

THE CRYSTAL STRUCTURE OF SOME METALLIC  
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## ABSTRACT

By making use of crystal structure as the criterion of isomorphism, argentite, hessite, eucairite, and naumannite are ruled out of the galena group because their structures are entirely different from that of galena. Clausthalite and altaite are isomorphous with galena, as their structures are similar. The isomorphism of the pyrite group is verified, except in the case of smaltite and chloanthite, which gave unsatisfactory data. Covellite and cinnabar are found not to be isomorphous. Cinnabar has a simple rhombohedral structure.

Argentite and acanthite are shown to have identical structures, and hence do not represent distinct mineral species.

Values obtained for the atomic radii of selenium and tellurium from the compounds PbSe and PbTe are Se 1.15 Å, and Te 1.27 Å.

## INTRODUCTION

The determination of the structure of a crystal is important in itself, but becomes of much greater significance when the structure can be correlated with chemical or physical properties, or when it has a bearing on certain conceptions which originated before such determinations were possible. Accordingly, in this investigation, not only was an attempt made to determine the structures of some of the metallic sulfides, but also the results so obtained were used as the criterion of isomorphism.

The mineralogist uses isomorphism as a convenient method of grouping minerals which have closely related properties. An isomorphous group is usually defined as one in which the members have analagous chemical compositions and crystalize in strikingly similar forms. Such a definition is capable of varied interpretations. Aside from certain groups where the isomorphism is very evident, it is a matter of opinion as to what compositions can be considered as analagous, or what forms are strikingly similar. In this investigation it was decided to use the crystal structure as the final test of isomorphism. This introduces nothing radically different into our conception of isomorphism. It is merely making use of a fundamental fact rather than a certain manifestation of that fact. The crystal form is ordinarily the outward expression of the inner structure, but if for any reason it furnishes evidence which is not

\* From a dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the University of Michigan, June, 1925.

well defined, the isomorphism should be based upon the structure itself.

This investigation covered the sulfides of a number of the metallic elements, and also included the closely related selenides and tellurides, as well as one arsenide and an antimonide. The term metallic sulfide is used in a general sense throughout the paper, and includes these similar compounds.

The equipment used in this investigation was an X-ray Diffraction Apparatus built by the General Electric Company. It is a self-contained unit, consisting of a high tension transformer and a water cooled Coolidge tube, with a molybdenum target. The radiation is rendered practically monochromatic by the use of a  $ZrO_2$  filter. The tube was ordinarily run at about 25 mil-amperes and from 30 to 35 kilovolts, and the exposures varied from 15 to 40 hours. The samples to be photographed were powdered and passed through a 200 mesh screen. In certain cases it was necessary to further grind the sample, and obtain finer material by suspension in water. The powder was placed in a glass tube, made by drawing out thin walled glass tubing to an outside diameter of about 1 mm.

#### THE GALENA GROUP

This group consists of a series of monosulfides, selenides, and tellurides of lead, silver, and copper, of which the more important members are as follows:

Galena	PbS
Clausthalite	PbSe
Altaite	PbTe
Argentite	$Ag_2S$
Hessite	$Ag_2Te$
Eucairite	$(Ag, Cu)_2Se$
Naumannite	$(Ag_2, Pb)Se$

The reason for including the galena group in this investigation was to determine whether or not the different members have the same structures. According to the theory of space groups it should be impossible for a compound like  $Ag_2S$  to have a structure similar to that of PbS. If the structures are different, similarity of crystal form is merely a coincidence, and does not indicate a fundamental relationship. In that case the compounds should not be considered isomorphous.

#### GALENA

Galena has the NaCl type of structure,<sup>1</sup> although no data have been published. The results secured by means of powder photo-

graphs are shown in Table I, where the spacings of the planes causing the reflections are given directly in Ångstrom units. The specimens used were as follows: (1) a cleavage fragment from an unknown locality; (2) an argentiferous galena from Colorado; (3) a non-argentiferous galena from Kansas; (4) material prepared artificially by precipitation from solution; (5) material prepared artificially by the direct union of the elements. There was no measurable difference between specimens (2) and (3). This was to be expected, for although the one from Colorado was classed as a good silver ore, the actual percentage of silver was not much over 0.1 per cent. The length of the side of the unit cube as determined from the average of the results from the plane 100 (2) was 5.93 Å.

The structure is made up of two interpenetrating face centered cubes, but the diffraction pattern is characteristic of a simple face centered cube arrangement. This is because the reflecting power of the S atoms is relatively so much less than that of the Pb atoms that they are practically negligible, and the pattern is determined by the Pb atoms alone. The theoretical and the observed intensities of the reflections from the different planes are shown in Table II.

#### CLAUSTHALITE

No specimen of natural PbSe was available, so the measurements were made on artificial material. The results are shown in Table I. It will be noticed that the interplanar distances are a little greater than in the case of galena, for the introduction of the larger Se atoms naturally causes an enlargement of the structure. The length of the cube side was found to be 6.14 Å. The diffraction pattern was quite similar to that of galena, except for some variation in the relative intensities of reflections from corresponding planes, due to the greater reflecting power of the Se as compared with the S atoms. Calculated and observed intensities are given in Table II.

#### ALTAITE

A specimen of the natural mineral from New Mexico was available but it proved to be Pb(Te, S) rather than PbTe. The spacings were larger than for either galena or clausthalite, but not as large as would be expected from the introduction of the larger Te atoms. Accordingly, artificially prepared material was measured, with the results shown in Table I.

The pattern obtained was different from those of the two preceding minerals. It indicated a simple cube arrangement rather

than a face centered cube. No reflections were secured from the planes 111, 311, and 331, whereas they were all present for galena and clausthalite, but this does not mean that it possesses a different structure. The Te atom is so much greater in its reflecting power that it cannot be ignored as was the S atom in galena. Both the Pb and the Te atoms must be considered. The effect of two interpenetrating face centered cube lattices, where both are nearly equivalent in reflecting power, is practically the same as that of a simple cube arrangement, with a cube edge only one half as long. Such a cube should give reflections from planes 100, 110, 111, 100(2), 210, and 211. To make these comparable with the larger cube, the order of reflection would have to be multiplied by two. These planes then become 100(2), 110(2), 111(2), 100(4), 210(2), and 221(2), and it will be seen in Table I that these are the planes which gave reflections for PbTe. The value for the spacing from the plane 100(2) gives 6.34 Å for the length of the unit cube edge.

Table I. VALUES OF INTERPLANAR DISTANCES IN Å UNITS

Plane	Galena PbS					PbSe	PbTe
	1	2	3	4	5		
100	a	a	a	a	a	a	a
110	a	a	a	a	a	a	a
111	3.42	3.40	3.40	3.42	3.40	3.55	a
100(2)	2.98	2.95	2.95	2.98	2.95	3.07	3.19
210	a	a	a	a	a	a	a
211	a	a	a	a	a	a	a
110(2)	2.100	2.085	2.085	2.100	2.085	2.17	2.26
100(3)	a	a	a	a	a	a	a
221	a	a	a	a	a	a	a
310	a	a	a	a	a	a	a
311	1.795	1.782	1.782	1.790	1.780	1.840	a
111(2)	1.720	1.708	1.708	1.720	1.700	1.760	1.845
320	a	a	a	a	a	a	a
321	a	a	a	a	a	a	a
100(4)	1.490	1.480	1.485	1.485	1.480	1.525	1.600
410	a	a	a	a	a	a	a
330	a	a	a	a	a	a	a
331	1.363	1.362	1.362	-	-	1.40	a
210(2)	1.329	1.328	1.328	-	-	1.360	1.430
211(2)	1.210	1.210	1.210	-	-	1.240	1.310

*Explanation of the table.*— All possible planes for a cubic structure with spacings greater than that of 211(2) are listed. The letter "a" signifies that no reflection was secured.

Table II. CALCULATED AND OBSERVED INTENSITIES OF REFLECTION

Plane	PbS		PbSe		PbTe	
	a	b	a	b	a	b
111	8.7	1	3.4	4	0.9	0
100(2)	10.0	1	10.0	1	10.0	1
110(2)	9.2	1	8.9	1	8.9	1
311	5.4	2	2.2	5	0.6	0
111(2)	3.7	4	3.7	3	3.7	3
100(4)	2.0	6	2.1	5	2.1	4
331	3.0	5	1.2	6	0.3	0
210(2)	6.3	3	6.0	2	6.1	2
211(2)	5.0	3	4.8	3	4.9	3

*Explanation of the table.*—The theoretical intensities (column a) were calculated by means of the intensity formula,<sup>2</sup> and the values were reduced to a scale of ten, so that the most intense reflections have the value 10. In the case of the observed values (column b) no attempt was made to measure the intensities quantitatively. On each film the most intense line (or lines) was given the value of 1, and the remaining lines were arranged in order of decreasing intensity with the values of 2, 3, 4, and so on, with 0 indicating complete absence. It will be seen that the order so obtained agrees closely with the order of the calculated intensities.

This table shows why the diffraction pattern from PbTe is of a different type than those of the other two. The intensities for planes 111, 311, and 331 are very low compared to those of the remaining planes. On a film where the others showed very distinctly, these three would be entirely obscured by the general blackening of the film. The pattern would consist, then, of only the planes 100(2), 110(2), 111(2), 100(4), 210(2), and 211(2). As mentioned before, if the order of these reflections is divided by two, these become the planes characteristic of a simple cube, the length of whose edge has been reduced by one half.

#### ATOMIC RADII OF Se AND Te

If in a compound selenium or tellurium is partly replaced by sulfur, or if lead is partly replaced by silver, as in the mineral *naumannite*, the size of the unit cell will be changed. Hence, any measurements as to the size of the atoms must be made on material in which the exact amount of the replacement is known, or on material where there is no replacement. This latter case is much simpler, and the data have been secured entirely from the artificially prepared pure PbS, PbSe, and PbTe.

There is no definite radius for the atom of a given element. In fact, the term "radius" is hardly justified, for it implies that the

atom is spherical. The actual meaning of the term can be explained as follows. As atoms occur in a structure, there is a certain distance between the centers of two adjacent atoms. If the two are alike, half of this distance is referred to as their radius. If they are unlike, a certain fraction of this distance is assigned to one of the atoms as a measure of its radius, and the remaining distance as the radius of the other atom.

If we assume that the S atom in the sulfides has a constant radius, then it is a simple matter to calculate the radii of Se and Te. In the mineral pyrite,  $\text{FeS}_2$ , the two S atoms are so placed that they are much nearer to each other than to any of the Fe atoms. This distance of nearest approach is 2.08 Å, so the radius of S is 1.04 Å. In galena, the distance from a Pb atom to a S is 2.96 Å. If 1.04 Å of this distance is assigned to the S atom, then the Pb atom must have a radius of 1.92 Å. Using this value in turn in the two compounds PbSe and PbTe gives 1.15 Å and 1.27 Å as the radii of Se and Te, respectively.

It might be considered that since pyrite and galena have different types of structures, the S atoms would not necessarily have the same radius in the two compounds. In that case the value of 1.04 Å would not hold for S in galena, and the values obtained for Se and Te would be wrong, although they would still represent the correct relative sizes in comparison to S.

#### ARGENTITE

The similarity of the crystal forms of argentite and galena is apparently good evidence for considering them isomorphous. The cube, octahedron, and dodecahedron are commonly observed on both minerals. However, argentite crystals are frequently distorted. Distortion usually refers to an unequal development of faces belonging to the same form, without any change in the angular position of the faces. In the case of argentite, the interfacial angles are sometimes distorted. For example, the specimen referred to as number 2 occurred in well formed crystals, which at first glance appeared to be octahedrons. Measurement of the angles showed, however, that instead of the theoretical value of approximately  $70^\circ$ , they were actually about  $63^\circ$ . The significance of this will be discussed later.

Six specimens of  $\text{Ag}_2\text{S}$  were used, as follows: (1) a crystal from Saxony, which appeared to be a cube in combination with a trigonal

trisoctahedron; (2) the steep octahedral crystal already mentioned, from Mexico; (3) and (4) massive specimens from an unknown locality; (5) material artificially prepared by precipitation from solution; and (6) material artificially prepared by the direct union of the elements. All six samples gave identical diffraction patterns of an unexpected type.

It is well known that the interplanar spacings in a cubic crystal have a very simple relationship. If  $a_0$  be the length of the side of the unit cube, or in other words, if  $a_0 = d_{100}$ , then the spacing for

any other plane  $hkl$  for any order  $n$  is equal to  $\frac{a_0}{\sqrt{(nh)^2 + (nk)^2 + (nl)^2}}$ .

This means that no matter what the absolute size of a cubic structure, the spacings are always in the ratio of  $\frac{a_0}{\sqrt{1}} : \frac{a_0}{\sqrt{2}} : \frac{a_0}{\sqrt{3}} : \frac{a_0}{\sqrt{4}}$ , etc.

It is accordingly possible to calculate the spacings for all possible planes in terms of  $a_0$ . In Table I, for instance, all planes with

spacings from  $\frac{a_0}{\sqrt{1}}$  to  $\frac{a_0}{\sqrt{24}}$  were listed. Not all of these gave reflections, however; but since there are no other possible planes with

spacings within the above limits, there can be no other reflections than those which correspond to these planes. Any additional reflection would correspond to a plane with impossible spacings.

If the spacings calculated from an extended series  $\frac{a_0}{\sqrt{1}} : \frac{a_0}{\sqrt{2}} \dots$

are plotted on a logarithm scale, then the differences due to the different values of  $a_0$  disappear. Whatever the absolute value of  $a_0$ , the relative spacings would be the same, and all cubic structures would be comparable. Such a plotting of the logarithms of the spacings might be referred to as a generalized cubic diffraction pattern. No matter how complex a cubic structure might be, it could not have lines in its diffraction pattern which did not correspond to this general pattern if they were plotted on a logarithm scale.

It was stated that the diffraction pattern from argentite was of an unexpected type. The spacings as determined from its pattern were plotted on the logarithm scale and there was no agreement with the generalized pattern. Not only do the lines occur in different positions, but their spacings are much closer together.

There are two possible explanations for this. As the interplanar spacings become smaller the lines of the pattern are much closer together. These lines correspond to planes of either high orders or of complex indices, and are usually secured from complex structures. The first explanation, then, would be that argentite has a complex cubic structure, and that its lines would match the generalized pattern in the region where the lines are very close together. Such a matching is difficult to detect because the error involved becomes as great as the distances between adjacent lines. This explanation, however, is not in accord with the available crystal structure data. Simple compounds appear to have simple structures, and there would seem to be no justification for assuming a simple compound like  $\text{Ag}_2\text{S}$  to have a complex structure. The second explanation is more reasonable: namely, that argentite is not cubic. Structures other than cubic are apt to have the lines in their patterns crowded close together. This is illustrated by comparing the cubic and orthorhombic systems. In the cubic, where the three axes are all equal, the planes 001, 010, and 100 are identical, as are also 110, 011, and 101; or 123, 132, 213, 231, 312, and 321; etc., while in the orthorhombic these would all be different, and would have different spacings. This fact makes the patterns of such crystals usually very complex, and the solution of their structures is difficult.

Doubt as to the true cubic character of argentite is suggested by the distorted angles observed on some crystals. Furthermore,  $\text{Ag}_2\text{S}$  occurs also as the mineral acanthite, classed by Dana<sup>3</sup> as orthorhombic, but possibly merely distorted argentite. Several specimens of acanthite were available and all gave diffraction patterns identical to those from argentite, indicating that there is no difference in structure between the two minerals. The apparently authentic cubic forms on argentite can be accounted for by assuming that  $\text{Ag}_2\text{S}$  has a high temperature cubic modification, which is unstable at lower temperatures. A crystal formed as cubic would retain its general outward form on cooling, but would undergo molecular readjustment, becoming a pseudomorph of acanthite after the high temperature form. This is somewhat similar to the case of the mineral leucite, which is cubic above  $500^\circ\text{C}$ . Below this temperature there occurs a readjustment, involving the formation of a complex twinned structure, composed of orthorhombic individuals. The outward form is still apparently cubic, with only very slight changes in the interfacial angles.



In regard to argentite, the uninterpreted diffraction pattern is insufficient to prove it to be orthorhombic. However, it is identical with acanthite, and both are entirely different from galena. The two probably have structures similar to orthorhombic chalcocite,  $\text{Cu}_2\text{S}$ . It should also be emphasized that even a high temperature cubic form could not be structurally isomorphous with galena, because two Ag atoms could not be equivalent to one Pb atom.

#### HESSITE

A specimen of hessite from Transylvania was available for investigation. This gave a diffraction pattern very similar to argentite, indicating that this mineral, also, is not isomorphous with galena. This furnishes additional proof that  $\text{Ag}_2$  is not equivalent to Pb in a crystal structure.

#### EUCAIRITE

There is no mineral corresponding to the composition  $\text{Ag}_2\text{Se}$ , so eucairite was used. The Ag and Cu selenides should be able to form mixed crystals, and it would be expected that  $(\text{Ag}, \text{Cu})_2\text{Se}$  would have the same structure as  $\text{Ag}_2\text{Se}$ . The specimen available was not pure. The eucairite was intimately mixed with an unknown mineral, and both were embedded in calcite. The latter was removed by treatment with dilute acid, while the former was partially removed by hand sorting under a magnifying glass. The diffraction pattern secured may not be due entirely to eucairite, but none of the lines agreed with the generalized cubic pattern. The introduction of the Cu atoms would change the crystallographic constants so that the pattern could not be expected to resemble that of argentite. While there is no direct proof of isomorphism with argentite, it is clearly established that eucairite is not isomorphous with galena.

#### NAUMANNITE

It was thought that the study of a compound such as this might throw some light on the relation of galena and argentite. If they are isomorphous, they ought to be able to form mixed crystals, with the Ag and the Pb in varying proportions. If they are not isomorphous, mixed crystals should not occur.

No specimen of naumannite was available, but the corresponding sulfide was prepared artificially. Two alloys of Pb and Ag were made, one with about 13 per cent and the other about 20 per cent

of Ag. These were finely divided, mixed with sulfur, and heated. The heat of the reaction drives off the excess sulfur not needed for combination.

The diffraction pattern from these two PbAg sulfides proved to be that of pure PbS, which was rather unexpected. It was expected that the pattern would either be that of a mixture of the two sulfides, or else correspond to a PbS structure with a different sized unit cell, because of the presence of the Ag atoms. Since the unit cell is of the same size, it must mean that there are no Ag atoms replacing Pb atoms in the structure.

There is a marked difference in the readiness with which lead and silver combine with sulfur. Molecular quantities of lead and sulfur unite rapidly with evolution of heat, while to form Ag<sub>2</sub>S it is necessary to use excess sulfur and prolonged heating. It may be that the lead in the alloy combined with the sulfur, while the silver did not. In that case the silver would be mechanically held in the PbS structure. It would not be present as crystallized silver, and hence would not give the silver diffraction pattern.

This again supports the conclusion that PbS and Ag<sub>2</sub>S are not isomorphous. The X-ray evidence in each case has indicated this fact. This does not establish the general conclusion that two monovalent atoms can never replace a single bivalent atom in a given structure, but it does prove it in this case, and further study of similar cases will probably show the same results.

#### THE PYRITE GROUP

This group consists of the following minerals:

Pyrite	FeS <sub>2</sub>
Hauerite	MnS <sub>2</sub>
Sperrylite	PtAs <sub>2</sub>
Ullmannite	NiSbS
Gersdorffite	NiAsS
Cobaltite	CoAsS
Smaltite	CoAs <sub>2</sub>
Chloanthite	NiAs <sub>2</sub>

These minerals occur in good crystals, the pyritohedron, cube, and octahedron being commonly observed. Their compositions are entirely analagous, and the series has long been considered as a well established case of isomorphism. It is only recently that any question has been raised as to the validity of this isomorphism.

Cobaltite occurs in perfectly formed crystals, and has been found by both the Braggs<sup>4</sup> and Mechling<sup>5</sup> to have the pyrite structure, but Schneiderhöhn<sup>6</sup> reports that it is not cubic at all. His examination of polished sections of the crystals by reflected polarized light revealed a structure made up of intimately twinned orthorhombic individuals. This, again, would seem to suggest a condition similar to the mineral leucite, which was referred to under the discussion of argentite as having high and low temperature modifications. If this be the true explanation, it would mean that the high temperature form was isomorphous with pyrite, rather than the ordinary or low temperature form. But, this does not explain the results secured by the Braggs and Mechling. It was thought that further investigation might settle this question.

#### PYRITE

The structure of pyrite has been worked out very thoroughly<sup>7, 8</sup>. Four molecules of  $\text{FeS}_2$  are associated with each unit cell. The Fe atoms lie at the corners and face centers of the unit cube, the length of whose edge is 5.38 Å. This unit cube can be thought of as divided into eight smaller cubes by passing planes through the center—from top to bottom, from side to side, and from front to rear. The alternate corners of one of these cubes will be occupied by the Fe atoms, and any diagonal through the center will always run from a corner occupied by an Fe atom to a vacant one. A sulfur atom is situated in each cube and lies on the diagonal toward the vacant corner, at a distance from it of approximately one fifth of the length of the diagonal.

A powder photograph of pyrite was made, and the diffraction pattern secured was used as the standard by which to judge the other members of the group. The planes represented in the pattern are shown in Table III, together with their observed intensities of reflection.

#### HAUERITE

This mineral was not included in this investigation. Its structure has been determined<sup>9</sup> and there is no question concerning its isomorphism with pyrite.

#### SPERRYLITE

The diffraction pattern from sperrylite is essentially the same as that from pyrite. There are differences in the relative intensities,

due to the difference in reflecting power of the Fe and S atoms, as compared with the Pt and As. The theoretical and observed intensities for the important planes are shown in Table III. For calculating the theoretical values it was assumed that the Pt and As atoms were both larger than the Fe and S in the same general proportion. Thus the As atoms should occupy the same relative positions on the diagonals of the small cubes as do the S atoms in pyrite. The observed intensities and those calculated on this basis agree fairly well, indicating that this assumption is approximately correct. The size of the unit cube of sperrylite was found to be 5.94 Å.

#### ULLMANNITE

Ullmannite is of interest because crystals have been observed which have lower symmetry than that of pyrite. The ordinary form is the cube, sometimes with pyritohedral striations. Miers<sup>10</sup> reports the occurrence of tetrahedral forms on crystals from Carinthia. The combination of tetrahedral and pyritohedral symmetry means that the crystals should be referred to the lowest symmetry class of the cubic system. The explanation has been given that this lower symmetry is due to the substitution of an Sb atom for one of the two S atoms. In pyrite the sulfur atoms are symmetrically placed with respect to three planes at right angles to each other. Since the Sb atom is not equivalent to the S in size, its substitution in alternate positions occupied by S would destroy this symmetry. No statement of an actual proof for this kind of a structure is on record, nor are there any data concerning the size of the unit cell.

The diffraction pattern is fairly similar to that of pyrite, and indicates that the structure is the same. The Sb atoms must occupy alternate positions with the S, for no other arrangement would be possible according to the theory of space groups.

Nickel has practically the same reflecting power as iron, but the presence of the antimony should make an appreciable difference in the relative intensities of reflection from pyrite and ullmannite. This is shown in Table III, where the observed intensities are given. In pyrite the planes 311, 211, and 210 have the intensities 1, 5, and 4 respectively, whereas in ullmannite these same planes are rated as 1.5, 2, and 1.

By assuming that the Sb atoms occupy the same relative position on the diagonals of the small cubes as do the S atoms in pyrite, the

calculated values do not agree closely with the observed intensities. For example, the reflection from the plane 111 was plainly visible, although not very intense, but according to the calculated value it should have been too weak to appear at all. Apparently, the positions have been slightly changed with reference to pyrite. The whole structure is, of course, on a larger scale because of the introduction of the larger Sb atoms. It is evident from a study of a three dimensional model of the structure that the Sb atoms would lie a little closer, and the S atoms a little farther from the vacant corners of the small cubes than do the S atoms in pyrite. By making such a change arbitrarily, the calculated results given in Table III were secured, and it will be seen that the agreement is fair.

The reflection obtained from the 100(2) plane gave a value of 5.91 Å for the length of the side of the unit cube.

#### GERSDORFFITE

The first specimen examined was from Austria and gave a diffraction pattern identical to those which were obtained from smaltite, indicating that it was  $\text{NiAs}_2$  rather than  $\text{NiAsS}$ . A second specimen, from Germany, proved to be gersdorffite. Its diffraction pattern is quite analogous to that of ullmannite, as would be expected. The side of the unit cube was found to be 5.68 Å. It should be pointed out that such dimensions as these refer only to the specimen examined. The size of the unit cell may vary greatly because of the extensive replacements which occur in the sulfide minerals. Gersdorffite, for example, may contain from 2 to 6 per cent of iron, small amounts of cobalt, and sometimes antimony. To obtain exact measurements of the unit cell, artificially prepared pure material would have to be used.

#### COBALTITE

The conflicting evidence in regard to cobaltite has already been stated. The diffraction pattern secured in this investigation was a cubic one, and gave a value for the side of the unit cell of 5.58 Å. This confirms the results obtained by the Braggs and by Mechling. As far as is known, none of the crystals used for X-ray analysis were examined by reflected light. It would be easy to conclude, therefore, that these are all cubic, while those examined by Schneiderhöhn are orthorhombic. This scarcely seems possible, for Schneiderhöhn found that without exception all crystals examined

were orthorhombic. On the other hand, crystals from widely different localities were used for X-ray analysis, and all were uniformly cubic. It would seem necessary to conclude that either the X-ray data are correct, and the observations of Schneiderhöhn wrong, or that his observations are correct, and the X-ray data wrong.

The method of examining polished sections of crystals by reflected polarized light is a sound one, and there seems to be no ground for doubting the results. On the other hand, judging from the large amount of consistent X-ray data obtained from all types of compounds, it would seem unwarranted to conclude that apparently authentic data can be secured which are not in accord with the structure producing them. If both results are correct, there must be some manner of reconciling them. Two possibilities suggest themselves. The first is concerned with the relative sensibility of the X-ray methods, and the second with the surface effects which may be produced by grinding and polishing mineral sections.

The first possibility can be explained as follows: chalcopyrite,  $\text{CuFeS}_2$ , crystallizes in the tetragonal system. Its axial ratio is 1:0.985, which is very nearly 1:1. Its diffraction pattern is, to all appearances, a cubic one, showing that X-rays, in the powder method at least, cannot distinguish between a cubic crystal and a tetragonal crystal with a value for the  $c$  axis so near to unity. It might be that the cobaltite structure is orthorhombic, but so nearly cubic that the X-ray data appear to be cubic.

Indirect evidence on this point can be obtained from pyrite and marcasite, the cubic and orthorhombic forms of  $\text{FeS}_2$ , respectively. Their diffraction patterns, although similar in some respects, show distinct differences, and that of marcasite could not be interpreted as belonging to a crystal isomorphous with pyrite. There is no orthorhombic mineral with the exact composition  $\text{CoAsS}$ . However, glaucodot is orthorhombic and differs from cobaltite in composition only in the presence of some iron, its composition being  $(\text{Co,Fe})\text{AsS}$ . It gives an entirely different pattern than does cobaltite. It is logical to conclude, therefore, that there is sufficient difference between cubic and orthorhombic  $\text{CoAsS}$  to distinguish their diffraction patterns, and that cobaltite, if really twinned orthorhombic, ought not to give a cubic pattern.

It might be well to state at this time that there is no possibility of cobaltite simulating a cubic structure by means of twinning. Twinning does sometimes result in "mimicry," as in the case of orthorhombic aragonite, which appears to be hexagonal, but this mimicry is in outward form only. The structure of each of the various individuals making up the whole is unchanged. A Laue photograph through a section of a twinned crystal might be affected, but in the powder method there would be no effect unless the twinning were sub-microscopic, in which case it could not be detected by optical methods.

The second possible method of reconciling the conflicting evidence is based on the assumption that cobaltite is metastable at ordinary temperatures. It is a well known fact that the grinding and polishing of metallographic sections may bring about decided changes in the surface layers of atoms. Alling<sup>11</sup> reports that the process of grinding brings about the change from the metastable orthoclase to microcline, with the development of the characteristic microcline twinning. In order to obtain results by the use of reflected polarized light a very high degree of polishing is necessary. It might be that this process brings about a superficially twinned orthorhombic structure, while the interior remains unchanged. The observations on these sections are not made by transmitted light. A change in a few atomic layers would be sufficient to be detected by optical methods, while no effect at all would be observed on the X-ray photograph.

In a transparent substance it would be easy to determine whether or not such a change was limited to the surface, by the use of ordinary petrographic methods. In opaque substances, it should be equally easy to determine if a structural change had occurred throughout the crystal, by the use of X-rays. The evidence actually secured indicates that such a change has not taken place. There seems to be no way in which evidence could be secured as to the surface structure by X-ray methods, for it would be impossible to obtain these surface layers, only a few atoms deep, separate from the remaining unchanged material.

It is not possible to prove at present if this second possibility is correct, or whether still another explanation might be found. The whole question of the dimorphous sulfide minerals is one deserving further study.

## SMALTITE AND CHLOANTHITE

These two minerals have the compositions  $\text{CoAs}_2$  and  $\text{NiAs}_2$ , respectively. The exact compositions represent the end members of a series of mixed crystals and rarely occur. The names smaltite and chloanthite are given to the various members of the series, depending upon which element predominates. There is so little difference between the Ni and Co atoms in size or in reflecting power that the diffraction patterns of the pure compounds should be very similar, and no difference at all should be observed when both Co and Ni are present in considerable amounts.

This was found to be true. Samples prepared from specimens from Germany, which qualitative tests showed to contain both Co and Ni, gave indistinguishable patterns. Specimens labelled "gersdorffite" and "skutterudite" also gave patterns of the same type, proving that they were actually either smaltite or chloanthite. In all, then, diffraction patterns were obtained from four samples.

These patterns are of a very puzzling nature. Except for two lines, they agree perfectly with a cubic arrangement. Calculations based on the density, the weight of a molecule, and the assumption that the unit cell contains four molecules, as does pyrite, give the length for the side of the unit cube of 5.96 Å, which checks closely with the value determined from the pattern.

However, the intensities of the reflections actually observed do not agree with those calculated for the pyrite structure. The reflection from plane 210 is strongest, while the calculated value is fourth, and that from 100(2) is absent, while for the pyrite structure it is quite strong, being rated second. These two variations do not present any special difficulties, for the former can be accounted for by the increase in reflecting power of the As as compared to the S atom, and the latter by assuming a slight change in the relative position of the As atoms. In pyrite the S atoms lie on the diagonals of the small cubes toward the vacant corners. If the occupied corners are considered as the origin, the co-ordinates of an S atom would be  $uuu$ , where  $u$  equals  $.338a_0$ . ( $a_0$  is the length of the edge of the unit cube). It is evident from a study of a three dimensional model that if larger As atoms be substituted for the smaller S, while Ni or Co are practically the same as Fe, the value of  $u$  would have to be less. In other words, the As atoms would not be so



relatively close to the vacant corners. By assuming  $u$  to have a value of about .350 instead of .388, the reflection from plane 100(2) disappears.

Other reflections have intensities that cannot thus be reconciled, however. The reflection from plane 211 is missing. If  $u$  were about .275, this could be expected, but if it is .350 as required by the plane 100(2), a medium strong reflection should occur. The reflection from plane 100(3) is present, although not intense, and that from 310 is very strong, but neither of these should be present for any values of  $u$  whatever in this type of structure. The reflection from 311 is weak, whereas it should be strong. In pyrite, this 311 reflection is the most intense, and no value of  $u$  can be assumed which will greatly reduce it.

The diffraction pattern presents two difficulties, then. Two lines do not fit in with a cubic pattern, and some of those that do fit do not have the intensities expected from the pyrite type of structure. The two lines are of such intensity that they cannot be ignored as being due to a trace of impurity. By assigning more complex indices to the planes, the pattern can be made to agree fairly well with a cubic arrangement, with the side of the unit cube 8.28 Å. But, a cell of this size would have to contain ten and a fraction molecules of either smaltite or chloanthite. The fraction might be due to a slight error in the density determination, but neither ten nor eleven molecules could be arranged in a cube with cubic symmetry.

It may be that we are not dealing with a homogeneous substance, and that the peculiar pattern is due to a composite effect. Extra lines in a diffraction pattern may be due to impurities. If the impurity is in solid solution the size of the unit cell might be changed but no new lines would appear in the pattern. If it is merely mechanically mixed with the substance, then each would give a pattern, the one superposed on the other. If it were present in only a small amount, only its most intense lines would appear.

Volkhardt<sup>12</sup> reports that when smaltite is treated with acid, a portion dissolves, leaving a residue with a higher percentage of arsenic—probably  $\text{CoAs}_3$ . Baumhauer<sup>13</sup> reports a zonal arrangement in smaltite crystals. Beutell<sup>14</sup> states that smaltite crystals examined by him consisted of an outer zone of  $\text{CoAs}_2$ , with  $\text{CoAs}_3$  and  $\text{Co}_2\text{As}_3$  on the inside. (In this same reference, Beutell says that skutterudite,  $\text{CoAs}_3$ , is probably not cubic, but occurs as a pseudomorph after smaltite). This zonal structure seemed to offer an explanation

for the extra lines in the smaltite pattern. If they corresponded to the chief lines of the skutterudite pattern, the whole question would be solved.

It has been impossible to secure a single crystal of skutterudite. Extremely small crystals were picked out from a specimen labelled skutterudite, but they gave the  $\text{CoAs}_2$  pattern, indicating that they were smaltite. Material consisting of an intimate mixture of skutterudite and smaltite was treated with sulfuric acid and  $\text{KClO}_3$ , according to the method of Parsons,<sup>15</sup> and a diffraction pattern secured from the residue, supposed to be  $\text{CoAs}_3$ . If this residue is skutterudite, it is quite certain that Beutell was right, and that it is not cubic, for the pattern was very complex. Moreover, there were no lines in positions which would account for the irregular lines from smaltite and chloanthite. . . . If this really is the skutterudite pattern, it is eliminated as a possible cause of the extra lines.

Attempts to prepare  $\text{NiAs}_2$  and  $\text{CoAs}_2$  artificially have failed so far. If this can be done, it will be possible to determine if the unusual pattern was due to material other than the two diarsenides. Until this is done, it is not likely that an exact determination of their structures can be made, and their isomorphism with pyrite cannot be proved from the structural standpoint.

TABLE III. OBSERVED AND CALCULATED INTENSITIES OF REFLECTION

Plane	Pyrite		Sperrylite		Ullmannite	
	Observ.	Observ.	Calc.	Observ.	Calc.	
111	5	x	550	x	12	
100(2)	2	2	970	3	227	
210	4	3	667	1	590	
211	5	4	310	2	320	
110(2)	3	2	870	4	119	
311	1	1	1434	1.5	325	

*Explanation of table.*—This table gives the observed values of the intensities of reflection from the most important planes of pyrite; and the observed and calculated values for the corresponding planes of sperrylite and ullmannite. For the observed values, 1 represents the most intense line. For the calculated values, the intensities are proportional to the number given. These numbers represent arbitrary units, and cannot be used in comparing the same planes from different minerals. The relative differences in the intensities for planes 311, 211, and 210 for pyrite and ullmannite is very apparent. The letter "x" indicates that the line was so obscured by the general blackening on the film that its comparative intensity could not be determined.

## CINNABAR GROUP

The two minerals cinnabar (HgS) and covellite (CuS) have been considered as forming an isomorphous group. Their compositions are analogous, and both crystallize in the hexagonal system. Groth<sup>16</sup> and Dana<sup>17</sup> refer cinnabar to the trigonal trapezohedral class, with an axial ratio of 1:1.1453. They assign to covellite a ratio of 1:1.1466, but express doubt as to the class of symmetry to which it belongs. In view of this uncertainty, it was thought that X-ray data might be able to determine whether covellite had the same structure as cinnabar or not. If it did, its symmetry would be clearly established.

## CINNABAR

There is a large difference between the reflecting power of the Hg and the S atoms, and it is to be expected that the diffraction pattern of cinnabar would be determined chiefly by the position of the Hg atoms. The pattern indicates a simple rhombohedral arrangement for these Hg atoms, with the actual lengths of the  $a$  and  $c$  axes 4.15 Å and 9.51 Å, respectively. This unit rhombohedron has an axial ratio of 1:2.29, which gives  $c$  a value just twice that which has been assigned to the crystals. In Table IV the spacings for the various planes which recorded reflections on the film are compared with the calculated values for a rhombohedron of the dimensions given above.

The customary calculations, involving the density of cinnabar, the volume of the unit cell, and the weight of one molecule of HgS, indicate that a single molecule is associated with this unit cell. If cinnabar possesses trigonal trapezohedral symmetry, then there is only one way of placing the two atoms, Hg and S, in the cell. The Hg atom would have the co-ordinates 000, and the S atom  $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ . In other words, there would be a Hg atom at each corner of the rhombohedron, and a S atom in the center. Each corner Hg atom would be shared in common by eight adjacent rhombohedrons, so that only one eighth of each atom would belong to an individual rhombohedron; but there are eight corners, so there would be a total of eight eighths belonging to each unit cell. The S atom at the center, would, of course, furnish one atom for every cell.

At first sight the steep rhombohedral character of the unit cell seems to represent a less simple structure than that of the similar compounds PbS (galena), which is face centered cubic. As a matter of fact, its structure is very much like that of galena. There is no

special significance to this similarity, except that it shows that there is no great difference in structure involved in this change to lower symmetry, and the type of bond between the atoms must be quite similar.

The rhombohedron of cinnabar could be thought of as a greatly distorted cube, but this would involve a change in the axial ratio (regarding the cube as a special rhombohedron with an angle of  $90^\circ$ ) from 1:1.22 to 1:2.29. (Figure 1a). This would mean that there was a considerable difference in the interatomic forces of the two compounds.

A more simple relationship between galena and cinnabar can be found. The points of a face centered cube can be connected so as to form a rhombohedron. (Figure 1b). This has an axial ratio of 1:2.45. A slight compression along the  $c$  axis would change this to a rhombohedron with the ratio found for cinnabar: namely, 1:2.29. The relative change involved is shown in Figure 1c.

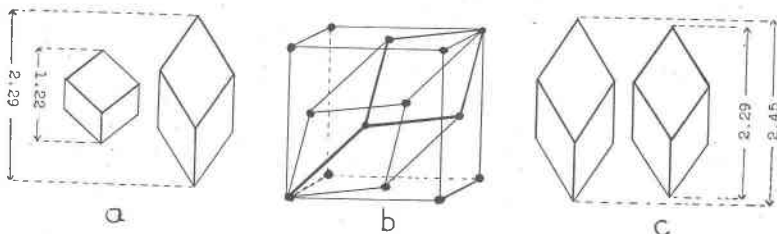


FIGURE 1

In this change the face-centered-cube positions of the Pb atoms in the galena structure become the rhombohedron-corner positions of the Hg in cinnabar. The S atom at the center of the galena cube would still be at the center of the rhombohedron. It is not easy to visualize the change from the old positions of the S at the middle of the cube edges in galena to the new position in the rhombohedron. However, they would fall into their proper places at the centers of adjacent rhombohedrons, and every position of the galena cube would have its equivalent position in the cinnabar structure. There is, therefore, a very close relation between the two structures. The two minerals cannot be considered isomorphous, because they are essentially different in their crystallographic properties, and yet a slight deformation will derive either structure from the other.

Cinnabar is optically active: that is, it rotates the plane of polarized light. This property is usually attributed to a spiral arrangement of the atoms which the rhombohedral structure found for cinnabar does not possess. It may be here, again, that we have a case in which a very slight deviation from the rhombohedral arrangement is not detected by the X-ray analysis, and yet is sufficient to make a marked difference in the optical properties.

#### COVELLITE

Because of the doubt as to the proper symmetry class to which covellite should be assigned, it was thought that a determination of its structure would show whether or not the symmetry was lower than that of cinnabar. The diffraction pattern was different than was obtained for cinnabar. This in itself is of no significance. In the cubic system all crystals can be compared if their spacings, as recorded on the diffraction patterns, are plotted logarithmically. In all the other systems crystals are not thus comparable unless they have the same axial ratios, for a very slight change in the ratio may make a marked difference in the position, or even in the number, of lines in the pattern. Covellite has an axial ratio similar to cinnabar, but there could very well be some difference in the pattern. The pattern secured, however, did not agree with a simple rhombohedral arrangement of any axial ratio whatsoever.

Attempts were made to secure Laue photographs to establish the symmetry and to give additional information as to the structure. Covellite has perfect basal cleavage, and the photographs were taken with the X-ray beam perpendicular to the cleavage plane. Instead of the usual pattern of spots, only streaks radiating from the center were secured. These are usually attributed to deformation of the crystal, so it may be that the rather soft plates were bent by handling. Even with careful manipulation, however, no better results were secured in repeated attempts.

The actual structure of covellite cannot be deduced from the available evidence, but it does seem clearly established that it is not isomorphous with cinnabar, and probably does have a different symmetry.

TABLE IV. OBSERVED AND CALCULATED SPACINGS FOR CINNABAR

Plane	Observed spacings	Calculated spacings
10 $\bar{1}$ 1	3.36Å	3.36Å
0001	3.17	—
01 $\bar{1}$ 2	2.87	2.865
11 $\bar{2}$ 0	2.08	2.074
10 $\bar{1}$ 4	1.98	1.980
02 $\bar{2}$ 1	1.764	1.764
11 $\bar{2}$ 3	1.73	1.735
10 $\bar{1}$ 1(2)	1.680	1.680
0001(2)	1.580	1.585
10 $\bar{1}$ 2(2)	1.440	1.432
2131	1.340	1.344
12 $\bar{3}$ 2	1.312	1.305
2025		

## SUMMARY

GALENA GROUP—Clausthalite and altaite have structures similar to galena, but with larger unit cells, while the other members of the group do not have the galena structure, and hence are not isomorphous with galena. They are probably orthorhombic. The existence of argentite and acanthite as two separate minerals is definitely disproven. The cubic form of argentite is explained as a pseudomorph after a high temperature form of  $\text{Ag}_2\text{S}$ .

PYRITE GROUP—Sperrylite has the same structure as pyrite, as does also ullmannite. The lower symmetry of the crystals of the latter is accounted for by the substitution of larger Sb atoms for half of the S atoms. Gersdorffite is very similar to ullmannite and has the same symmetry, although no crystals have been observed which showed this. The X-ray data indicate that cobaltite likewise has the pyrite structure, with the same symmetry as ullmannite. A possible explanation is given to account for the optical data which apparently contradict the X-ray evidence concerning the crystal form of cobaltite. Smaltite and chloanthite should be isomorphous with pyrite, but the X-ray data are decidedly unsatisfactory, and no explanation could be found for the diffraction patterns, although it may be that the crystals were not homogeneous.

CINNABAR GROUP—A simple rhombohedral structure is deduced for cinnabar from the X-ray data. The unit rhombohedron has an axial ratio twice that usually given to the crystals, and contains one molecule of  $\text{HgS}$ . Although the structure of covellite was not

determined, the evidence showed that it is unlike that of cinnabar, and that they are not isomorphous.

#### CONCLUSIONS

Isomorphism is essentially a means of classification, and its validity depends upon the extent to which it is based on fundamental rather than superficial facts. The ordinary conception of isomorphism antedates any knowledge of actual crystal structure. In an attempt to get at more fundamental relationships than were evident from the crystal form, there were introduced such ideas as equivalent parameters<sup>18</sup> and topical axes for molecular distance ratios<sup>19</sup>; but still more fundamental than these is the structure itself, of which all these others are merely expressions. Since there is now a means of determining the structures, it is possible to base isomorphism directly upon them.

Ordinarily the crystal form can be regarded as fundamental, but apparently there are cases where this cannot be done. The crystals of argentite are either pseudo-cubic, or, if the structure be assumed to be complex cubic and not orthorhombic, their resemblance to the crystals of galena is merely a coincidence. This likewise applies to hessite, eucairite, and naumannite. In the pyrite group, the lower symmetry of ullmannite is not due to any fundamental difference in structure. It still has the pyrite structure, and should be considered isomorphous with it.

If structure is to be the criterion of isomorphism, we should no longer have isomorphous groups in which the members have a different number of atoms. An exception to this might have to be made to cover the substitution of a group such as  $\text{NH}_4$  for a single monovalent atom. The indications are that this group functions as a crystallographic entity as well as a chemical entity<sup>20</sup> and can occupy a position in a structure analogous to that occupied by a single atom; but in no way could two Ag atoms in  $\text{Ag}_2\text{S}$  occupy a position corresponding to one Pb atom in  $\text{PbS}$ , without violating the principles of space group theory.

Not only can the structure be used instead of the crystal form in determining isomorphism, but it also has a direct bearing on the analogy in chemical compositions. Apparently similar compounds may have the same number of atoms with the same valences, and yet have different structures, as  $\text{HgS}$  and  $\text{CuS}$ . This means that valence alone is not sufficient to determine the analogy in composi-

tion. Hg and Cu do not occur in the same family of the periodic table, and the atoms themselves are not of analogous types, so there is no reason to expect the two compounds to have similar structures. On the other hand there are cases of isomorphous groups with elements from different families. It would seem best, then, to make the criterion of analogy the similarity of interatomic forces, which, in turn, means similarity of crystal structures.

In the majority of cases the old definition of isomorphism will suffice, but the analogy in chemical composition must be understood as applying only to such compounds as have analogous structures, as well as similar chemical natures. Moreover, it must be remembered that while the crystal form ordinarily is an accurate expression of the structure, it may be at variance with it. In such cases the criterion to be used must be the more fundamental of the two, the crystal structure.

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