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THE USE OF ZONE THEORY IN PROBLEMS OF SULFIDE MINERALOGY, PART II; THE RESISTIVITY OF CHALCOPYRITE

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Abstract

Resistivity vs. temperature measurements on chalcopyrite indicate a very small activation energy for donor impurities. In a sulfur-free atmosphere dissociation occurs at a lower level of thermal energy than does intrinsic semiconductivity, suggesting a relatively large energy gap between the valence and conduction bands. Attempts to maintain equilibrium sulfur vapor pressure during resistivity measurements in order to obtain the exact band gap energy were unsuccessful. Total absence of *p*-type conductivity was noted. This implies that chalcopyrite will not occur with a cation deficiency, but will deviate from stoichiometry only with a cation excess.

Introduction

In two earlier papers (Frueh, 1954; 1955) a more or less qualitative use of zone theory was applied to several problems in sulfide mineralogy. An explanation, based on the relation between the band gap energy and the energy connected with a vacancy or interstitial impurity, was presented for the stable existence of non-stoichiometric compounds. In one example, AgCuS, it was apparent from the calculated electron-to-atom ratio necessary to fill the valence band that if this compound existed with the exact stoichiometric composition, some of the electrons would have to lie in the conduction band at a somewhat higher energy level. This might require more energy than that necessary to remove a silver atom, and, as indicated by experimental observation, the stable composition of stromeyerite would be $Ag_{1-x}CuS$, where x has some value between 0 and 0.1.

A similar explanation was advanced for the size and shape of the stability field of digenite (Cu_9S_5)-bornite (Cu_5FeS_4)-chalcopyrite ($CuFeS_2$). In the field from digenite to chalcopyrite the same structural type is maintained, despite the increase in the iron-to-copper ratio, by the omission of sufficient metal atoms to avoid increasing the electron-to-atom ratio beyond the capacity of the valence band.

To expand this theory and put it on a quantitative basis, a knowledge of the magnitude of the energy gap between the valence band and the conduction band is necessary. As the excess or deficiency of atoms in a non-stoichiometric compound may be treated as impurities, it would also be beneficial to have quantitative data regarding the impurity levels.

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All of this information can be secured experimentally from the measurement of the variation of electrical characteristics with temperature.

Electrical measurements have been obtained and the band structure determined for a number of semiconductors that are of interest to the electronic industry, and in a few cases, such as PbS (Scanlon, 1953; Bloem, 1956; Bloem and Kröger, 1956) and FeS_2 (Marinace, 1954; Sasaki, 1955; Otsuka, 1957), they have also been of direct interest to the mineralogist. There are many data to be obtained from naturally-occurring sulfides before optimum use can be made of existing theory. This paper contains the results of initial attempts to elucidate the band structure of chalcopyrite by this method.

Since much information on the theory and technique of the determination of band structure from the variation of electrical properties with temperature is contained in texts on semiconductors (Dunlap, 1957; Shockley, 1950) and in solid state physics texts, it will suffice here to give a brief résumé of the properties to be measured and their relation to the band structure.

At low temperatures and high purity, semiconducting materials are good insulators of electricity. They are represented in band theory (Fig. 1) as having their valence bands filled; there is a forbidden energy gap between the top of the valence band and the bottom of the conduction band. As we raise the temperature, enough energy is given to the pure semiconductor in the form of heat to lift the electrons at the top of the valence band across the energy gap to the conduction band. The material becomes a conductor because the electrons now in the conduction band are free to conduct, and because the holes left in the valence band permit a net movement of the energy states in the valence band. The latter can be looked upon as conduction by positive holes. Thus, this type of conductivity, called intrinsic semiconductivity, is made up of two types of carriers: electrons, or negative carriers; and holes, or positive carriers, that are simultaneously activated when the temperature of the sample reaches the intrinsic range.

The total conductivity is expressed mathematically by $\sigma = e(n\mu_n + p\mu_p)$, where e is the electronic charge (1.6×10^{-19} coulombs), n the number of electrons or negative carriers, p the number of holes or positive carriers, and μ_n and μ_p their respective mobilities. For intrinsic conductivity $n = p \sim \exp - \Delta E / 2kT$, where ΔE is the energy gap between the valence band and the conduction band, k the Boltzman constant, and T the absolute temperature. As resistivity is the reciprocal of conductivity, $\rho = 1/\sigma$, it follows that ΔE can be obtained from the slope of the curve $1/T$ vs. $ln\rho$, if we assume that the change in mobilities μ_n and μ_p with temperature is small compared to the change in the number of carriers, n and p.

If we are utilizing natural samples, the possibility of obtaining very pure ones is quite remote. We must, therefore, be aware of the conductivity that arises from impurities. Also, as pointed out above, a stoichiometric excess or deficiency can be looked upon as an impurity, and therefore the activation energies of the impurity levels are a necessary and important part of the total energy picture of a non-stoichiometric compound. There are two types of impurity or extrinsic semiconductivity. One is due to the presence of an impurity which, when activated, can donate an extra electron to the band structure of the host semiconductor. This is called donor, or *n*-type, impurity and can be caused by an atom of a greater number of valence electrons in substitution solid solution. When activated, the extra electron would have to be accommodated in the conduction band, and thus an *n*-type semiconductor would be created. The extra electron might also be donated by the presence of a cation in interstitial solid solution, or even by a stoichiometric excess of cations.

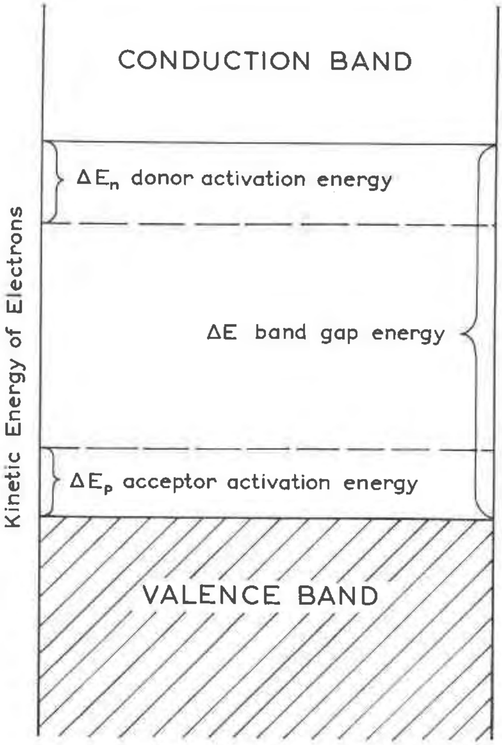

Fig. 1. Band scheme for semiconductor.

The other type of extrinsic semiconductivity is due to the presence of an impurity which, when activated, will capture or accept an electron from the valence band, thus causing *p*-type, or acceptor, semiconductivity. Thus an atom substituting in a position in the structure normally occupied by one with a higher number of electrons will, when activated, act as an acceptor. The same effect can be produced by a deficiency of cations, probably resulting in vacancies (Schottky defects) which will trap electrons and cause holes in the valence band.

Two of the commonly used experimental methods for determining the type and number of carriers, and hence the kind of semiconductivity, are the determination of the Hall effect and the determination of the thermoelectric power. In the former, use is made of the fact that the holes and electrons travel in opposite directions in a sample plate during current flow. When a magnetic field is applied normal to the face of a plate, both holes and electrons will be deflected to the same side. From a measure of the sign and magnitude of the potential difference across the plate (perpendicular to both the current flow direction and the direction of the magnetic field) both the type and density of the carriers can be determined.

When a temperature difference is maintained between the ends of a specimen, an e.m.f., the thermoelectric power, is measured in millivolts/°C. by means of metal leads (usually copper) connected to the ends of the specimen. By convention, the sign of the thermoelectric effect is taken as positive if the electric current flows in the same direction as the thermal current. A positive thermoelectric sign indicates the presence of *p* carriers, while a negative one indicates *n* carriers. For most semiconductors the thermoelectric power is independent of the composition of the metal leads.

The activation energy of both types of impurity (ΔE_n or ΔE_p) can be determined by a method similar to that for determining the band gap energy: that is, from the slope of the curves in the temperature ranges where an increase in conductivity is due to the activation of only one type of carrier. Samples containing both types of impurity, in cases where both are activated over the same temperature range, are not suitable for this determination.

EXPERIMENTAL METHODS

Ideally, resistivity measurements for elucidating the band structure should be made from oriented single crystals. As there are additional energy states connected with the surfaces and interfaces of semiconductors, it is best to avoid multicrystalline samples. In an anisotropic crystal the band structure may also be anisotropic, and the energy gaps will have to be determined in different directions to get the correct picture.

Large, well-formed single crystals of chalcopyrite from French Creek, Pennsylvania; Cornwall, England; and Ugo, Japan, were used. Samples were prepared from these crystals by slicing with a toothless band-saw blade to which #600 abrasive powder, mixed with water and glycerine, was applied. The crystal was mounted on a little dolly that was pulled forward by the weight of a few small washers on a string over a pulley, thus holding the crystal against the moving saw blade with a very light pressure. Sections were cut in various orientations, and two sample sizes, 1×0.2×0.1 and 2×0.5×0.2 cm., were utilized.

Resistance was measured by a null method to avoid the effect of contact resistance. A schematic diagram of the circuit used is illustrated in Fig. 2. Hall effect measurements were made by varying the slide wire potentiometer until a potential null was found, and then applying a 7000 Gauss field. All measurements were repeated after reversing the current flow through the crystal, and the results were averaged to remove any thermoelectric effect due to a possible thermal gradient in the sample.

The crystal holder, Fig. 3, was fashioned from Lavite, and gold leads were used throughout. The holder was inserted in a small furnace consisting of a vacuum bottle of Monel metal, with Kanthol windings on a ceramic core inserted in the bottle. The two-inch outside diameter of the vacuum bottle permitted it to be inserted between the poles of an electromagnet. Provision was made to introduce an inert atmosphere into the furnace.

A similar holder, for resistivity measurements alone, was constructed to fit into a silica tube, which in turn was fitted into a horizontal tubular furnace. The tube was sealed at one end, and the other end was connected to a source of H_2S for the maintenance of sulfur vapor pressure.

RESULTS

From the sign of the very small Hall effect, all the samples appeared to be *n*-type conductors at room temperature. This is in agreement with the results of other workers (Telkes, 1950) who found that, without exception, all of the twenty-two different samples of chalcopyrite measured had a negative thermoelectric effect.

Resistance measurements were made at temperatures only as low as −50° C., and from the negative slope of the $1/T$ vs. $\log \rho$ curve in this region it was evident that the *n* carriers were already activated. It can be concluded that the donor impurity level of chalcopyrite lies very close to the bottom of the conduction band, the ΔE_n being very small.

Resistance measurements were made up to 350° C. The resistance slowly increased with temperature (Fig. 4), due to the interaction of the carriers with increased thermal vibrations of the lattice, until a temperature of about 310° C. was reached. At this point the resistance reached a maximum; then, as the temperature increased, the resistance rapidly decreased, indicating a marked increase in the number of carriers.

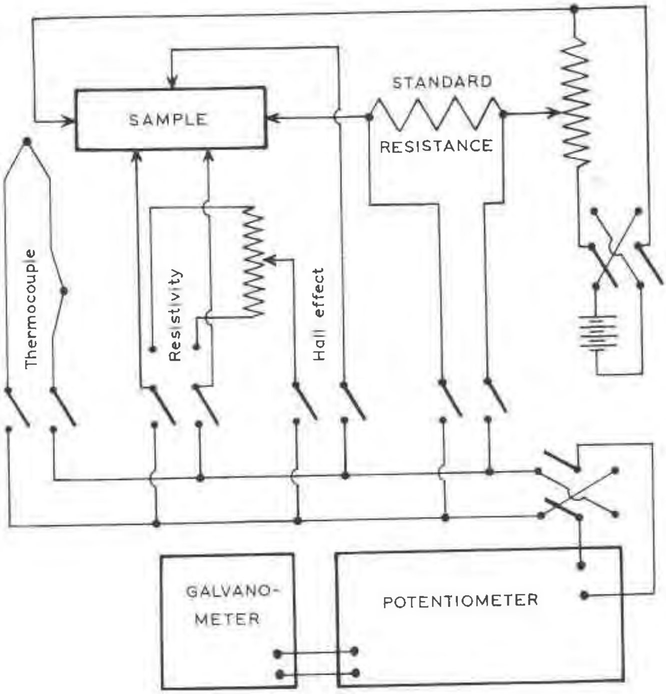

Fig. 2. Circuit diagram for Hall effect and resistivity measurements.

Upon cooling the sample, the high resistance is not recovered, but the sample returns by a lower path to a resistance considerably lower than its initial room temperature resistance. If the same sample is reheated, the curve obtained upon the previous cooling is followed until 310°, when, with increasing temperature, the resistance decreases rapidly. Again the resistance is not recovered when the sample is cooled. These runs were re-

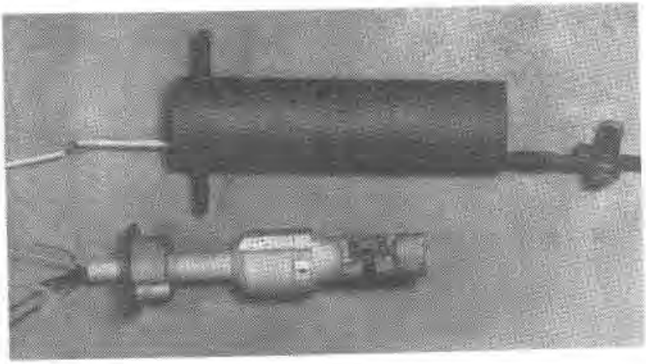

Fig. 3. Furnace and holder for Hall effect and resistivity measurements.

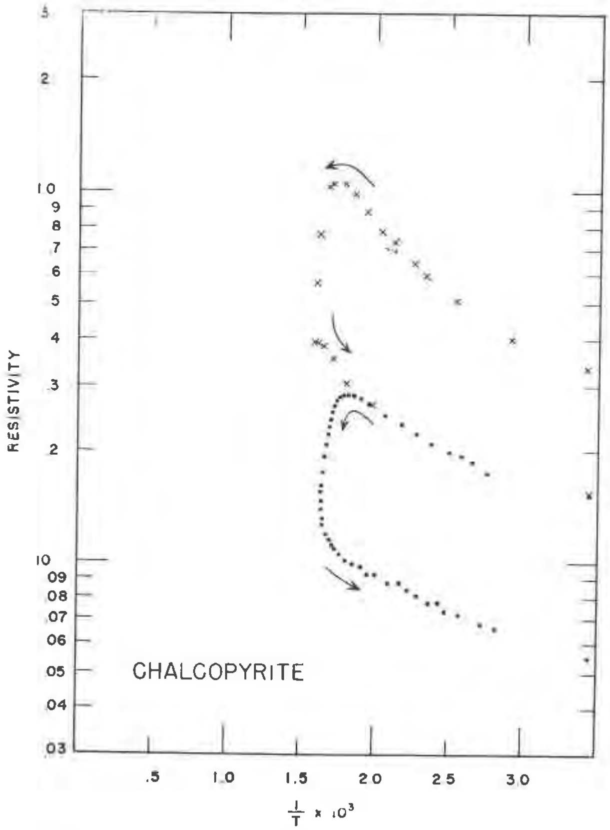

FIG. 4. Resistivity of chalcopyrite as a function of temperature in inert atmosphere. x = first run; • = second run.

peated several times with similar result until the sample became brittle and would crumble under the pressure of the electrical contacts.

It was found from a series of independent runs that the resistance curves were reproducible on heating and cooling as long as the temperature (310°) where the curve reaches its maximum resistance was not exceeded. It was also found that if a temperature higher than 310° C. is maintained for a long period of time, the resistance continues to drop, the crystal becomes brittle, and the electrical contacts are lost.

From these experiments it is evident that the creation of more electrical carriers above 310° C. is not an equilibrium process due to intrinsic semiconductivity, but rather appears to be a process in which additional carriers are caused by a deviation of stoichiometry due to partial dissociation and loss of sulfur. A similar effect was noted by Scanlon (1953) in PbS where it was found that carriers were created by dissociation shortly after the intrinsic range was reached. Data necessary to determine the energy gap could be obtained only in the small range of temperature between where intrinsic conductivity started and dissociation took place. However, in chalcopyrite the dissociation appears to take place before the intrinsic range is reached, and therefore some means of preventing dissociation is necessary before data for the determination of the band gap energy can be obtained.

Resistance measurements were attempted in a sulfur vapor atmosphere (H_2S-H_2). It was soon found that too high a sulfur vapor pressure resulted in the formation of an outside coating of covellite, CuS, and the growth of pyrite, FeS_2, within the sample. There are no data available at present on the exact sulfur vapor pressure in equilibrium with stoichiometric chalcopyrite at these temperatures.

An attempt to maintain the equilibrium vapor pressure was made by isolating a sample of chalcopyrite, to which electrical leads had been connected, in a sealed tube partially filled with finely powdered chalcopyrite. It was hoped that the fine powder about the walls of the tube would be a little warmer than the isolated sample in the middle of the tube, thus dissociating first and forming a sulfur vapor pressure that would be just enough to maintain the composition of the slightly cooler single crystal. The curve (Fig. 5) again shows lack of reversibility, and it must be assumed that the equilibrium vapor pressure is not maintained by this method.

In an investigation of the system Cu-Fe-S, Merwin and Lombard (1937) found the dissociation pressure curve for $CuFeS_{1.95}$ from 550° to 625° C. Preliminary tests were made by these investigators at temperatures from 375° to 525° C. and at sulfur pressures of 1 to 50 mm. Only above 500° C. and at pressures above 40 mm. did the results indicate systematic changes. Merwin and Lombard found that the reaction of chalcopyrite involving the absorption of sulfur lagged greatly at the lower temperatures and pressures because pyrite, one of the reaction products, was slow to crystallize, whereas loss of sulfur began without apparent lag.

They also found that samples of $CuFeS_2$, heated within the range of 10 mm. to 610 mm. and from 525° to 625° C., contained small amounts of pyrite, whereas samples 0.5% by weight lower in sulfur were homogeneous. Therefore, they concluded that in this range chalcopyrite of theoretical stoichiometric composition is not quite stable.

More recently, Hiller and Probsthain (1956) found from thermal and x-ray powder studies that, when heated without a controlled sulfur pressure, the disordered phase of $CuFeS_2$, stable above 550° C., slowly loses sulfur up to 720° C. when an end product poorest in sulfur is reached. This compound, which has a formula $Cu_{17+x}Fe_{17+x}S_{32}$ ($x \approx 0.6$), inverts upon cooling to a cubic phase ($a=10.58$) which is still based upon face-centered close-packed sulfur atoms.

There appears to be no conflict between the results of the present research and that of earlier workers, except that the much greater sensitivity of electrical measurements allows one to detect the loss of sulfur at a much lower temperature. The loss of sulfur before the advent of the intrinsic range supports the theory that the non-stoichiometric composition with extra donor atoms, in the form of a stoichiometric excess of cations, is the more stable or lower energy compound under low sulfur vapor pressure and elevated temperature conditions. This is because a relatively greater energy is required to lift the electrons across the band gap than to include and activate them in the donor level. The low activation energy of the donor-type impurities, and either the high activation energy of lack of acceptor-type impurities, as evidenced by the fact that all samples give only negative Hall and thermoelectric effects, imply that

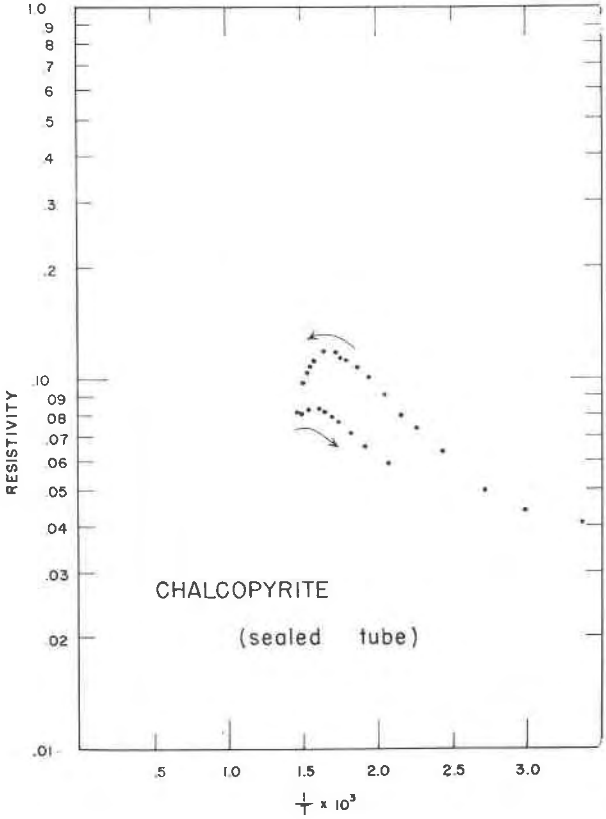

FIG. 5. Resistivity of chalcopyrite as a function of temperature in a sealed tube.

the variation of stoichiometry in chalcopyrite will always be on the sulfur-deficient side and never cation-deficient.

Until an accurate equilibrium sulfur vapor curve for chalcopyrite from 300° C. and up is known, and resistivity is measured in a controlled atmosphere, it will be impossible to obtain the exact band gap energy by this method. However, electrical measurements (Bloem and Kröger, 1956) provide a very sensitive method for determining the vapor pressure curve. Attempts should also be made to "dope" chalcopyrite, perhaps with minute amounts of phosphorus, to see if acceptor impurities can be synthetically created and the ΔE_p determined.

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