm to vibrate, and a sound is heard.

APPARATUS

Every available mineral that showed any possibility as a detector, was examined and tested on a radio receiving set arranged as in Figure 2.

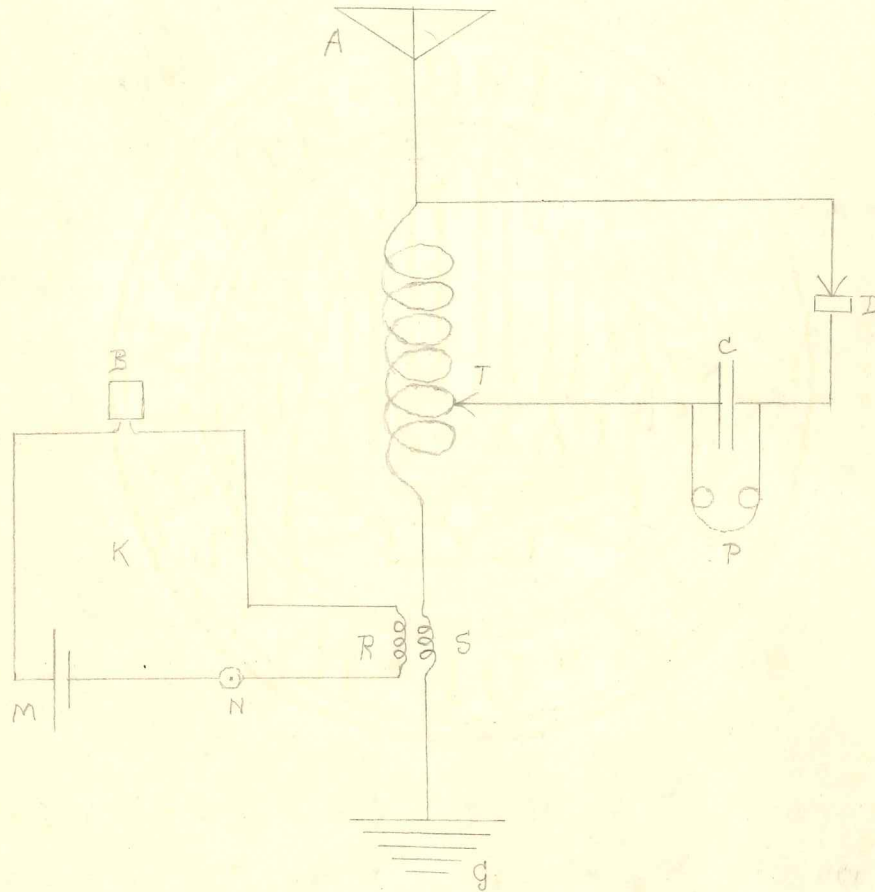


Figure 2

- | | |
|----------------------------|-----------------------------|
| A aerial | B buzzer |
| D detector crystal | N push-button |
| T tuning-coil | M dry cell |
| C condenser | R primary excitation coil |
| P phones | S secondary excitation coil |
| K buzzer excitation system | |
| G ground | |

The set is so arranged that oscillations in the receiving circuit can be induced from the buzzer circuit, in case none of the nearby sending stations are in operation. The buzzer circuit consists of a push-button, buzzer, a single dry cell, and a primary excitation coil of seven turns. In the ground-wire of the radio receiving set, there is a secondary coil, which also contains seven turns. When the buzzer is in action, an oscillating series of waves are set up in the buzzer circuit. The small primary coil causes an induced oscillating series of waves in the whole radio circuit. As it is the function of detectors to allow the oscillations to pass only in one direction, there occurs a relative building up of power on one side of the detector. The magnitude of this distortion in the equilibrium of the circuit, is recorded by the vibration of the diaphragms in the phones.

The set is tuned so that no sound of the buzzer can be heard in the phones when an ordinary conductor is placed across the detector terminals. On the other hand, when an active or detecting crystal is placed across the circuit, a record of the oscillations of the buzzer is transmitted to the ear. The experimental work is, therefore, not dependent upon the broadcasting stations. It is only necessary to press the push-button, and the record in the phones immediately tells whether or not the crystal is detecting. In addition, the set is tuned and ready,

without any adjustment, to receive any message that may come in on the standard broadcasting wave length.

In the work of testing the various crystals, it is found that, in some cases, on a given crystal, only a few points possess the ability to detect. Two galena crystals, equal in purity and apparent crystal form, may yield totally different results. Usually only a few points, on such a crystal, prove to be active. It is true, therefore, that a negative result on a given mineral does not prove that all tests on that mineral will be negative.

Some crystals will detect only when the pressure of the contact point is slight; others require considerable pressure to produce results.

In the list of minerals tested and found to be detectors, their sensitiveness ranged from zero up to that of the best crystals of galena and pyrite. Crystals that are able to receive radio broadcast news, clearly and distinctly, are called "excellent" detectors. Crystals which give persistent, though relatively weak results with radio broadcast news, are termed "fair" detectors. Other crystals, which give negative results with radio broadcast news, yet are able to detect the stronger buzzer oscillations, are called "poor" detectors.

In some cases, an electric potential across the detector, serves to raise the crystal from the "fair" to the "excellent" class of detectors. Carborundum is an example of this class.

As conductors of electricity, those crystals which possess a conductivity approaching that of copper, are termed "high" conductors. When the substance possesses a conductivity more nearly approaching that of galena, it is said to have "medium" conductivity. Crystals which show the approximate conductivity of pyrite, are called "low" conductors. The remaining crystals are classed as non-conductors.

TABLE I

Name	Composition	Crystal System	Conductivity	Detectivity
Aluminum	Al	Isometric	High	Lacking
Antimony	Sb	Rhombohedral	High	Lacking
Arsenic	As	Rhombohedral	High	Lacking
Bismuth	Bi	Rhombohedral	Medium	Lacking
Cadmium	Cd	Isometric	High	Lacking
Chromium	Cr	Isometric	High	Lacking
Cobalt	Co	Isometric	High	Lacking
Copper	Cu	Isometric	High	Lacking
Diamond	C	Isometric	None	Lacking
Gold	Au	Isometric	High	Lacking
Graphite	C	Hexagonal	Medium	Lacking**
Iron	Fe	Isometric	High	Lacking
Lead	Pb	Isometric	High	Lacking
Magnesium	Mg	Hexagonal	Low	Lacking
Manganese	Mn	Isometric	High	Lacking
Mercury	Hg	(Amorphous)	Medium	Poor
Nickel	Ni	Isometric	High	Lacking
Platinum	Pt	Isometric	High	Lacking
Silicon	Si	Hexagonal	Low	Excellent
Sulphur	S	Orthorhombic	None	Lacking
Tellurium	Te	Rhombohedral	Low	Lacking
Tin	Sn	Tetragonal	High	Lacking
Tungsten	W	Isometric	Medium	Lacking

** Functions as a coherer.

Name	Composition	Crystal System	Conductivity	Detectivity
Zinc	Zn	Isometric	High	Lacking
Carborundum	SiC	Hexagonal	Low	Fair
Alabandite	MnS	Isometric	None	Lacking
Argentite	AgS	Isometric	Low	Poor
Arsenopyrite	FeAsS	Orthorhombic	High	Lacking
Bismuthinite	Bi ₂ S ₃	Orthorhombic	Low	Lacking
Bornite	Cu ₅ FeS ₄	Isometric	High	Fair
Chalcocite	Cu ₂ S	Orthorhombic	Medium	Poor
Chalcopyrite	CuFeS ₂	Tetragonal	Medium	Poor
Cinnabar	HgS	Rhombohedral	None	Lacking
Cloanthite	NiAs ₂	Isometric	High	Lacking
Cobaltite	CoAsS	Isometric	Medium	Lacking
Covellite	CuS	Hexagonal	High	Lacking
Galena	PbS	Isometric	Medium	Excellent
Hessite	Ag ₂ Te	Isometric	High	Lacking
Linnaeite	Co ₃ S ₄	Isometric	High	Lacking
Löllingite	FeAs ₂	Orthorhombic	High	Lacking
Marcasite	FeS ₂	Orthorhombic	Low	Lacking
Millerite	NiS	Rhombohedral	High	Lacking
Molybdenite	MoS ₂	Hexagonal	Low	Excellent
Niccolite	NiAs	Hexagonal	High	Lacking
Orpiment	As ₂ S ₃	Monoclinic	None	Lacking
Pentlandite	(Fe,Ni)S	Isometric	High	Lacking
Pyrite	FeS ₂	Isometric	Low	Excellent
Pyrrhotite	Fe _n S _{n+1}	Hexagonal	High	Lacking

Name	Composition	Crystal System	Conductivity	Detectivity
Realgar	AsS	Monoclinic	None	Lacking
Smaltite	CoAs ₂	Isometric	High	Lacking
Sphalerite	ZnS	Isometric	None	Lacking
Stibnite	Sb ₂ S ₃	Orthorhombic	None	Lacking
Sylvanite	(Au,Ag)Te ₂	Monoclinic	High	Lacking
Ullmanite	NiSbS	Isometric	High	Lacking
Wurtzite	ZnS	Hexagonal	None	Lacking
Boulangerite	Pb ₅ Sb ₄ S ₁₁	Orthorhombic	None	Lacking
Bournonite	[Pb,Cu ₂]Sb ₂ S ₆	Orthorhombic	None	Lacking
Enargite	Cu ₃ AsS ₄	Orthorhombic	Low	Lacking
Jamesonite	Pb ₂ Sb ₂ S ₅	Orthorhombic	Low	Lacking
Proustite	Ag ₃ AsS ₃	Rhombohedral	None	Lacking
Pyrargyrite	Ag ₃ SbS ₃	Rhombohedral	None	Lacking
Stannite	Cu ₂ FeSnS ₄	Isometric	Low	Poor
Tennantite	Cu ₃ AsS ₃	Isometric	Medium	Lacking
Tetrahedrite	Cu ₃ SbS ₃	Isometric	Low	Poor
Zinkenite	PbSb ₂ S ₄	Orthorhombic	Low	Lacking
Atacamite	Cu ₂ Cl(OH) ₃	Orthorhombic	None	Lacking
Fluorite	CaF ₂	Isometric	None	Lacking
Halite	NaCl	Isometric	None	Lacking
Sal Ammoniac	NH ₄ Cl	Isometric	None	Lacking
Brookite	TiO ₂	Orthorhombic	Low	Poor
Cassiterite	SnO ₂	Tetragonal	None	Lacking
Chromite	FeCr ₂ O ₄	Isometric	None	Lacking
Cuprite	Cu ₂ O	Isometric	None	Lacking

Name	Composition	Crystal System	Conductivity	Detectivity
Franklinite	$Zn(Fe, Mn)_3O_4$	Isometric	None	Lacking
Göthite	$FeO(OH)$	Orthorhombic	None	Lacking
Hausmannite	Mn_3O_4	Tetragonal	Low	Lacking
Hematite	Fe_2O_3	Rhombohedral	Low	Lacking
Ilmenite	$FeTiO_3$	Rhombohedral	Low	Poor
Limonite	$2Fe_2O_3 \cdot 3H_2O$	(Amorphous)	None	Lacking
Magnetite	Fe_3O_4	Isometric	High	Lacking
Manganite	$MnO(OH)$	Orthorhombic	None	Lacking
Octahedrite	TiO_2	Tetragonal	None	Lacking
Plattnerite	PbO_2	Tetragonal	Low	Lacking
Psilomelane	$H_4MnO_5^+$	(Amorphous)	Low	Fair
Pyrolusite	MnO_2	Orthorhombic	Low	Poor
Rutile	TiO_2	Tetragonal	None	Lacking
Zincite	ZnO	Hexagonal	Low	Fair
Azurite	$2CuCO_3 \cdot Cu(OH)_2$	Monoclinic	None	Lacking
Bismutite	$Bi_2(OH)_2CO_3$	(Amorphous)	None	Lacking
Cerussite	$PbCO_3$	Orthorhombic	None	Lacking
Malachite	$CuCO_3 \cdot Cu(OH)_2$	Monoclinic	None	Lacking
Rhodochrosite	$MnCO_3$	Rhombohedral	None	Lacking
Siderite	$FeCO_3$	Rhombohedral	None	Lacking
Smithsonite	$ZnCO_3$	Rhombohedral	None	Lacking
Anglesite	$PbSO_4$	Orthorhombic	None	Lacking
Brochantite	$CuSO_4 \cdot 3Cu(OH)_2$	Orthorhombic	None	Lacking
Chalcanthite	$CuSO_4 \cdot 5H_2O$	Triclinic	None	Lacking
Crocoite	$PbCrO_4$	Monoclinic	None	Lacking

Name	Composition	Crystal System	Conductivity	Detectivity
Carnotite	$K(UO_2)VO_4 \cdot H_2O$	Orthorhombic	None	Lacking
Hübnerite	$MnWO_4$	Monoclinic	None	Lacking
Mimetite	$(PbCl)Pb_4(AsO_4)_3$	Hexagonal	None	Lacking
Pyromorphite	$[PbCl]Pb_4(PO_4)_3$	Hexagonal	None	Lacking
Scheelite	$CaWO_4$	Tetragonal	None	Lacking
Uraninite	(Rare earths)	Isometric	None	Lacking
Vanadinite	$(PbCl)Pb_4(VO_4)_3$	Hexagonal	None	Lacking
Vivianite	$Fe_3(PO_4)_2 \cdot 8H_2O$	Monoclinic	None	Lacking
Wolframite	$(Fe, Mn)WO_4$	Monoclinic	None	Lacking
Wulfenite	$PbMoO_4$	Tetragonal	None	Lacking

In addition to the crystal detectors listed above, several couples were found to be excellent detectors. Among these are zincite-bornite, zincite-chalcocite, zincite-chalcopyrite, and bornite-psilomelane.

MINERAL DESCRIPTION

GALENA

Galena or lead glance, is composed of lead sulphide. When found with a perfect cubical cleavage, it is very near to the theoretical PbS , though the presence of AgS in small amounts, does not alter the crystal habit. It is lead-gray in color and has a metallic lustre.

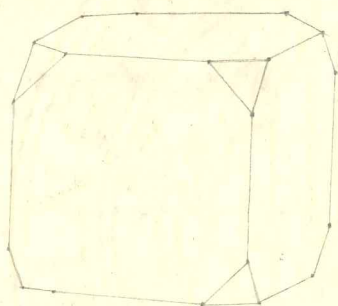


Figure 3

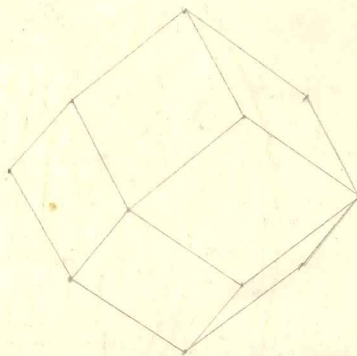


Figure 4

Galena crystallizes in the isometric or cubic system, and is usually found in the form of cubes. Occasionally, crystals are seen wherein the cube is beveled by an octahedron. (Figure 3) Less commonly, the rhombic dodecahedron is seen. (Figure 4) Galena often occurs in granular form, and is then spoken of as "steel galena."

The hardness of galena lies between that of the minerals selenite and calcite, and it is therefore one of the softer minerals. The specific gravity is 7.5.

Galena is a brittle mineral. It breaks into cubical shapes when cleaved, and the cleavage surfaces are

brilliant. For this reason, it is said to possess perfect cleavage in three directions at right angles to each other.

When it is fractured, or broken in some direction other than the cleavage directions, the surfaces produced are slightly curved. This type of breaking is usually spoken of as conchoidal or subconchoidal fracture. It is on these curved surfaces that the most persistent and reliable results are obtained as wireless detectors.

Among the minerals capable of detecting oscillating electric waves, galena is one of the best conductors of electricity. In order that galena may detect, the contact point must touch the crystal with a very delicate pressure. As the pressure of the point is increased beyond a certain point, the detectivity decreases, though the conductivity still continues to increase.

When galena is pulverized, and held in a suitable container, it will detect, even though a moderate pressure is applied. Galena is a highly sensitive detector and ranks with the very best when it is in perfect adjustment.

The delicate pressure of the contact point, and its consequent ease of being thrown out of adjustment, constitute the chief objection to the use of galena as a detector for radio work.

PYRITE

Pyrite is a disulphide of iron. When fresh, it is brass-yellow in color. The powdered mineral is greenish or brownish black. The lustre is metallic, often brilliant.

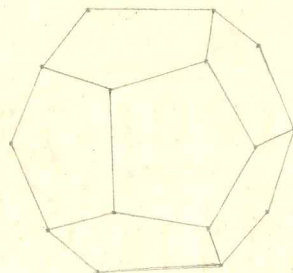


Figure 5

Pyrite crystallizes in the isometric system, and it is found either in the form of cubes or pentagonal dodecahedrons. The latter form is often called the pyritohedron. (Figure 5)

Pyrite is a hard mineral, its hardness lying between that of the minerals orthoclase and quartz. It is, therefore, too hard to be scratched by a knife-blade. The specific gravity varies from 4.5 to 5.1.

Crystals of pyrite do not cleave into forms bounded by plane surfaces. The mineral is brittle, and it fractures with decidedly curved or conchoidal faces.

Pyrite is a relatively poor conductor of electricity. A considerable amount of pressure can usually be applied to the contact point before it reaches its maximum of detecting. This is due, partly to the hardness of the

crystal, and partly to the fact that it is a poor conductor of electricity. When pyrite is pulverized, it will not function as a detector.

Pyrite slowly alters to a mineral of the same chemical composition. The secondary mineral is called marcasite. Crystals may show all gradations from pyrite to marcasite, even though the original shape of the pyrite crystal is preserved. Great periods of time are required to accomplish this change, yet the process is constantly going on.

The transition of pyrite into marcasite is accomplished by an internal rearrangement of the molecules. This action is accompanied by an increase in volume, and the color becomes more pale.

While marcasite is a better conductor of electricity than pyrite, it will not detect. If the alteration of pyrite to marcasite has proceeded to any extent, the crystal is worthless as a detector.

Among all of the specimens tested, none of the crystals of the pyritohedral form were found to be detectors.

SILICON

Crystalline silicon is an electric furnace product. It does not occur in nature owing to its great affinity for oxygen. It is lead-gray in color, and possesses a very brilliant metallic lustre. The powdered substance is also lead-gray.

Silicon crystallizes in the hexagonal system, in the form of needle-like crystals. They are usually six-sided elongated double-pyramids.

Silicon is a hard substance and possesses about the same hardness as pyrite. The specific gravity is 2.42.

Silicon is brittle, and it breaks with a conchoidal fracture. It does not possess any definite cleavage.

Crystalline silicon offers a great resistance to an electric current, and it is an extremely low conductor. On the brilliant crystal face, it requires a considerable amount of pressure to obtain the maximum detectivity. The hardness and poor conductivity account for this phenomena.

As with the other substances, it is the conchoidal surfaces of silicon which yield the most reliable results as detectors. The "high spots" and the "low spots" are noticeably superior to the intermediate points.

In the powdered form it acts as a detector, though great pressure must be applied before the best results are obtained.

MOLYBDENITE

Molybdenite is a sulphide of molybdenum answering to the chemical formula MoS_2 . It is lead-gray in color, with a bluish cast on the fresh surfaces. It has a metallic lustre, and resembles graphite in its appearance. It is greasy to the touch, and it soils the hands. In the powdered form it is bluish-gray. The specific gravity is 4.7 to 4.8.

Molybdenite crystallizes in the hexagonal system, in the form of double-pyramids. It has a perfect cleavage in one direction, causing it to break down into plate-like forms or laminae. These laminae are flexible, and an irregular surface is produced when they are torn across the cleavage directions.

The detectivity does not appear to depend upon the surface touched by the contact point, though slightly better results are obtained on the irregular surfaces. The nature of the surface touched, and not the direction through the crystal, seems to be the ruling factor that produces the best results.

CARBORUNDUM

Carborundum is a carbide of silicon, SiC. It is colorless when pure, though the commercial variety is colored brown or black. It has an adamantine lustre. The powdered substance is colored gray or greenish-gray.

Carborundum is one of the hardest substances known, being little inferior to diamond in this respect. The specific gravity is 3.23.

Carborundum crystallizes in the hexagonal system, in the form of six-sided plates. It has no definite cleavage, and it breaks with a conchoidal fracture.

It is a poor conductor of electricity. The detecting properties are not shown until a strong pressure is applied. It is not satisfactory for radio work unless a potential of four to six volts is established across the crystal. When this is done, it is one of the most reliable of crystal detectors, for the pressure of the contact point prevents it from getting out of adjustment.

Pulverized carborundum mixed with bornite is a more sensitive detector than either ingredient taken separately.

PSILOMELANE

Psilomelane is composed of a hydrous manganate, and possibly answers to the formula, H_4MnO_5 . It does not have a constant composition, and it usually contains some potassium or barium. The mineral is black in color, and has a dull earthy appearance. It does not occur in crystal form.

Its conductivity is about equal to that of pyrite. It is irregular and unreliable in its detecting properties, though, occasionally, a specimen will be found that yields excellent results. Good results are obtained with a psilomelane-bornite couple.

ZINCITE

Zincite is an oxide of zinc, ZnO . It is deep red in color, and has an adamantine lustre. The powdered mineral is orange in color.

Zincite crystals belong to the hexagonal system, though well shaped crystals are seldom met with. Zincite has one good cleavage, and sometimes other fair cleavage directions. The fracture is subconchoidal.

Zincite is a poor conductor of electricity. It is practically a nonconductor on a fractured surface or in the powdered form. The solid, or darker spots, are the only ones that will function as detectors.

When used with a metal contact point, zincite is a weak and unsatisfactory detector. If a crystal of bornite

chalcocite, or chalcopyrite is used to make the contact with the zincite, a sensitive detector is produced. This arrangement is spoken of as a couple.

BORNITE

Bornite, Cu_5FeS_4 , is a copper-red mineral with an iridescent tarnish. It is often called "peacock copper." It is dark-gray in the powdered form. It is a soft mineral, and can easily be scratched with a knife.

Bornite crystallizes in the isometric system, but good crystals are rarely seen. It has no cleavage, and it breaks with a conchoidal fracture.

It is the best conductor of electricity among all the known detectors. As a detector it is usually unsatisfactory, and an exceedingly delicate contact is required to make it function. Apparently it is too high a conductor to make a good detector.

MERCURY

If a steel point lightly touches the surface film of mercury, an excellent detector is sometimes obtained. It is questionable whether mercury is the real detector in this case. It may be the film of some amalgam that does the detecting.

The following minerals are detectors of powerful oscillations, but none of them are capable of receiving radio broadcast news,-

Argentite

Ilmenite

Brookite

Pyrolusite

Chalcocite

Stannite

Chalcopyrite

Tetrahedrite

DEDUCTIONS

An examination of the table of detectivity will show the relation of composition to detecting power. Silicates, phosphates, halogen salts, sulphates, and carbonates are nonconductors and nondetectors of weak oscillations, such as are used in radio work. Crystals that will detect, are confined to elements, sulphides, and oxides. The presence of arsenic or antimony appears to be injurious to both conductivity and detectivity. Beyond this point, all generalizations on the relation of composition to detectivity seem to meet with immediate and glaring exceptions.

Detectors are not confined to any crystal system. Of the substances found to be detectors, six belong to the isometric system, one to the tetragonal, four to the hexagonal, one to the rhombohedral, three to the orthorhombic, and the remainder are amorphous.

The conductivity of electricity through simple isometric crystals and amorphous substances is equal in all directions. These substances are said to be isotropic because their optical or electromagnetic properties are independent of the orientation.

Crystals of all other systems are anisotropic with respect to their conductivity of electromagnetic vibrations. The maximum or minimum ease of vibration lies parallel to the long direction of the crystal in the tetragonal, hexagonal,

and rhombohedral systems. This long direction of the crystal, (or the shortest in the case of tabular crystals) is an axis of electromagnetic symmetry. Such crystals are called uniaxial. Crystals belonging to the orthorhombic, monoclinic, and triclinic systems possess two axes of electromagnetic symmetry, and are called biaxial.

While pyrite and galena crystallize in the isometric system, they do not always possess the full symmetry of that group. A cube of pyrite is really a combination of forms, and their interference with each other is shown by the striations on the crystal faces. Crystals that have formed under a strain are never truly isotropic, and it is practically certain that a small amount of double refraction exists in a cube of pyrite. It is noticeable that galena crystals which show a strain are more liable to function as detectors.

When two anisotropic crystals are placed in series, and in the proper orientation with respect to each other, the current is cut off. If one of these crystals is rotated through ninety degrees, a good conductor may result. The effect is similar to that of a Nicol prism.

Evidently an electric current behaves in an unusual manner, when it enters a crystal that is anisotropic. It appears to be plane polarized, just as a ray of light is polarized in the same type of substance.

It is a fact worthy of notice that the best detecting crystals are low conductors of electricity.

Detectivity appears to be produced by a rectifying action within the crystal. It is possible that it is due to total internal reflection of one of the polarized rays.

In general, crystal detectors yield the best results when conchoidal surfaces are used to make the contact. The high spots and the low spots on such a surface are generally superior to the intermediate points. The required contact pressure varies directly with the crystal hardness, and inversely with the conductivity.

Crystal detectivity appears to be tied up with molecular structure. The ultimate solution of the problem would therefore seem to involve a further study of the basic principles of physical science.

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