

THE CRYSTAL STRUCTURE OF  
MINERALS AND INTERMEDIATE METALLURGICAL PRODUCTS  
AS A GUIDE TO THE IMPROVEMENT OF ORE DRESSING AND  
METALLURGICAL PROCESSES.

by

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## INTRODUCTION

The importance of metals to our present day world is undeniable. It follows then that the recovery of metals from the mineral deposits of the earth is of primary necessity to modern civilization. There is thus nothing unreasonable in the statement that the mineral and metal industries constitute one of the fundamental building stones of our economic structure.

That system of knowledge to which the present status of the metal industry is due, and to which it must look for future developments and economies is the science of metallurgy. This science deals with the solution of economic problems in the treatment of ores and the production of metals. Although metallurgical science frequently employs such terms as atoms, entropies, isotherms, and the like, - its ultimate aim is to economically extract metals from their ores and to prepare the extracted metal for use in commercial purposes.

It is true that while Nature is abundant, little or no exact knowledge is required. Rich ores mined and smelted in days past did not require extremely refined methods. But Nature cannot and does not remain externally lavish. Rich ore bodies are rapidly being exhausted; moreover, the economic situation has changed, so that now it is imperative that every available particle of metal be taken from the ore. Each small detail of the processes must be worked out. All of the tricks that Nature exercises in tucking away the smaller fractions of valuable constituents must be thoroughly understood, so that these smaller fractions can be routed from their hiding places and turned out into the world as useful metal.

And thus it is that metallurgy has been forced to grow from a crude art,



in ancient times making use of loosely built stone furnaces and invocations to sundry gods, to its present state of efficient production, where invocations are addressed to chemists, mineralogists, microscopists, and all branches of engineering.

As pointed out by R. E. Head,<sup>(1)</sup> the metallurgists job now is to tear down cheaply and in a few hours what has taken Nature countless centuries to produce. And this cannot be done blindly and without some degree of understanding of the materials being worked upon. Consequently we find an ever increasing need for a constantly improving technique and refinement of methods in both the laboratory and the plant. There was a time when rough qualitative tests sufficed for all operations. Then came exact quantitative chemical analyses which determined how much of the various metals were present. But the treatment of low grade ores necessitated concentration of the minerals themselves, and it became a matter of extreme importance as to not only what metals were present, but how were they present - in what minerals and how were these minerals distributed throughout the ore. At this point we find the introduction of the microscope as a metallurgical tool directly applicable to the solution of problems in the economies of ore dressing. Head,<sup>(2)</sup> Head and Crawford,<sup>(3)</sup> and various others<sup>(4)</sup> have shown repeatedly the almost indispensable value of microscopic investigations in ore dressing operations.

As ores become leaner, metallurgical knowledge must confine itself to smaller and smaller dimensions of matter. In other words, fundamental information must be obtained for direct application in present day and future metallurgical operations. Thus we find such work as that on Flotation Fundamentals<sup>(5)</sup> as done at the Utah Engineering Experiment Station, and other papers on flotation,<sup>(6)</sup> and such work as Ralston's<sup>(7)</sup>

on Iron Oxide Reduction Equilibria, and Maier's<sup>(8)</sup> on the Thermodynamics of Zinc, beginning to appear.

Since 1912, a new branch of knowledge has developed which should prove to be of immense value to metallurgy, namely, the study of the structure of crystals. In the field of fabrication metallurgy, remarkable progress has already been obtained. Some general discussions of this branch of crystal studies are included in the attached bibliography.<sup>(9)</sup> At the present time, however, very little has been done in the realm of process metallurgy - that is, the recovery of metals from their ores. But that such studies can be expected to bring forth fundamental information on problems met with in the recovery of metals is certainly not very far from a high probability. In view of this situation, work on the problem entitled, "The Crystal Structure of Minerals and Intermediate Metallurgical Products as a Guide to the Improvement of Ore Dressing and Metallurgical Processes" has been started in the Department of Mining and Metallurgical Research of the University of Utah.

## Purpose, Scope, and Division of the Problem

All metallurgical processes involve the treatment of matter in the solid state. The mode of treatment and the results obtained depend upon the physical and chemical properties of the solids under consideration just as much as they depend on those properties of the other substances employed in the operations.

Now the behavior of a solid under any conditions, whether in the furnace, leaching heap, or flotation cell is intimately tied up with its structure. Calculations made on the basis of the electrostatic forces between atoms in a crystal lattice have led to the evaluation of physical constants in good agreement with experimental values. <sup>(10)</sup> Born and Lande <sup>(11)</sup> have shown how to determine these forces. <sup>(12)</sup> Kossel has been able to account for many properties of chemical compounds on the basis of similar conceptions. <sup>(13)</sup> Eucken remarks: "-- on the whole, evidence has been produced for at least the heteropolar substances that the so-called chemical forces are identical with the forces which determine the coherence of the crystal." <sup>(14)</sup> Bragg has shown that the only properties which are not directly related to the crystal structure are those few which depend upon the atomic forces alone. Another viewpoint of fundamental interest to metallurgy, especially to the theory of flotation, has been expressed by Bragg as follows: <sup>(15)</sup>

"We must bear in mind also that there is something even more important than the solid itself. Namely the boundary between solid and liquid or gas. It is here that a vast number of changes continually take place which are essential to the processes of Nature, animate and inanimate. At the surface the free disorder of the liquid comes into contact with the solid and its constrained regularity. The two phases meet, interchange existences and exert mutual influences just as land and sea mutually encroach and affect each other. That is why the study of surface actions,



of catalysis, and of colloidal phenomena are of such intense interest and importance. Now this surface action is greatly influenced by the orientation of the molecules of the solid; one face of a crystal for example has not the same properties as another. We cannot expect to understand the behavior of the surface unless we know what is at the back of it in the solid, and whether the regularity of the solid is continued to the surface absolutely or is modified as it approaches the open, and how the molecule presents itself to the liquid or gas outside, and what are the special properties of the portions so presented."

A moments thought will convince one that the variety of solids encountered in metallurgy is exceedingly great. Consequently the scope of the present problem is indeed very wide, and it cannot be hoped to more than give a few general indications of possible results and to introduce the problem in its more general aspects.

An immediate division into two main branches is apparent from the title of this paper:

1. The crystal structure of minerals.
2. The crystal structure of intermediate metallurgical products.

The present discussion shall take up the following subjects in the order named:

1. The crystalline state, in which a brief description of the general ideas of crystal structure will be attempted.
2. Crystal structure studies and mineralogy.
3. Crystal structure studies and intermediate metallurgical products.
4. The present experimental work.

THE CRYSTALLINE STATE

(1)

That state of matter characterized by a definite and repeated arrangement of atoms, ions, or molecules, vibrating about fixed positions in a spatial lattice, is called the crystalline state. Such a definition might perhaps include the liquid crystals, but they shall not be considered at this time. It is to be noticed that the isotropic materials, the glasses, found so frequently in metallurgical slags, cannot come under the above classification. These latter are occasionally more appropriately called under-cooled liquids.

With the exceptions of glasses, practically all solids are crystalline. The old distinction between amorphous and crystalline material has almost completely disappeared. Thus amorphous carbon has been proven to be distinctly crystalline. The term amorphous now is synonymous with isotropic and applies only to the glasses and perhaps to various transition states between random molecular arrangement and the regular arrangements characteristic of crystals.

Colloidal suspensoids have been found to be dispersions of minute crystals, characteristic x-ray diffraction patterns having been obtained for sols of  $As_2O_3$ , Au, Ag, etc. <sup>(16)</sup> Gels, rubber, resins, etc., occasionally show diffraction effects which Clark <sup>(17)</sup> suggests are indicative of incipient crystal form. Hence it is to be expected that the colloidal minerals generally will be crystalline in nature. With very few exceptions then, most of the solids found in mineralogy and metallurgy are sure to be made of crystalline material. And mattes, metals, ores, fume, drosses, sinters, refractories, etc., are generally crystal-

line and should be amenable to the methods of crystal analysis.

In 1782 the original principle of crystallography was stated by Abbe Haüy to be that "— every single substance, definitely chemically constituted, possesses its own crystalline form."<sup>(18)</sup> Through the work of many men the science of crystallography was developed until it became an indispensable tool in the study of minerals. The science of the external geometrical complexes of crystals had conceived of some regular internal arrangement of atoms as an explanation of the constancy of crystal form. Reasoning from this conception, together with the ideas as to the number of atoms in a unit volume of substance,  $\nabla$  Laue,<sup>(19)</sup> in 1912, predicted that, if x-rays were short electromagnetic waves similar to light, they should be diffracted by the regular array of atoms in a crystal. Friedrich and Knipping<sup>(20)</sup> performed the experiment of passing a beam of x-rays through a crystal placed in front of a photographic plate and discovered, in addition to the image caused by the main undeviated beam, a series of diffraction spots. This result proved both the nature of x-rays and that crystals were composed of a regular arrangement of atoms. Two enormous fields of investigation were thus opened: the intimate structure of crystals, and x-ray spectroscopy. In the hands of the Englishmen, W. H. and W. L. Bragg, the former rapidly became an exact science. It thus became possible to determine the exact distance between the atoms and their relative positions in a crystal.

It is not the purpose of this paper to discuss the methods of crystal analysis. For a general account of the entire theory of methods and results, reference should be made to the very readable book by Sir Wm. Bragg, - "Introduction to Crystal Analysis."<sup>(21)</sup> For details of the



various methods, Wyckoff's book,<sup>(22)</sup> and various other books and papers,<sup>(23)</sup> should be consulted.

Hauy's original principle still stands as correct. Each chemical entity has its own peculiar crystal form, or better, arrangement of atoms. The crystallographers have shown that there are only 32 possible symmetry operations, that is, any more than this results in a repetition. These 32 operations repeated on 14 possible space lattices result in 230 possible space groups. A space group may be defined as a spatial distribution of atoms, which, as a whole, possesses crystal symmetry, and in which each like atom is situated in exactly the same way in relation to its surroundings as every other atom of the same kind. An indefinite but uniform repetition of these space groups results in the macroscopic crystal as we ordinarily think of it. The space group always contains some small whole number of molecules, but since they are indefinitely repeated, the term molecules loses much of its usual significance from the standpoint of crystal structure. The 230 space groups have been deduced by a Schoenflies,<sup>(24)</sup> Fedorov,<sup>(25)</sup> Barlow,<sup>(26)</sup> Hilton,<sup>(27)</sup> and the theory has been discussed by Kreutz,<sup>(28)</sup> Schoenflies,<sup>(29)</sup> Niggli,<sup>(30)</sup> and Wyckoff,<sup>(31)</sup> Wyckoff has developed the analytical geometry of the space groups and has tabulated the results as coordinates of equivalent points.<sup>(32)</sup> Astbury and Yardley have prepared diagrams of all of the groups.<sup>(33)</sup> A knowledge of space groups is essential to a complete understanding of crystal structure but finds its chief application in the actual determinations from x-ray data.

#### LATTICE TYPES

The phrase, "arrangement of atoms," used so repeatedly in the preceding discussion must be modified in accordance with the following ideas:

Crystals may be either ionic, homopolar, molecular, or metallic.

In the first type, characterized by most of the inorganic salts, the positive atom has given up one or more electrons to the negative atom so that there results a positive ion and a negative ion. These ions are then held together in the crystal by electrostatic forces. Hence, with certain reservations, the ionic crystals, as they are called, may be thought of as an assemblage of incompressible spheres. This conception leads to many interesting conclusions, some of which shall be briefly discussed in a later paragraph.

Homopolar crystals are those in which the various valence electrons of the constituent atoms are shared by both positive and negative atoms. And the forces which hold the crystal together are in this case, similar to the forces between atoms in a chemical molecule. Homopolar crystals are inclined to be mechanically weaker than the ionic.

Molecular lattices are made up of an arrangement of molecules in a space lattice. The crystal bonds are then similar to residual valencies, and the crystals of this class are usually soft and possessed of low melting points.

The metallic lattice is conceived as a "negative field of free electrons in which are imbedded the atomic kernels." <sup>(34)</sup> Such a conception permits of ready explanation of the electrical properties of metallic substances. Bernal <sup>(35)</sup> has given a critical discussion of the metallic state in which he is inclined to subdivide metallic lattices into "metallic ionic, metallic homopolar," and truly metallic types.

There are, of course, various intermediate conditions between any of the above lattice types. But it can be seen that such a division allows many of the properties of the crystal to be explained. The ionic

lattices are generally capable of much more simple interpretation than any of the others. Metallurgical crystals are usually of the ionic or metallic types.

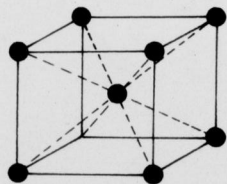
#### GENERAL TYPES

It is becoming general to identify crystals more conveniently by referring them to certain types, the types being named after some typical representative. Figure I shows a few of the metallic types while Figure II shows a few of the more common heteropolar or ionic types. A description of various crystal structure types can be found in a paper by Gruner.<sup>(36)</sup>

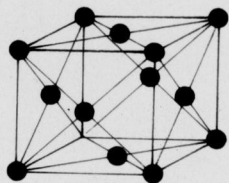
As a result of the numerous investigations on the crystal structures of a great number of compounds, generalizations can already be made. Of extreme interest and importance is the work of Goldschmidt and his co-workers on the relations between crystal structure and chemical constitution. Goldschmidt<sup>(37)</sup> states a general thesis or fundamental law that

"- The structure of a crystal is determined by the ratio of numbers, the ratio of sizes, and the properties of polarization of its building stones. As the building stones of crystals we visualize atoms ( or ions ) or groups of atoms." Numerous investigations have been made on the sizes of atoms and ions within crystals. The results are plotted in Figure III from data of Goldschmidt brought to this laboratory by Dr. N. W. Taylor. The actual order of magnitude of these radii are of course dependent upon the structure of the atoms themselves. It will be noticed that the radii are periodic functions of the elements. Also, it is interesting to observe that the size of the positive ions is less than the size of the corresponding atom, and that the negative ions are considerably larger than their parent atoms. This is to be expected when it is remembered that a positive ion has lost one or more electrons, and a negative ion

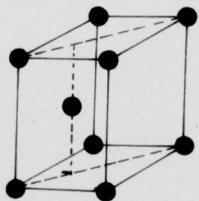




UNIT CELL OF  $\alpha$  Fe  
(CSCL TYPE)

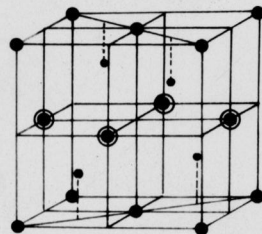


UNIT CELL OF Cu  
(FACE CENTERED CUBE).

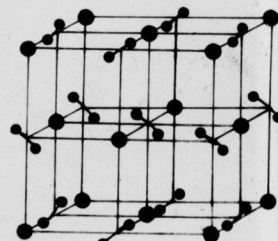


HEXAGONAL CLOSEST PACKED  
UNIT CELL OF Mg, Co, etc.

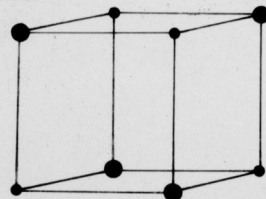
FIGURE I



● = Cu ⊙ = Fe • = S  
CHALCOPYRITE  
(ZnS TYPE)



● = Fe • = S  
PYRITE  
(PYRITE TYPE)



● = Pb • = S  
GALENA  
(NaCl TYPE)

FIGURE II

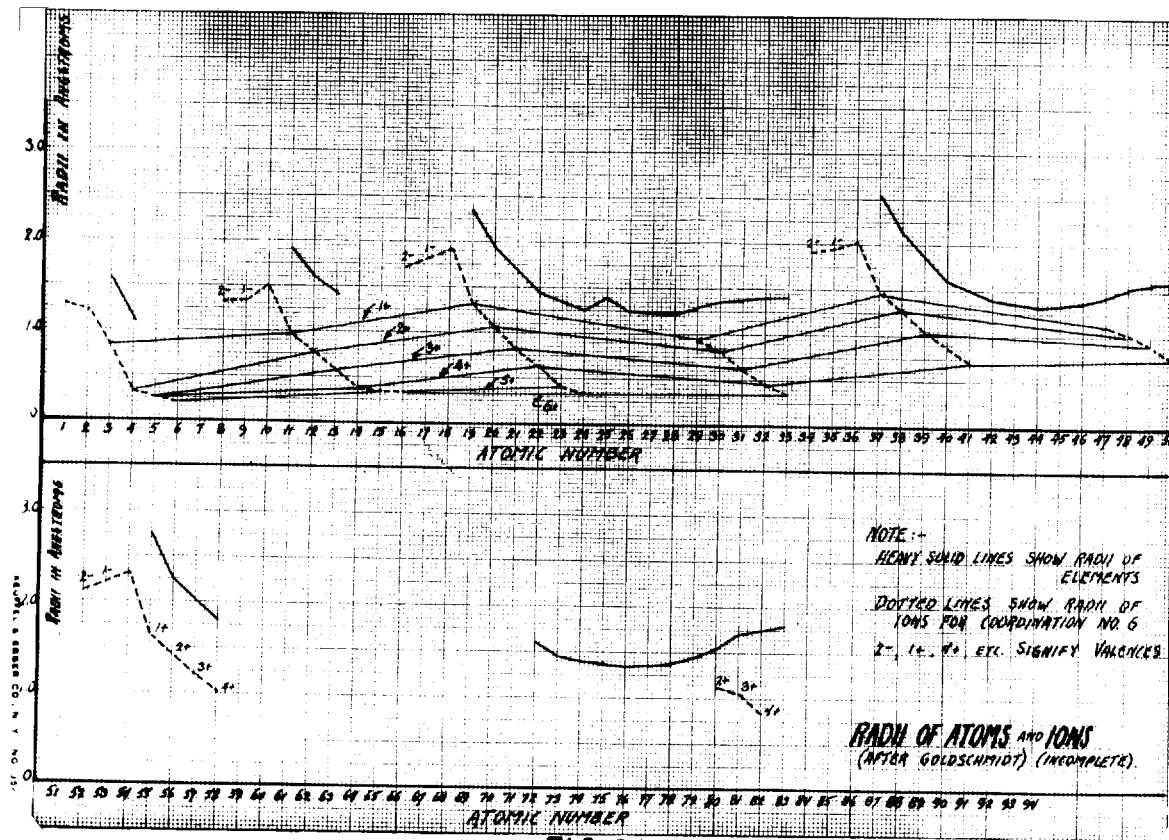


FIG. III

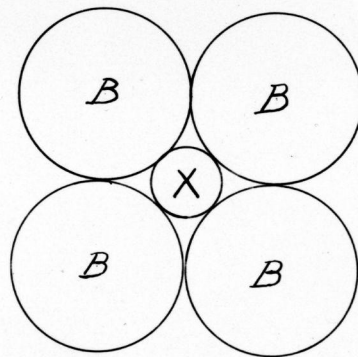
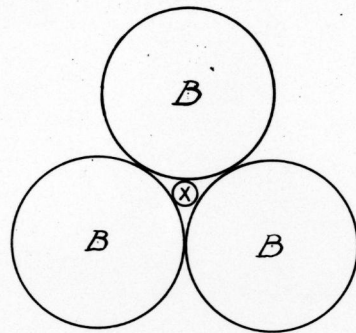


FIGURE IV



gained electrons. However, the real significance of these data to crystal structure is more pertinent to the present discussion.

If we consider only truly ionic crystals, we can, for the present, think of them as being composed of rigid spherical ions in contact with each other. The sketches then in Figures I and II are not exactly correct. The black balls represent only the centers of the atoms or ions. Their shells or "spheres of influence" can be considered to extend until they are in contact with each other. Now, on this basis, a geometrical analogy to the structure of crystals can be set up which approaches the actual conditions. <sup>(37)</sup> If we confine our attentions to two dimensions, it can be seen that circles of two different sizes can be arranged so that one circle of radius X is in contact with as many circles of radius B as is possible. ( See Figure IV ) With a certain ratio between the two sizes, three B. circles can be arranged around one X circle. This ratio is X:B greater than 0.15. However, if this ratio exceeds 0.22, four B. circles can be arranged around one X circle. Considerations of this sort extended to three dimensions can be applied to ionic crystals. A systematic relationship has thus been found in many cases between structure and radii ratios in crystals. This leads to a possibility of predicting crystal structures for compounds which have not yet been determined, at least it gives a hint toward the type of structure they may be expected to have. And we come to an understanding of isomorphism in going from one compound to another. Furthermore, it is readily perceived that some few atoms within some crystal may be very easily replaced by other atoms of the same size without altering the structure other than by stretching or contracting the distance between centers in case the atoms or ions are not exactly the same size. Such is what happens in the case of solid solutions. For an extended

treatment of this very fruitful phase of the study of crystals, reference should be made to the work of Goldschmidt<sup>(38)</sup> and others.<sup>(39)</sup>

This hasty presentation has been given only to show a most general idea of the possibilities of such a science, as but a slight amount of thought will enable one to see many applications in the realm of minerals, particularly with regard to impurities and association. Thus, cannot it be possible that the individuals in the iron-copper-sulfur series of minerals are not exact chemical entities? The literature shows two and sometimes more different formulae for bornite. Crystal structure analyses of two samples,<sup>(40)</sup> one with the composition  $\text{Cu}_3\text{FeS}_4$  and the other  $\text{Cu}_3\text{FeS}_3$ , showed exactly the same type of structure with but a slight decrease in the edge of the unit cell in the case of the former. Reference to the curves of radii will show that divalent Cu and divalent iron have very nearly the same ionic sizes. It would seem that a rather wide range of solid solubility of iron or copper in bornite might be possible. Chalcopyrite likewise appears in several different colors. This may have a similar explanation. If this idea of solid solution is true, we might expect variations in the properties and hence metallurgical behavior in minerals from different localities. Further, whitneyite has been shown to be a mixture of a solid solution of Cu and As and algodonite.<sup>(41)</sup> Thus the formula  $\text{Cu}_3\text{As}$  is practically meaningless.

In a recent paper,<sup>(42)</sup> Head, Crawford, and Thackwell have shown the case of an ore containing 7.5% manganese which had resisted all attempts at economical concentration. Careful microscopic examination revealed no manganese minerals except traces of manganese oxide minerals. Reasoning from a knowledge of the composition and variations in minerals, these men decided that the manganese was contained in siderite, the predominating

mineral in the ore. Selection of siderite grains under the microscope followed by chemical analysis, proved their contention and accounted for practically all of the manganese. Reference to the curves of atomic radii (Fig. III) will show the close similarity between the sizes of the divalent iron atom and the divalent manganese atom. It is readily conceivable how a certain amount of manganese could replace iron atoms in the siderite lattice. These examples will suffice for the present. Doubtless Nature is replete with similar obscurities, and x-ray results, coupled with the microscope and other tools, are already on the road toward an explanation of these occurrences.

#### CRYSTAL IMPERFECTIONS

The picture of a crystal we have obtained from x-ray data is one involving a perfect continuum from the single unit cell or space group, to the large crystal. And now science, who seems at times to be somewhat of a practical joker, informs us that if a crystal were as we have pictured it, we would not be able to know anything about its structure from x-ray effects. Theoretical considerations, substantiated by experiment, have shown that diffraction phenomena would be difficult to obtain if the alignment of atoms were geometrically perfect. <sup>(43)</sup> Bragg has shown that a freshly cleaved rock salt surface gives a great deal less x-ray reflection than one which has been ground, that is, subjected to distortion. <sup>(43)</sup> This and other ideas have led to the conceptions of perfect and imperfect crystals. The perfect represent, apparently, a practical impossibility. All known crystals thus fall into the imperfect class.

Hence we find a new picture for a crystal. The complete crystal is believed to be built from small blocks, each of which possesses in itself the exact structure as revealed by the x-ray methods, but each block

( assumed to be of the order of 1 micron in size ) is separated from its neighbors by a small space. Ewald and Smekal in Germany, and Zwicky, Goetz, and others in this country have accordingly developed the idea of a mosaic crystal structure. Zwicky<sup>(44)</sup> gives thermodynamic reasons for a regular series of deviations from the ideal crystal state, and points out several experimental indications of such conceptions. Goetz<sup>(45)</sup> studied cleavage faces and etch figures on single crystals of Bismuth and came to the conclusion that the crystals were built of "blocks of a definite size, which size is independent of the perfection of the crystal, so long as the crystal is not plastically deformed." Joffe<sup>(46)</sup> attributes all "disturbing phenomena" in the mechanical properties of crystals to irregularities of structure of heterogeneous bodies. Smekal<sup>(47)</sup> is probably the most enthusiastic worker on crystal imperfections. He has shown the relation between many physical and chemical properties of crystals to their discontinuous structure, and divides properties into those dependent entirely on the lattices and those dependent upon the spaces between the unit blocks.

There is not at present very much experimental evidence as to the existence of the unit blocks. Tensile strength calculated from the forces between atoms in a crystal by the method of Born are always many times greater than obtained by experiment. Traube and co-workers<sup>(48)</sup> have observed that a crystal, upon going into solution, first disintegrates into a large number of particles of colloidal dimensions which are identified with the unit blocks of Smekal. Wood<sup>(49)</sup> has observed Bragg reflections of visible light from  $KClO_3$  crystals which indicates the existence of a regular superstructure within the material. The density of crystals calculated from x-ray data is generally higher than the density determined by the usual methods, which signifies that there must be some

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free spaces within the crystals. Dean has shown that the amount of hydrogen sulfide adsorbed on 80 mesh galena can be accounted for by assuming a monomolecular layer to be adsorbed on unit blocks containing  $4 \times 10^{-12}$  molecules per block.

Dean has discussed the possible metallurgical consequences of such a discontinuous structure. Thus it might be expected that the "work of crushing a mineral to a given size will depend on the size of the unit blocks in it." Leaching reactions will depend upon the size of the unit blocks, or better, upon the amount surface exposed to the action of the solvent which will in turn be a function of the size of the blocks. Flo-tation phenomena will be influenced by the fact that the interstitial faces are probably already covered by a film of adsorbed gas before any treatment whatever is given the mineral in the mill. Dean further points out that the independence of the rate of leaching of chalcocite on the particles may be explained by the conception of unit blocks. That is, the solution can possibly penetrate into the large lumps by means of the spaces between the blocks with the result that the actual surface of contact between solid and solvent is the same for coarse material as for fine.

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CRYSTAL STRUCTURE AND MINERALOGY

( 2 )

There is no complete listing, in English, of the crystal structures already known. Ewald and Hermann <sup>(53)</sup> have published a comprehensive compilation of structure data and are adding to it continually. Wyckoff lists about three or four hundred inorganic compounds in the "International Critical Tables." Wyckoff also has a rather complete bibliography on crystal structure studies for the years up to and including 1923 in his book, "The Structure of Crystals." Morse <sup>(54)</sup> recently published a bibliography of crystal structure studies.

Kerr <sup>(55)</sup> has described equipment and methods of using x-rays as a tool in determinative mineralogy. Each mineral, if it is a definite chemical entity, produces its own peculiar x-ray pattern. Kerr suggested that standard films could be prepared from pure known materials. Unknown samples could thus be photographed under the same conditions and their patterns compared with the standards. Hull, <sup>(56)</sup> whose method Kerr was using, says that a crystal present in proportions under 10% in a mixture of crystals will not satisfactorily produce its pattern on top of the pattern of the preponderating crystal. Thus small amounts of a some one mineral cannot be definitely located in mixtures by the x-ray method. Even if over 10%, of various minerals are present in a mixture, the x-ray examination usually gives only qualitative data. However, x-rays should prove of advantage in identifying very finely dispersed minerals which are too small or too stubborn to be influenced by microscopic etch

or stain reagents. Thus R. E. Head, at these laboratories, has come upon some leached chalcocite grains which show a rather large amount of some mineral phase distributed in bands which are just beyond the resolving power of the microscope and consequently not able to be identified by the usual methods. X-ray analysis of these grains should show at once if another phase is actually present and should permit of its definite determination. It is in such work that the x-ray study of crystals should prove to be an aid to the microscope.

Applications of crystal structure studies to the relations between the various individual minerals in a "Group" has been shown in a preceding paragraph, ( See page 12 ) in which possibilities of solid solutions were discussed. The occurrence of solid solutions in minerals is not rare. Thus in the plagioclase feldspars a continuous series of solid solutions exists between albite and anorthite. Here one sodium and one silicon in equivalent amounts replace one calcium and one aluminum, with no change in the type of structure. Krieger <sup>(57)</sup> has studied the series calcite, rhodochrosite, on this basis. The tennantite-tetrahedrite relations are undoubtedly explainable on the same basis. Molybdenum is found to replace some of the tungsten in scheelite. The radii of Mo and W ions are practically the same. Ca is known to be present in Wulfenite, more than likely, according to the ionic radii, taking the place of some Pb ions. Teallite, Franckeite, and cylindrite are in the same category. There is no necessity of listing all of the possibilities. The direct metallurgical significance of such phenomena is that crystal structure studies either by the microscope or by x-rays, will permit determining the best method of concentration or separation of the valuable constituents of an ore. That is, chemical analysis will show that certain metals are present. And knowledge of the structure in which the metal

is confined will determine if physical or chemical means of separation are necessary.

In the flotation of minerals we find a great wealth of conflicting theory. In spite of the tremendous achievements in the floating of minerals in the last twenty years, there is yet no satisfactory explanation of the general phenomena and each mine and mill has its own individual problems, the experience gained at one mill serving only to indicate the general mode of procedure at another mill. That the crystal structures of the minerals are involved in the causes governing flotation cannot, it is believed, be disproved. But as to what part they play, there is, at present, no information available.

That phenomenon or group of phenomena which are classified under the name of adsorption, play as is well known, an exceedingly important role in all flotation processes. The forces at the surfaces of crystals have considerable influence on at least some types of adsorption as was shown by Langmuir. <sup>(58)</sup> Polanyi <sup>(59)</sup> has considered adsorption from a similar standpoint. <sup>(60)</sup> Mukherjee and <sup>(61)</sup> Fajans have studied the double layer at the boundary of crystalline materials. Kruyt and Van der <sup>(62)</sup> Willigen found that silver iodide sols were stabilized only by salts which were isomorphous with Ag I. Their experiments included the preparation of the sol in the presence of each of the following salts: KI, KBr, KCl, KCN, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, K<sub>3</sub>Fe(CN)<sub>6</sub>, KNO<sub>3</sub>, K<sub>2</sub>SO<sub>4</sub>, K<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>HPO<sub>4</sub>, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>. All of the suspensoids flocculated rapidly except those prepared in the presence of the first six salts given above. This is taken as an indication of the influence of isomorphism on the stability of sols. That is, those ions are adsorbed which tend to form isomorphous salts with the adsorbent. However, Freundlich <sup>(63)</sup> points out that this rule, which had

been formulated before by Marc, does not "relate to truly isomorphous substances but to 'homomorphous' ones. These have very similar crystalline forms and hence can crystallize together in parallel overgrowths, while they can scarcely form solid solutions with one another, and do not mutually act as nuclei in cases of supersaturation." However, in general the literature on the relations between crystal structure and adsorption phenomena is most scarce. And it is this type of knowledge which should be had to aid in building a complete picture of flotation mechanisms. An attempt was made to discover some relationships between structure and flotation results by tabulating the influences of various ions on certain minerals along with the crystal structures of the mineral and the adsorbed material, the data being taken from the literature. No significant dependences could be noticed, although this is not necessarily discouraging because most flotation tests have been made with a view toward determining the effect of reagents rather than of the minerals themselves.

Not alone do lattice properties come into play in adsorption phenomena. If crystals are built of unit blocks, the blocks are probably possessed of a coating of adsorbed material which might influence even more strongly than the lattice energies, the ability of the mineral to further adsorb the flotation reagents. It is well known that crystals forming in the presence of impurities have a tendency to adsorb a certain amount of the impurities. In fact this tendency is so pronounced in some cases as to prevent certain faces from growing. Thus a small amount of urea in  $\text{NaCl}$  solutions will cause the salt to crystallize in the form of octahedra rather than the normal cubes. In the presence of diamine sky blue, potassium alum crystallizes in perfect cubes. <sup>(64)</sup> It can presumably happen that the adsorbed material is isomorphous or homomorphous with the crystallizing substance and hence alternate layers of crystal and adsorbed substance can be formed.

It is in this manner that we might expect minerals to form from magmatic waters; crystallizing not as a perfect continuum<sup>n</sup> but as a series of blocks separated by thin layers of adsorbed material. And this adsorbed material might be either another mineral or some gas, depending upon conditions. If this substance which is adsorbed is taken into the lattice of the crystal, in contradistinction to the picture of unit blocks and their coatings, we would expect to find a change of the lattice constants as shown by x-ray analysis. Foote, Blake, and France<sup>(64)</sup> studied the influence of diamine sky blue on the lattice constants of potassium alum and found no change due to the adsorbed dye. This led them to feel justified (with reservations as to the outcome of future experiments) in assuming that the dye is adsorbed interstitially rather than by replacement of the ions in the unit cell.

Galena is known to contain considerable quantities of  $H_2S$ . Its odor can frequently be detected upon freshly broken specimens. Verde<sup>(65)</sup> in studying PbS contact detectors found that a large quantity of hydrogen sulphide was given off by artificial galena when under a vacuum and heated to  $500^{\circ} C$ . On the basis of the assumption of unit blocks, this gas might be expected to be contained on their surfaces. Work is now being done by Gross and St. Clair on the adsorption of this gas on natural galena at the Utah Engineering Experiment Station in cooperation with the U. S. Bureau of Mines. One phase of the problem will be to determine if the lattice constants of a degassed and a saturated sample of galena are the same. If so, as in the case of the potassium alum, it can perhaps be assumed that the gas is present in the interstices between the unit blocks. Hence, as pointed out by Dean,<sup>(66)</sup> the amount of gas taken up by a given sample should serve as a measure of the size of the unit blocks.



It is doubtful if x-ray methods will permit of any study of the actual surface layers of mineral samples. Clark Brugman, and Kaufmann<sup>(67)</sup> have been able to study alloy surfaces by reflecting x-rays from them at very small angles of incidence. But in such substances, the surface effects looked for are many atomic layers deep. Mineral surfaces cannot be expected to have much more than a monomolecular film and any diffraction effects from this film might well be overshadowed by the effects from the main part of the crystal. One tool which may prove of some service in such work is the electron beam. Hupp<sup>(68)</sup> in Germany, and Davisson, and Germer<sup>(69)</sup> in this country have obtained diffraction phenomena by a beam of electrons reflected from metal surfaces. Davisson and Germer give evidence, from this method, of a regular arrangement of oxygen atoms adsorbed upon clean nickel surfaces.

Adsorbed substances possibly have some influence on the solubility of the adsorbent,- an effect which would play a part in the leaching of ores. Tammann<sup>(70)</sup> remarks that two or three layers of mica molecules are rendered supersoluble by cleavage. This may be attributed to the fact that the molecules on a fresh cleavage surface may not have time to adjust themselves to a condition of minimum energy before solution takes place. However, such adjustment might consist in the adsorption of ions of the solvent until all bonds or excess lattice forces at the surface of the solid are satisfied. In general, an aggregate of unit blocks with adsorbed coatings would not be expected to have the same solubility characteristics as the same material without the coatings. But, any hindrance offered to solution from this standpoint is probably completely hidden by the increase in the rate of solution to be expected from the enormously increased surface due to the blocks.

The actual lattice structure of a mineral unquestionably has some

bearing on its behavior in leaching operations. DeJong <sup>(71)</sup> has worked out the structure of bornite and found it to contain 32 cuprous and 8 cupric ions in the unit cell. Surely these two kinds of ions will not go into solution with the same ease. Covellite, crystallizing in the hexagonal system, is <sup>known</sup> to contain six CuS in the unit cell. <sup>(72)</sup> Davey states -- " --2 of the 6 Cu 'atoms' occupy isolated positions in the lattice. Such structure invites speculation as to the ionic state of Cu and S., for instance: Are the two isolated Cu really neutral atoms and not ions; must 4 of the 6 sulfurs carry only  $\frac{1}{2}$  of the normal negative charge in order to keep the crystal as a whole neutral?" Sullivan <sup>(73)</sup> has shown that when chalcocite dissolves, one half of the Cu is rapidly liberated, no free sulphur being released, but that the Cu:S ratio does not then stay at 1:1 and the remainder dissolve as CuS. The actual happening is that more Cu is liberated alone until the ratio Cu:S is less than 1:1 reaching the value of 0.81:1 at times. If there is any basis to Davey's "invitation to speculation" it might find some backing in this effect noted by Sullivan. That is, perhaps some of the Cu atoms are different than the others in CuS; the two "isolated" coppers dissolving more readily and independently of the sulfurs.

The mechanical strength of mineral crystals is a function of their structure. Not much more than this can be said at the present time in relation to the effect of crystal structure on grinding. Grinding may cause allotropic changes in a mineral, however. Schlegel and Gantzckow <sup>(74)</sup> found that wurtzite was converted into zinc blende by the mere act of pulverizing.

CRYSTAL STRUCTURE AND INTERMEDIATE  
METALLURGICAL PRODUCTS  
(3)

In intermediate metallurgical products we come upon physical-chemical systems of pronounced complexity. Mattes, slags, sinters, drosses, speiss are all composed of many components and the phases present range from material in the metallic state, through intermetallic compounds, to nonmetallic elements and compounds, distinct or in solid solution with each other. A complete understanding of these materials will probably require the working out of all the possible binary systems, then the ternary, quaternary, and so on, indeed a Herculean task. X-ray crystal analysis would serve to distinguish each phase in the solids. The structures of a great many of the individual substances likely to be present are already known as can be seen by reference to any of the structure data compilations previously mentioned ( See page 16 ). And from the laws of crystal chemistry and other physical chemical data a great many predictions can possibly be made. This field of metallurgical investigation is truly enormous and it is not surprising that it has not been touched.

The entire preceding discussion has been given in an attempt to show the possible importance of crystal structure studies to mineralogy and process metallurgy. In spite of the fact that the structures of a great number of crystalline solids are already known and tabulated, very little has been done in the interpretation of such data from the standpoint of their metallurgical application. And the conceptions of crystal imper-

fections are still in the controversial stage with practically no direct bearing on minerals or metallurgical products.

The words, "crystal structure studies" as used in the paper mean not only the mere determination of the atomic positions within the crystals nor only the discovery of the presence or absence of crystal imperfections, but the development of fundamental information concerning the behavior of all metallurgical solids under any conditions. Naturally then, it is a matter of primary importance to know just what the nature of the solids can be, what forces hold them together, what forces must be overcome to take them apart, and what forces do they exert on their surroundings.

It is obvious that the field is relatively new. Hence it has been possible only to draw inferences and suggestions from work done on other products with no connection to metallurgy and to attempt to show how similar work, carried out on materials of metallurgical importance, should prove to be of great value in the furtherance of metallurgical knowledge.

#### PRESENT EXPERIMENTAL WORK

The present work has been done in relation to the ideas of crystal imperfections. It is believed that these ideas have been sufficiently discussed in preceding paragraphs and require no further general treatment in this section.

R. S. Dean has prepared a program of investigations on imperfections in mineral crystals in which it is hoped to determine a number of physical properties on each of many different mineral samples. The properties to be investigated are those which might be directly influenced by the presence of the assumed superstructure of crystal discontinuities

or imperfections. For instance: Pycnometer density, x-ray density, microscopic characteristics, electrical conductivity, temperature coefficient of electrical conductivity, ability to adsorb gases, critical sizes for floatation, grinding, and leaching, etc. are to be determined on the same samples. In this way it is expected that information as to number, size, and effect of the unit blocks in crystalline minerals can be obtained.

This report is confined to the electrical conductivity and its temperature coefficient; the work on the other phases of the problem is being done by other investigators at these laboratories.

#### Mosaic or "Unit Block" Structure and Electrical Conductivity.

(75) Koenigsberger, and Rasch and Hinrichsen, (76) observed that the electrical conductivity of solid salts at different temperatures could be represented by an equation such as:

$$\ln K = \frac{B}{T}$$

Eq. (1). or  $K = AC \frac{e^{-E}}{T}$

Where K is the specific conductivity, A, B and E are constants and T is the temperature. That is, the relation between the logarithm of the specific conductivity and the reciprocal of the temperature proved to be linear. However, this relation holds only between certain temperature limits. It also holds only for ionic conductors. Above some minimum temperature a break occurs in the curve  $\log K$  vs.  $1/T$ .

(77) Smekal has pointed out that this break in the curve can be explained on the basis of the assumption that crystals are built of small blocks separated from each other by interstices or "Lockerstellen." Ionic conductors then, at the lower temperatures, conduct electricity by



virtue of mobile ions within the interstices, but above some critical temperature ions from the lattices of the unit blocks themselves take a part in the conduction, with the result that both types of ions are involved, and the slope of the temperature-conductivity curve is changed. The conductivity can be better represented by the equation:

$$\text{Eq. (2)} \quad K = A_1 e^{-\frac{E}{T}} + A_2 e^{-\frac{E}{T^2}}$$

Where the first term on the right hand side refers to that part of the conduction due to the "Lockerionen" and the second term to that due to the lattice ions. This view has been challenged by Jost, who states<sup>(78)</sup> that electrolytic conductance of good conducting AgI crystals is not influenced by limiting surfaces, and that the conductivity of such salts does not depend on internal boundaries. Phipps and Leslie<sup>(79)</sup> performed transference experiments on NaCl over a wide range of temperature and maintain that the break in the curve occurs at a point where the Cl ions begin to carry a part of the current, the Cl ions not having taken any appreciable part in the conduction up to that point. Their data fit Equation (2) above. But they are inclined to interpret the equation in such a way that the first term represents the conduction due to one kind of lattice ions, and the second due to the other kind of lattice ions, thus neglecting the influence of "Lockerionen" if present.

Regler,<sup>(80)</sup> in accordance with the ideas of Smekal concerning unit blocks, considers that a great part of the resistance of high resistance bodies, and solid insulators exists in the transition regions between the blocks. The actual conductivity of the lattice material is believed to be considerably higher than measurements on gross crystals show. He points out that deviations from Ohm's law can be explained on the basis of

a discontinuous structure. In fact it is postulated that a discontinuous structure will not permit Ohm's law to be obeyed by metallic conductors. Selliger<sup>(80)</sup> has remarked that deviations from Ohm's law are only apparent and arise from polarization phenomena. Joffe<sup>(81)</sup> holds a similar view and has shown that conductivity in poorly conducting salts does follow Ohm's law.

Regler also, in a paper on the electrical properties of galena crystals,<sup>(82)</sup> reported experiments which were intended to show that galena crystals, possessed piezo-electric properties. The unit blocks are supposed to expand under the influence of a potential applied in one direction, and to contract with opposite polarity. This expansion is then thought to occasion a decrease in the transition resistance between the unit blocks while the contraction under opposite polarity causes an increase in the transition resistance, with the combined result that current will be carried with more ease in one direction than in another, and rectification of an alternating current is thus made possible. In the same paper were reported experiments which showed that the amount of current carried by a crystal of galena was dependent upon the applied pressure. This was attributed to a squeezing together of the unit blocks resulting in a better contact between them and a consequent lower resistance of the crystal as a whole. The effect of pressure on deviations from Ohm's law was also studied by Regler. According to these studies, conductivity in galena does not follow Ohm's law until a certain minimum pressure is reached, presumably that pressure at which the unit blocks come into intimate contact or at least as close as possible.

These papers and others show that both the mechanism of electric

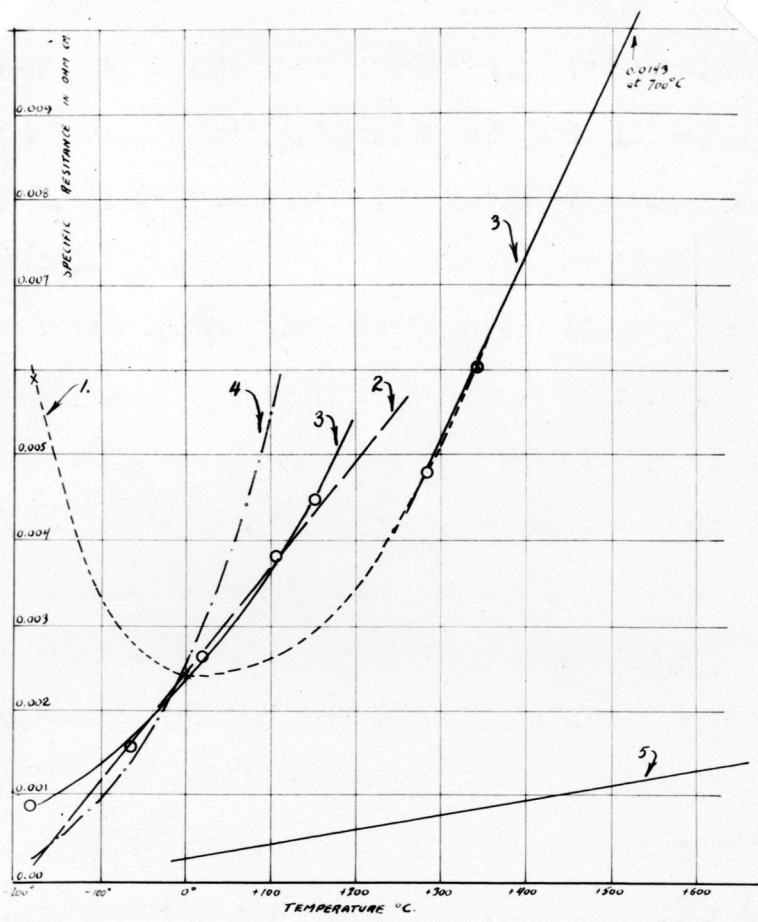
conduction and the concept of unit blocks are still matters of controversy. However, as Smekal has pointed out, <sup>(83)</sup> any disturbance of the lattice structure will produce a hindrance to the migration of electrons in electronic conductors. Consequently a study of the electric conductivity of metallic minerals should give an indication of the presence or absence of a mosaic structure.

THE ELECTRICAL CONDUCTIVITY OF  
GALENA

Galena has been chosen as the first material to be investigated, chiefly because of the simplicity of its crystal structure.

The electrical conductivity of galena and crystallized lead sulfide has been studied by Hittdorff, <sup>(84)</sup> Braun, <sup>(85)</sup> Doelter, <sup>(86)</sup> duMoncel, <sup>(87)</sup> Weigel, <sup>(88)</sup> Bernfeld, <sup>(89)</sup> Beijernick, <sup>(90)</sup> Buff, <sup>(91)</sup> Koenigsberger, <sup>(92)</sup> Streintz, <sup>(93)</sup> Streintz and Wesley, <sup>(94)</sup> Streintz and Wellick, <sup>(95)</sup> Wesley, <sup>(96)</sup> Hulzinga, <sup>(97)</sup> Baedeker, <sup>(98)</sup> Reichenheim, <sup>(99)</sup> Padoa, <sup>(100)</sup> Collet, <sup>(101)</sup> Guinchant, <sup>(102)</sup> Koenigsberger and Schilling, <sup>(103)</sup> van Aubel, <sup>(104)</sup> James, <sup>(105)</sup> Gehlhoff and Neumeir, <sup>(106)</sup> Pierce, <sup>(107)</sup> Goddard, <sup>(108)</sup> Coursey, <sup>(109)</sup> Koenigsberger and Reichenheim, <sup>(110)</sup> Wakasaburo, <sup>(111)</sup> Regler, <sup>(112)</sup> Tubandt, <sup>(113)</sup> Frey, <sup>(114)</sup> Vrede, <sup>(115)</sup> Lapinski, <sup>(116)</sup> and others.

Figure V shows some of the results of these investigators. van Aubel <sup>(104)</sup> says that there is a minimum in the temperature-resistance curve at  $-189^{\circ}\text{C}$ . Landolt and Bornstein and also the International Critical Tables, in reporting the measurements of Koenigsberger and Reichenheim show a minimum in the curve between  $+20^{\circ}$  and  $-180^{\circ}$ . James <sup>(105)</sup> shows a pronounced break in the curve at  $+180^{\circ}$  and attributes it to a transition from  $\alpha$  PbS to  $\beta$  PbS. Streintz <sup>(93)</sup> noticed that the conductivity was higher after heating and cooling and assumes the presence of a metastable form. Lapinski <sup>(116)</sup> also says that heating and cooling lowers the resistance. The most significant statement is probably that of Harvey <sup>(117)</sup> who, in working with comparative resistances of different minerals, found a variation of over 300,000% in the figures for seventeen different samples of galena.



1. INTERNATIONAL CRITICAL TABLES (AS TABULATED)
2. " " (CALCULATED)
3. KOENIGSBERGER AND REICHENHEIM REFERENCE (110)
4. FREY REFERENCE (114)
5. GUINCHANT " (102)

FIGURE V



(93) Streintz showed that the passage of D.C. through galena is accompanied by the electrolytic formation of metal threads, particularly if AgS is present. Koenigsberger and Schilling (103) said that conduction is certainly electronic. Tubandt (113) has shown that the latter is correct from the standpoint of transference experiments. Heaps (118) has found a pronounced Hall effect in Galena crystals. And the metallic luster of galena crystals lends more substantiation to the idea that galena conducts electronically.

(119) Coblenz found that one specimen of galena was not photoelectrically sensitive. Case (120) found that galena was sensitive to light.

Workers on galena from the standpoint of its ability to rectify A.C. report various experimental results which are in disagreement with each other.

In view of all of these results, it can be seen that, in general, very little definite information has been obtained on the electrical properties of galena or lead sulfide.

The aim of the present work was to determine the temperature, resistance relations for different samples of galena. The discussion of the work of others on this subject points to but one significant fact, namely: The independent determination of any of the electrical properties of galena is practically meaningless unless supplemented by measurements on other physical and chemical properties of the same sample. Accordingly this work has been done on samples from specimens which are now being investigated from the standpoint of their other properties, as mentioned before.

#### METHOD

The method chosen for the measurements is that in which the potential drop is measured across a prism of galena when carrying a known current.

That is, the sample is connected in series with a known standard resistance and the potential drop determined across both by means of a Leeds and Northrup type K potentiometer. This method eliminates the usual effects of contacts. It was believed that variable contact resistance had been the cause of many of the variations in the work of other investigators. This is not unreasonable since galena is known to conduct differently in different directions. Any contact potential developed at one electrode would thus not necessarily be exactly balanced by the contact potential at the opposite electrode.

#### EFFECT OF VARIOUS TYPES OF CONTACTS

Even though a potentiometric method was employed, electrical contacts proved to be the greatest source of trouble. It was discovered that the location of both current and potential contacts was a matter of fundamental importance to the particular value of resistance obtained. The ordinary method of clamping the specimen between the two current electrodes and then determining the potential drop across two needles at a fixed distance apart cannot be employed. Readings obtained in this fashion were found to vary over a wide range by merely shifting the needles, or even by lifting the needles from the surface and then replacing them in exactly the same position in so far as could be determined by microscopic observation. And also, concordant readings could not be obtained if the same specimen were removed from the clamp and then immediately replaced. Mercury, lead amalgam, silver foil, Pt. foil, graphitizing, gold leaf pads, electrolyte solutions, were all tried with indefinite results.

## PRESSURE EFFECT

There was some indication that contact pressure was a factor of pronounced importance. This idea was strengthened by the reported experiments of Regler (See p. 27). Accordingly a clamp was designed which permitted small crystals of galena to be subjected to pressures of the same order ( 0. to 1 Kg. ) as employed in Regler's experiments. Measurements of current passed by the crystal for different pressures confirmed Regler's observations, i.e., more current was passed at higher pressures. However, it could scarcely be maintained from such experiments that the resistance of galena was a function of such small pressures. It was believed that the change in the amount of current carried was a function of the gross contact between the entire crystal and the electrode material rather than in the change in contact pressure between the unit blocks, ( See p. 27 ). Attempts to measure the drop across the crystal for a fixed current were made by driving two Pt-Ir needles, held securely in place by means of set screws, into the side of the crystal. However, only contradictory results were obtained, the resistance showing at one time a decrease with pressure and at another an increase. It was decided that such discrepancies were due to the impossibility of securing fixed contacts. Vibrations of the building in which the work was being done were sufficient to change any one reading tenfold or more. Consequently advantage was taken of a fact employed by Coblenz<sup>(119)</sup> in making electrical contact with galena crystals, namely: That a copper wire, heated to incandescence and touched to a galena surface will fuse into the material and form a firm bond. This method made fixed potential contacts possible. It was later found out that leads could be attached in this way by touching a fine Cu wire (No. 30) to a piece of galena and short-circuiting both across

the house lighting circuit with a variable resistance of a few ohms interposed.

In order to determine more definitely the effect of pressure, an apparatus was built similar to that used by Regler but permitting welded potential contacts to be taken from the centers of the ends of the specimen. It is shown diagrammatically in Figure XV.

The current was adjusted for each reading so that it was constant for any one set of observations. Results of determining the IR drop across the welded potential leads for two different samples of galena are shown in Tables I and II.

It can be readily seen that the resistance of galena does not change with the order of pressures used, at least any variations are smaller than the other variations encountered.

It was further observed that Ohm's law is followed by galena at any of the pressures employed. Thus there does not seem to be any indication of unit blocks in galena from the standpoint of pressure-conductivity relations.

However, reproducible readings of specific resistance could not be obtained on any one sample with the apparatus employed above. A mere resetting of the top brass block sufficed to change the figures. Nevertheless, for any one setting of the specimen in the holder, and with no great vibrations of the apparatus, consistent results were always found in so far as pressure effects were concerned.

The inability to get reproducible readings was finally traced to two causes. (1) Galena was found to possess a high thermoelectric force toward copper. (2) The location of the current contact proved to be as

TABLE I

Showing the effect of pressure on the resistance of Galena  
Sample No. 14.4 ( Joplin, Mo)

Current for all readings 10 milliamperes.

Total Pressure in Grams.	Resistance in ohms.
90	0.0124
200	0.0120
400	0.0103
500	0.0110
700	0.0110
900	0.0110
700	0.0110
500	0.0105
200	0.009
90	0.0130

TABLE II

Showing the effect of pressure on the resistance of Galena  
Sample No. 89808-3 (U.S.N.M.)

Current for all readings 10 milliamperes.

Total Pressure in Grams.	Resistance in ohms.
90	0.0371
200	0.0357
400	0.0383
600	0.0365
800	0.0377
1000	0.0363
1300	0.0369

**Note:** 0.01 ohm corresponds to an IR drop of 0.1 millivolt with  
a current of 10 milliamperes. Hence, all variations in the  
above resistance readings amount to variations in measured  
potential of some 0.01 millivolts.

important as the location of the potential contacts.

#### THERMAL EFFECT

It has been observed by Reglar<sup>(82)</sup> that galena develops a thermal EMF against brass of  $2.4 \times 10^{-4}$  volts per degree. In the present work, while attempting to plot equipotential lines on the surface of a large specimen of galena by means of a series of 49 wires welded to the surface, it was found that readings were impossible when the specimen was merely allowed to lie on the laboratory table. Immersion in an oil bath was resorted to in order to prevent temperature effects from interfering. It was observed that when a balance was obtained on the potentiometer, the approach of an electric lamp to one of the potential contacts caused a galvanometer deflection, which could be reversed by bringing the lamp in the neighborhood of the other potential contact. No attempts were made to measure the intensity of this effect because the temperature difference between both ends of the specimen could not be determined. However, the fact was evident that a constant temperature bath was necessary.

#### GEOMETRICAL EFFECTS

Further attempts to plot equipotential lines with the block at uniform temperature were abandoned due to the fact that the differences in potential between one point and another on the surface were so small as not to be detectable. Currents of 10, 20, and 30 milliamperes were employed. Further increases in the amount of current passing would induce heating effects which would only complicate the results.

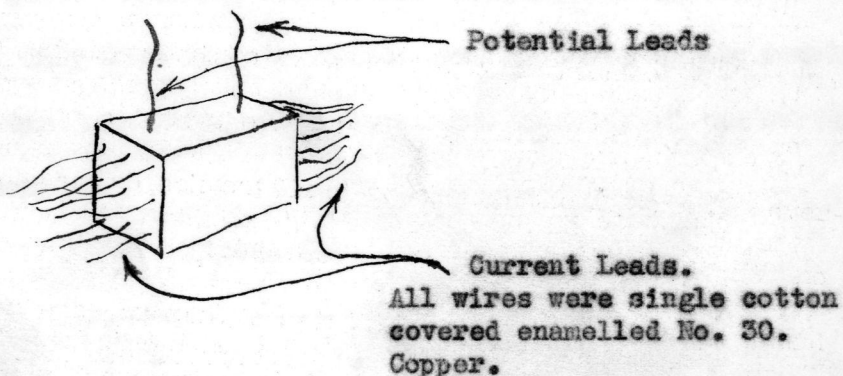
But, before reliable readings could be obtained on any specimen at even room temperature, it was necessary to determine the influence of the location of both current and potential contacts. The welded contact seemed



to be one of very great advantage in that it was rigidly fixed to one definite point. Accordingly, small right prisms of various galena samples were ground. Current leads were welded to the ends and potential leads to one side. The welding current, 3 to 6 amps., was passed into the crystal between the end and the potential lead on that end so that no change in the structure could be occasioned within the region whose resistance was to be measured. Such a set up gave, upon measuring the IR drop between the potential leads, very constant and reproducible results when immersed in a constant temperature bath. However, it was believed that, if the current were passed through another set of leads welded next to those already present, a different reading would be obtained.

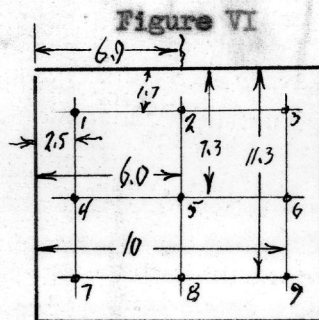
To verify this, somewhat larger prisms of galena were ground. The potential leads were welded on one side as before. But several wires were welded on each end for current leads. The accompanying sketch, Figure XVI, shows the general appearance of the specimen with the wires welded as described.

FIG. XVI

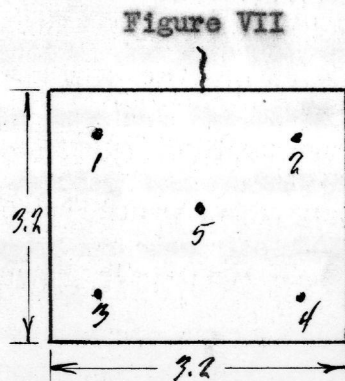


The ends of the crystal were labeled B and T. The location of the current points can be understood by referring to Figure VI. The distances shown on the diagram are in millimeters and represent the

average of the measurements from both ends, using one side and the top of the prism as reference lines. The sample used was from specimen No. 81805 from the U. S. National Museum. The sample was mounted by suspending it, by means of the wires forming the various leads, in a cylindrical copper can immersed in the heating or cooling medium, which was contained in a Dewar flask. Low temperatures were obtained with the aid of  $\text{CO}_2$  and ether mixture -- high temperatures by means of a resistance furnace in which the can was placed. Both high and low temperatures were measured with an iron - constantan thermocouple.

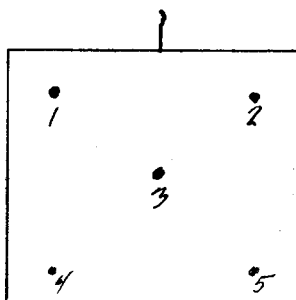


A sample of galena from St. Joseph Lead Company was treated in a similar fashion. Only five current points were employed as the sample was considerably smaller. Figure VII shows the location of the current points for this sample.



Now, just as a matter of comparison, a prism of a bismuth tin alloy was fixed to copper leads in exactly the same way. The copper wire was welded to the alloy by immersing the wire in a drop of zinc chloride solder flux and short circuiting the wire and the alloy across the power lines for a second or less. The location of the current points in this case can be seen by reference to Figure 8.

Figure VIII



Figures IX, X, and XI show the potentials obtained across the potential leads for the various current leads at room temperature. This gives some idea of the current distribution in the galena. It will be observed that the Bi-Sn alloy shows a similar distribution of current.

Figures XII, XIII, and XIV, are typical curves plotted from the results of temperature-resistance measurements. The actual numerical results are shown in Tables III, IV and V. It is interesting to note that none of the individual current points show the same temperature coefficient. This is true for the Bi-Sn alloy as well as the galena samples. The curves showing temperature-resistance relationships when all of the current leads are used probably represent the closest



TABLE III

Sample NO. 81805-8 (U.S.N.M.)

Contact Combination	CO <sub>2</sub> -ether Mixture.		Ice Water		Room Temp.		Hot Water		Furnace		Furnace.	
	Ohms.	Temp.	Ohms.	Temp.	Ohms.	Temp.	Ohms.	Temp.	Ohms.	Temp.	Ohms.	Temp.
A.	0.-----	-80°	0.0386	0.5°	0.0412	24.2°	0.0530	61.5°	0.1273	153°	0.1314	197.5°
F.	0.01345	-80	0.02295	1.1	0.0426	25	0.0571	76.5	0.-----		0.1120	198.9
1.	0.0119	-75	0.0305	0.5	0.0415	24.2	0.0672	73				
2.	0.0254	-75	0.0451	0.5	0.0550	24.2	0.0725	70				
3.	0.0162	-77	0.0263	0.5	0.0330	24.2	0.0381	69.5				
4.	0.0032	-77	-----		0.0100	24.2	0.0163	68				
5.	0.0008	-78	0.0055	0.5	0.0084	24.2	0.0144	67.5				
6.	0.0018	-78	0.0072	0.5	0.100	24.2	0.0147	65				
7.	0.0022	-79	0.0060	0.5	0.0071	24.2	0.0101	64.5				
8.	0.0007	-79	0.0050	0.5	0.0073	24.2	0.0091	64				
9.	0.0037	-78	0.0063	0.5	0.0075	24.2	0.0082	62				
A.			0.0391	0.5	0.0407	24.2	0.0532	61.5	0.1417	153	0.1556	197
F.	0.01375	-80	0.02295	1.1	0.0410	25	0.0576	76.5			0.0960	199.8
1.	0.0150	-75	0.0288	0.5	0.0400	24.2	0.0535	73				
2.	0.0278	-75	0.0442	0.5	0.0515	24.2	0.0715	70.5				
3.	0.0199	-77	0.0259	0.5	0.0320	24.2	0.0396	69				
4.	0.0092	-78			0.0110	24.2	0.0175	68.5				
5.	0.0018	-78	0.0063	0.5	0.0083	24.2	0.0172	67				
6.	0.0011	-78	0.0055	0.5	0.0095	24.2	0.0152	66				
7.	0.0069	-79	0.0052	0.5	0.0075	24.2	0.0112	64				
8.	0.0033	-78	0.0052	1.0	0.0064	24.2	0.0116	64				
9.	0.0063	-78	0.0062	1.0	0.0068	24.2	0.0091	62.6				
Averages			0.0398	0.5	0.04095	24.2	0.0531	61.5	0.1345	153	0.1435	197
Both	0.0136	-75	0.0229	1.1	0.0418	25	0.0574	76.5			0.1040	199
Relatives	0.0266	-75	0.0446	0.5	0.0552	24.2	0.0720	70				
5.	0.0013	-78	0.0059	0.5	0.0083	24.2	0.0158	67				
9.	0.0020	-78	0.0051	1.0	0.0068	24.2	0.0102	64				

A. refers to readings made by using all current contacts and taking potential from the top side  
 F. refers to readings made by using current contacts, 1,2,3,4,6,7,8,and 9. Potential across center of ends,  
 i.e. contacts No. 5.

TABLE IV

Sample No. 14-7 (Joplin, Mo.)

Contact Combination	CO <sub>2</sub> -ether Mixture		Ice Water		Room Temp.		Hot Water		Furnace		Furnace.	
	Ohms.	Temp.	Ohms.	Temp.	Ohms.	Temp.	Ohms.	Temp.	Ohms.	Temp.	Ohms.	Temp.
T end Positive	A.	0.0015	-69°	0.0031	1.0	0.0041	25°	0.0056	76°	0.0084	218.3°	
	F.	0.0025	-77	0.0053	4	0.0065	25	0.0086	74	0.0156	212.8	
	1.	0.0018	-69	0.0030	1	-----	---	0.0042	71			
	2.	0.0006	-70	0.0029	1	-----	---	0.0046	69.5			
	3.	0.0012	-71	0.0024	1	-----	---	0.0042	68			
4.	0.0023	-76	0.0032	1	-----	---	0.0058	67.5				
B end Positive	A.	0.0017	-69	0.0030	1	0.0041	25	0.0065	76	0.0166	221.1	
	F.	0.0029	-77	0.0047	4	0.0055	25	0.0075	74.5	0.0186	214	
	1.	0.0013	-69	0.0027	1	-----	---	0.0066	71			
	2.	0.0035	-70	0.0051	1	-----	---	0.0081	69.5			
	3.	0.0013	-71	0.0024	1	-----	---	0.00423	68.5			
4.	0.0006	-76	0.0022	1	-----	---	0.0043	67.5				
Averages for Both Polarities.	A.	0.0016	-69	0.0030	1	0.0041	25	0.0061	76	0.0125	220	
	F.	0.0027	-77	0.0049	4	0.0058	25	0.0081	74	0.0171	213	
	1.	0.0016	-69	0.0029	1	-----	---	0.0054	71			
	4.	0.0015	-76	0.0027	1	-----	---	0.0051	67.5			

A. refers to readings made by using all current contacts and taking potential from top side.

F. refers to readings made by using current contacts 1,2,3, and 4. Potential taken across the center of the ends, i.e., contacts No. 5.

TABLE V

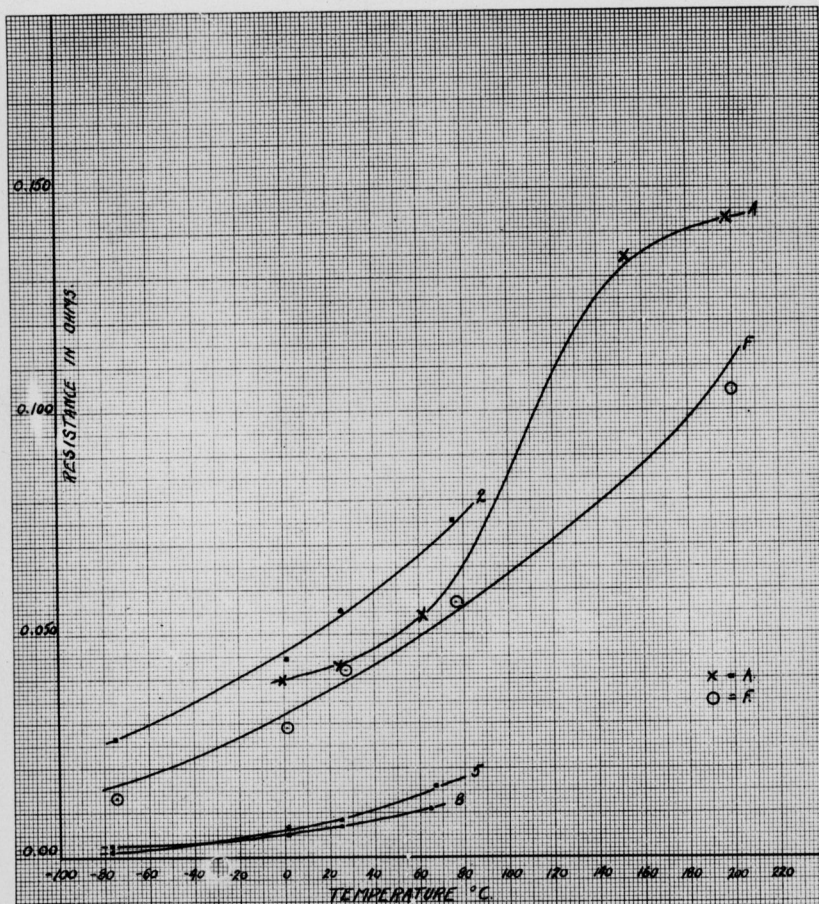
Bi-Sn Alloy ( 1% Sn )

Contact Combination	CO <sub>2</sub> -ether Mixture		Ice Water		Room Temp.		Hot Water		Furnace	
	Ohms.	Temp.	Ohms.	Temp.	Ohms.	Temp.	Ohms.	Temp.	Ohms.	Temp.
<i>T end Positive</i> A.	0.00023	-73°			0.00031	29°	0.00037	73°		
	F.	0.00021	-73			0.00033	29	0.00033	66	
	1.	0.00037	-73			0.00051	29	0.00050	71	
	2.	0.00037	-73			0.00050	29	0.00050	70	
	3.	0.00025	-73			0.00031	29	0.00031	69	
	4.	0.00016	-73			0.00017	29	0.00020	68	
5.	0.00015	-73			0.00017	29	0.00017	67		
<i>B. end Positive</i> A.	0.00025	-73			0.00033	29	0.00037	73		
	F.	0.00015	-73			0.00033	29	0.00033	65.5	
	1.	0.00037	-73			0.00051	29	0.00051	71	
	2.	0.00037	-73			0.00050	29	0.00050	70	
	3.	0.00020	-73			0.00031	29	0.00033	69	
	4.	0.00008	-73			0.00017	29	0.00020	68	
5.	0.00008	-73			0.00015	29	0.00017	67		

A. refers to readings made by using all current contacts and taking potential from top side.

F. refers to readings made by using current contacts 1,2,4, and 5. Potential taken across the center of the ends, i.e., contacts No. 3.

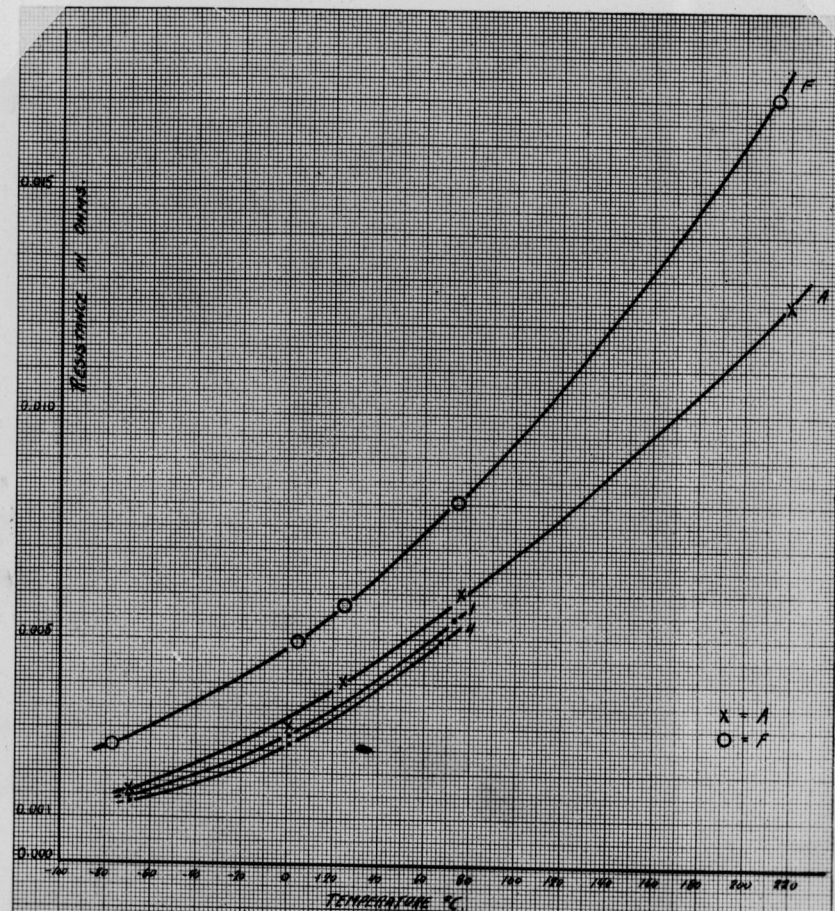




CURVE SHOWING RELATION BETWEEN TEMPERATURE AND RESISTANCE FOR VARIOUS CONTACT COMBINATIONS. GALENA SAMPLE NO. 81805-B

PLOTTED FROM AVERAGES OF READINGS FOR BOTH POLARITIES. DATA FROM TABLE III. A, F, X, S, B, REFER TO CONTACT COMBINATIONS. (SEE TABLE III)

FIGURE XII



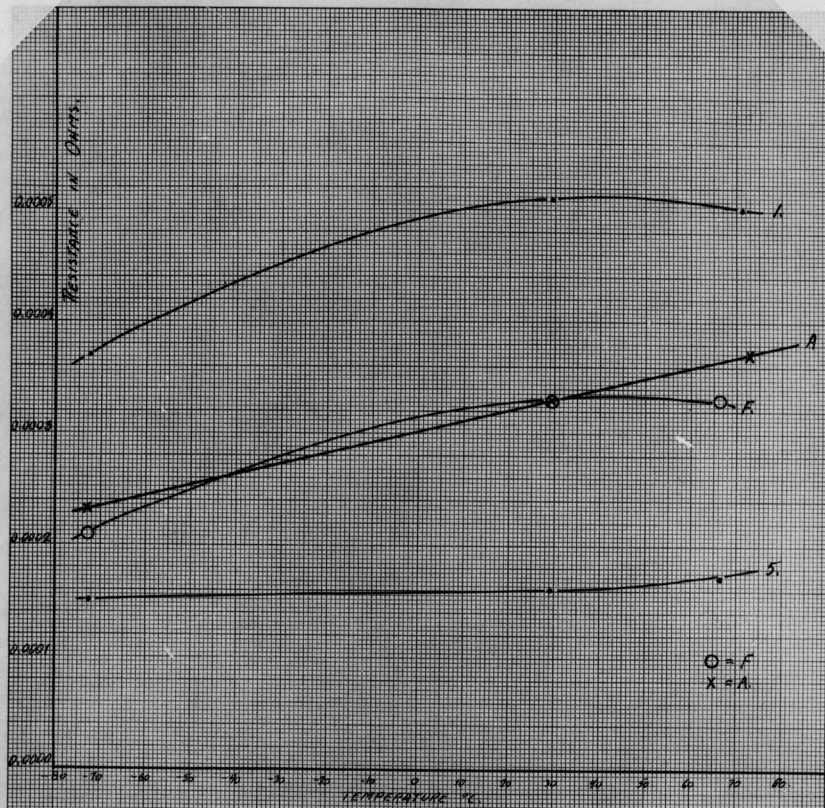
CURVES SHOWING RELATION BETWEEN TEMPERATURE AND RESISTANCE FOR VARIOUS CONTACT COMBINATIONS. GALENA SAMPLE NO. 19-1.

DATA FROM TABLE II REFERRED FOR BOTH POLARITIES. TABLE III

A, F, I, and J REFER TO CONTACT COMBINATIONS

FIGURE XIII





CURVE SHOWING RELATION BETWEEN TEMPERATURE AND RESISTANCE FOR VARIOUS CONTACT COMBINATIONS. BI-SM ALLOY (1% Sn).

DATA FROM TABLE IV.

1, 5, A, and F REFER TO CONTACT COMBINATIONS. (SEE TABLE III.)

FIGURE XIV

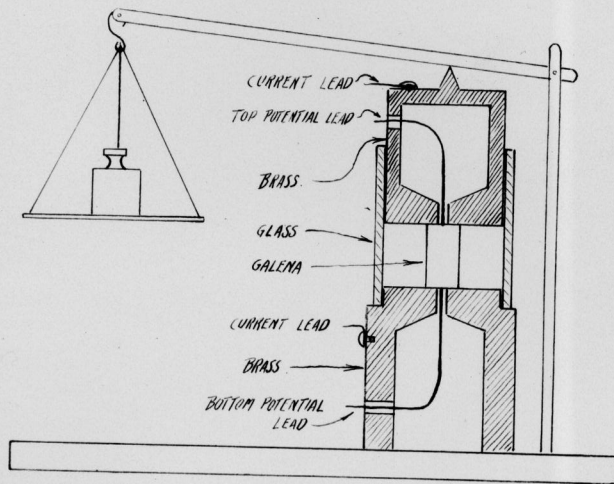
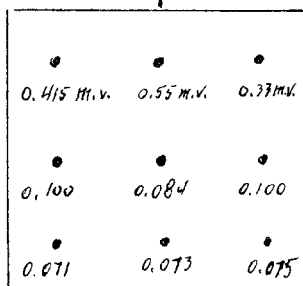


FIGURE XV

approximation to the true condition. Thus, these curves for the Bi-Sn alloy are strictly straight lines. This conforms to the behavior of metallic conductors in the temperature range employed. But similar curves for galena do not show this linear relationship. In general, they are more nearly horizontal at the lower temperatures and the slope increases rapidly with increasing temperature. This unquestionably shows deviations from straight metallic conduction in the case of galena. The exact interpretation of the bend in the galena curve is difficult. It is perhaps qualitatively important from the standpoint of the conception of aggregate structure. But quantitative interpretation is practically impossible with this method of attack.

Reference to any of the curves, or better to Figures IX, X, and XI will show that the potential reading is very delicately adjusted to the distances between the nearest current leads and the line along which the potential is measured. Now, unless all points; that is, the entire surface of the sample can be used for sending in the current, it is impossible to calculate the specific resistance.

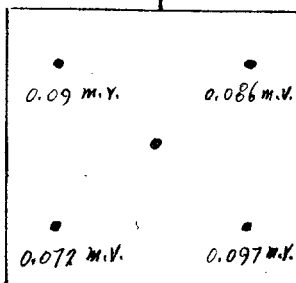
Figure IX



Sample 81805 U. S. N. M. (-8)

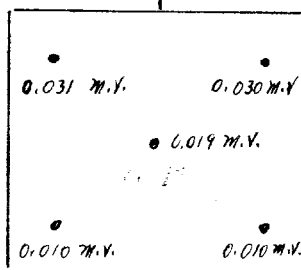
Diagram showing the potential measured across the fixed potential leads for the different pairs of current leads. Current in all cases 10 M. A. Temperature - 24.2° C.

Figure X



Sample- galena from St. Joe Lead Co. No. 14-7  
 Diagram showing the potential measured across the fixed potential  
 leads for different pairs of current leads. Current in all cases  
 30 M. A. Temperature  $1^{\circ}$ .

Figure XI



Sample Bi - Sn Alloy (approx. 1% Sn)  
 Diagram showing the potential measured across the fixed potential  
 leads for different pairs of current leads. Current in all cases 60  
 M. A. Temperature -  $29^{\circ}$ .

Preliminary experiments had been made at the beginning of this work in which right prisms of galena were copper-plated, the Cu ground from all but two ends, and soldered connections made to those ends. This made a plane contact over the entire area of each end of the prism. At that time the method was abandoned because of the extreme mechanical weakness of the joint. Also the welded contact was not then known, and both potential and current contacts had been taken from the same drop of solder, which was not desirable since the readings thus included the drop through the solder and the Cu galena interfaces. However, it was discovered that the Cu plate and solder connection could be made satisfactorily if small copper wire were used. The small wire was sufficiently pliable to take all of the strain and transfer but very little to the Cu - galena bond.

The copper-plated end offers a current contact which covers all points of the end of a crystal as the copper is deposited in all corners and irregularities of the surface. The experiments on the location of current contacts had proved that this is the desirable condition.

A section of galena, sawed from a large block and ground to square cross section by mounting with balsam on a piece of key steel, was again sawed to give two samples from the same portion of the same specimen. Both samples were copper-plated under identical conditions, and leads soldered to the ends as previously described. Two potential leads were welded into one side of each prism. The current was passed through the copper-plated contacts and potential measurements made with the following results:

Sample No.	M.A.	Sp. Res.	Temp.
14-13	20.0	0.00182	24 <sup>o</sup>
14-14	20.0	0.00139	24 <sup>o</sup>

The specific resistance, calculated in accordance with the usual formula,

$$P = R \frac{l}{a}$$

(Where P = Specific Resistance, (Ohm-Cm), R = resistance of sample in Ohms, l = distance between potential leads, and a = area of cross section) shows a difference of 0.00043 ohms or 31% of the higher value.

It was evident that either the method was at fault or else the conductivity of galena varies from point to point.

A new potential contact was welded into the sample 14-13 at a point on a line with and between the two original contacts.

Measurement of the IR drop between the new contact and one of the old ones gave, when calculated to specific resistance, 0.00221 ohms-cm. Likewise a new measurement on the two original contacts gave a figure of 0.00231 ohm-cm.

This proved conclusively the inadequacy of the welded contact. The change in resistivity is believed due to the interposition of the new contact in the path of the current. Microscopic observation of several of the welded contacts in cross section showed that the wires penetrated into galena to different depths. This factor seems to be beyond control. The cross section showed the wire partially dissolved and cemented into a sheath of black material, probably a mixture of copper sulfide and metallic lead.

These last experiments, together with those on the effect of contact location, confirmed the futility of attempting to measure the specific

conductivity of galena. Only comparative measurements can be made and they can be but rough approximations.

#### RESISTANCE AND TEMPERATURE

It was believed that perhaps some constancy might be obtained in the results of temperature coefficient measurements. In spite of the fact that the welded leads penetrated to different depths, they were adopted as the most reliable contact. The maximum observed discrepancies which were probably partly or entirely due to the welded contact, amounted to only about 30%. Needle contacts had shown inconsistencies of 1000% or more. The copper-plated current contacts were also retained as the best. Six different samples were ground to the same cross sectional area by mounting on key steel as before. They were copper-plated, dried, and leads soldered and welded all under the same conditions. Resistance readings were made at CO<sub>2</sub>-ether, ice water, and room temperatures, and at temperatures between 150° and 210° C. The samples were mounted in the same way as for the experiments on the location of contacts (See page 35.) Readings were made as shown in Tables VI, VII, VIII, IX, X, and XI.

It will be observed that apparently an irreversible change takes place upon both heating and cooling of some of the samples. The effect due to heating has been observed by others (See page 29), but has usually been a decrease in resistance. Perhaps the increase observed in some of the present cases is due to oxidation. However, some samples show a decrease, and it would seem unlikely that one specimen of galena



TABLE VI

Sample No. 98110-1 (U.S.N.M.)

Current 20 milliamperes.  
Readings reported in the order taken.

Resistance in ohms.	Temperature °C.	Polarity.
0.0884	19	B-
0.0882	19	T-
0.2070	205	B-
0.2068	205	T-
0.0899	21.5	B-
0.0892	21.5	T-
0.0832	0.7	B-
0.0843	0.6	T-

TABLE VII

Galema sample No. 13.

Current 10 Milliamperes.  
Readings reported in the order taken.

Resistance in ohms.	Temperature °C	Polarity
2.1598	19	B-
2.1610	19	T-
3.2743	156.5	B-
3.3085	158	T-
2.5538	21	B-
2.5483	21	T-
2.4613	3	B-
2.4577	3	T-
1.7177	-70 (approx)	B-
1.7060	-70 "	T-
1.4063	23	B-
1.3656	23	T-

TABLE VIII

Sample 17589-6 (U.S.N.M.)

Current 30 milliamperes

Readings reported in the order taken.

Resistance in ohms	Temperature °C	Polarity
0.0629	19	B-
0.0655	19	T-
0.0785	0.7	B-
0.0774	0.7	T-
0.0832	23	B-
0.0849	23	T-

TABLE IX

Sample 13208-2 (U.S.N.M.)  
Current 10 milliamperes.  
Readings reported in the order taken.

Resistance in ohms	Temperature °C	Polarity
1.1145	19	B-
1.106	19	T-
1.864	166	B-
1.929	174	T-
1.410	0.6	B-
1.415	0.6	T-
1.327	24	B-
1.3287	24	T-
2.4545	-70 (approx)	B-
2.3093	-70 "	T-
1.400	23	B-
1.382	23	T-

TABLE X

Sample 81805-9 (U.S.N.M.)  
Current 10 milliamperes.  
Readings reported in the order taken.

Resistance in ohms.	Temperature °C	Polarity
0.2906	19	B-
0.2908	19	T-
0.3747	151	B-
0.3856	152	T-
0.304	0.2	B-
0.313	0.2	T-
0.326	24	B-
0.328	24	T-

TABLE XI

Sample 14-10 (Joplin, Mo.)  
Current 30 milliamperes.  
Readings reported in the order taken.

Resistance in ohms.	Temperature. °C	Polarity
0.0035	19	B-
0.0035	19	T-
0.0094	164	B-
0.00846	165	T-
0.00294	0.8	B-
0.00300	0.8	T-
0.00333	23	B-
0.00360	23	T-
0.0236	-70 (approx)	B-
0.0241	-70 "	T-
0.055	24	B-
0.055	24	T-

should be much more resistant to oxidation than another. Furthermore, all of the samples appeared bright and untarnished after the heating. Lapinski (loc. cit.) has observed crystal growth in pressed PbS powders at  $215^{\circ}$ - $225^{\circ}$  C, and remarks that such growth takes place without heating, although very slowly. But this phenomenon has always been accompanied by a decrease in the resistance.

Water vapor or other gases may be driven off from within the interior of the crystal. Lapinski observed this in the case of his pressed powders. And also the changes due to cooling may be due to a condensation of the adsorbed gases within the crystal.

The effect of minute impurities can be considerable, and it is not unreasonable that changes in phase relationships between galena and its impurities should take place on heating. That is, some impurity, naturally retained as a distinct phase, may enter the galena lattice at some higher temperature and exist thereafter as solid solution. Head (See page 47) has observed minute NaCl crystals on cleaved galena surfaces. Perhaps with a stretch of the imagination, NaCl might go into solution in PbS. The structures of the two materials are of the same type and the dimensions of the respective lattices are not far different.

Streintz and James had postulated two allotropic modifications of galena as cause of the change on heating and cooling. It is not believed that there is at present any x-ray evidence of such possibilities. This question is to be studied by x-rays at a later date.

It will be noticed that there are great differences in the resistances of the various samples. Even though we assume that any particular measurement is accurate to only 30%, the values measured

range from 0.003 to 1 ohm for the crystals showing the usual cleavage and up to 2 ohms in the case of sample 13 which was composed of an aggregation of small crystals. This corresponds to a range of variability of 100,000%.

Such variations cannot be definitely explained and are probably due to part or all of several causes. Impurities are perhaps one of the greatest sources of variation. These may be present as: (1) Solid solutions in the lattice. (2) Mechanical inclusions between planes of weakness in the crystal. (3) Dispersions throughout the crystal, or (4) Adsorbed material.

(1) The solution of any metal in another is known to cause a marked decrease in the conductivity of the original metal. Such is probably what may be expected in the case of solid solutions <sup>of</sup> other material in galena.

(2) Head <sup>(17)</sup> has recently observed minute NaCl crystals on cleavage faces of some of the minerals employed in this work. Lead carbonate has also been found on freshly cleaved galena surfaces of other specimens. Tubandt <sup>(80)</sup> has shown that the conductivity of  $PbCl_2$  is increased 47 fold due to an admixture of 0.1% KCl, and that the KCl does not take part in the conduction. Similar effects are certainly not impossible for electronic conductors.

(3) Dispersed material in galena will obviously change its conductivity. Metallic lead has been found in the form of minute globules in galena. The mixture of Pb and PbS should not conduct in the same degree as pure PbS.

(4) As to adsorbed material, it is quite evident, assuming the unit block idea, that the current will be conducted by either the ad-

sorbed layers, the lattice proper, or both. In any case a change in the resistivity will be occasioned by a change in size or shape of the blocks. Vrede has shown that complete removal of the gases from crystallized PbS by repeated sublimations under a vacuum, prevents the rectifying effect from being observed.

Gross crystal defects such as voids, cracks, and large planes of foreign inclusions will be expected to add their effect on conductivity measurements. A sister sample of U.S.N.M. 13208, (Table IX) was found to be hollow although the natural crystal appeared to be a compact solid cube. Head has found and described similar voids in some of the samples used in this work. Frequently upon copper-plating specimen, heavy planes of foreign material have been found, although macroscopic observations of the unplated crystal showed no such planes.

Head has also observed and described uniform striations and vein-like lines on clean, freshly cleaved surfaces. The striations are interpreted by him to be slip planes. Such slip planes are regions of distortion and consequently will influence conductivity measurements.

In general there are many variables to be tied down before an exact interpretation can be given to conductivity measurements of natural galena crystals.

#### DETECTOR ACTION

Galena, as is well known, possesses the ability to rectify small alternating currents. The various theories regarding this phenomenon are not pertinent to the present paper. However, it might be expected that this action should produce a pronounced effect on the resistance measurements with direct current. Such was found to be the case in practically all experiments wherein point contacts were used to send the current



through the crystals. For instance, see Tables III, IV and V. The measured potential is generally different for opposite directions of the same current strength.

But reference to Tables VI, VII, VIII, IX, X, XI, show, that when the current is supplied by copper-plated contacts of equal area, little or no detector action is noticeable. The copper-plated ends seem to automatically eliminate any discrepancies in resistance measurements due to unipolar conduction. This suggests that the detector action is very closely related to the well known point to plane effect.

#### SUMMARY

- (1) The effect of small pressures on the conductivity of galena has been studied by a potentiometric method. Within the limits of the pressures employed no change in the resistance of galena can be detected at different pressures. Likewise conduction in galena obeys Ohm's law for all pressures used in the experiments.
- (2) Galena was found to possess a high thermo-electric force against copper.
- (3) The location of contacts on galena crystals has been found to be of fundamental importance to the values of resistance determined by potentiometer measurements.
- (4) Some evidence that irreversible changes take place in galena crystals upon either heating and cooling or cooling and heating is shown by resistance measurements made at various temperatures.
- (5) Resistance measurements have been found to be the same for either direction of current flow when copper-plated current contacts of equal area are used.
- (6) Possible causes of the many variations in the conductivities of

of natural galena crystals have been briefly discussed.

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