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*IRON-IRON INTERACTION IN  
IRON-CONTAINING ZINC SULPHIDE*

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INLAND WATERS BRANCH

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MINERAL SCIENCES DIVISION

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## IRON-IRON INTERACTION IN IRON-CONTAINING ZINC SULPHIDE

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### ABSTRACT

The behaviour of iron in ZnS has been studied through the effect of iron concentration on magnetic and electrical properties†. Specimens containing iron in amounts varying from 0.09 to 16.16 atom per cent have been synthesized. These were found to be homogeneous by electron-probe microanalysis and under the reflecting microscope.

At lower iron concentrations the synthetic and natural iron-bearing sphalerites are paramagnetic and their magnetic susceptibilities vary with the iron content in a linear manner. At higher iron concentrations these iron-bearing sphalerites become increasingly antiferromagnetic and their magnetic susceptibilities vary in a non-linear manner. The antiferromagnetic behaviour may be comparable to that observed in Mn-bearing ZnS and is probably the result of similar magnetic ordering of the substitutional iron.

Electrical conduction for a natural iron-bearing sphalerite has been found to result from migration of low-mobility holes rather than by electrons. This observation is consistent with the mechanism known as d-band conduction, which attributes electrical current to the flow of holes in the d-bands of transition metals. This type of conduction is possible in iron-containing ZnS through the interaction of  $\text{Fe}^{3+}$  with  $\text{Fe}^{2+}$ , with the  $\text{Fe}^{3+}$  in either the tetrahedral or the octahedral position.

### INTRODUCTION

The properties of zinc sulphide containing iron have been the subject of a number of investigations, stemming from both technological and mineralogical interests. Zinc sulphide has been employed industrially for many years as a phosphor, and the role of iron is that of a "killer centre", (Jaffe & Banks 1964) i.e. its presence quenches the luminescence. A mineralogical application was noted by Kullerud (1953) when he suggested that the iron content of the cubic modification (sphalerite) formed in equilibrium with pyrrhotite, could be used as a geothermometer. The method has proven unsuccessful however, and a re-examination of the FeS-ZnS solvus (Barton & Toulmin 1966, and Boorman 1967), has produced a result differing from the one upon which Kullerud's proposal was based.

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The presence of iron also affects the lattice parameter of sphalerite, causing an increase in the unit-cell edge (Skinner 1961) which is proportional to the iron content. The question of the linearity of the relationship between iron content and cell edge has been discussed by several authors (van Aswegen & Verleger 1960; Krause 1961; Boyle & Jambor 1963; Kullerud 1964; Barton & Toulmin 1966). Hardness measurements as a function of iron content have produced conflicting results (Henriques 1957; Young & Millman 1964). The optical absorption spectra of iron-containing zinc sulphide have been studied by Low & Weger (1960) and Manning (1967). The latter author concluded that iron entered the lattice substitutionally as  $\text{Fe}^{2+}$  and interstitially as  $\text{Fe}^{3+}$ , the ratio  $\text{Fe}^{2+}/\text{Fe}^{3+}$  in two natural samples being approximately 10. Magnetic susceptibility studies (Stutzer *et al.* 1918; Spokes & Mitchell 1958) have shown that sphalerite, which in the pure state is diamagnetic (*Int. Crit. Tables* 1929; Larach & Turkevich 1955), becomes paramagnetic upon addition of iron. A comprehensive summary of these and other properties of zinc sulphide has been made by Nickel (1965).

The multitude of observations made on the effects of iron in zinc sulphide have raised many questions regarding the fundamental processes associated with the electron interactions which take place. The substitution of  $\text{Fe}^{2+}$  for zinc should not drastically affect the semiconducting properties of the mineral. On the other hand, the presence of even small quantities of  $\text{Fe}^{3+}$  in an interstitial site should liberate a significant number of electrons (three for each  $\text{Fe}^{3+}$ ), which might be expected to transform the material from the status of an insulator to that of a semiconductor. The electron processes are strongly influenced by the interactions between the iron atoms themselves and can be studied through magnetic susceptibility measurements.

The purpose of the present investigation is to present evidence that will provide some understanding of the nature of the interactions associated with the presence of iron in zinc sulphide. We have measured the electrical conductivity, thermoelectric power, and magnetic susceptibility of a number of specimens, both natural and synthetic, containing iron in amounts varying from 0.09 to 16.16 atom per cent. The results of these measurements have been combined with existing theories of semiconductivity and magnetism to present an hypothesis upon which the behavior of iron in zinc sulphide can be based.

### THEORY

The interactions of the iron atoms within the zinc sulphide lattice take place through electrons and it is therefore natural that properties

which depend upon the state of the electrons should be studied. One such property is the electrical conductivity, which, in company with other transport properties, can be used to determine the number of charge carriers per  $\text{cm}^3$  responsible for conduction, and their mobility. Magnetic susceptibility is also characteristic of the state of the electrons and is particularly useful in establishing the type of interaction between electrons in the  $d$ -shell of transition elements. It can be used to determine both the  $d$ -shell electron configuration of the atoms themselves and also the nature of the coupling between electrons associated with different atoms.

#### *Electrical transport equations*

Zinc sulphide, like most other minerals, is a semiconductor. The high resistivity at room temperature classifies it as an insulator, which differs from a semiconductor only in the magnitude of its resistivity. Semiconductivity can be distinguished from metallic conduction by its temperature dependence; the resistivity of a semiconductor decreases with increasing temperature, whereas the reverse is characteristic of a metal.

With a single type of charge carrier present the conductivity may be expressed as

$$(1) \quad \sigma = ne\mu$$

where  $\sigma$  is the conductivity,  $n$  is the density of charge carriers,  $e$  is the electronic charge and  $\mu$  is the mobility, defined as the velocity per unit electric field. The temperature variation of the conductivity arises through the dependence of  $n$  and  $\mu$  on temperature. In the majority of semiconductors, the dependence of  $\mu$  on the temperature is small, and the variation of  $\sigma$  is due primarily to the variation of  $n$ . However, in compound semiconductors where one of the species is a transition element, it is often found that  $n$  remains virtually constant with temperature and the conductivity depends primarily on the mobility. This is the case for iron-containing ZnS and the mobility takes the form

$$\mu = \mu_0 e^{-E/kT}$$

where  $E$  is an activation energy and  $k$  is Boltzmann's constant. The model which best describes the process involves a temperature variation of mobility based on the diffusion of charge carriers through the lattice. Mobility and diffusion coefficients are connected by the Einstein relationship

$$\mu = De/kT$$

where  $D$  is the diffusion coefficient. From diffusion theory

$$\begin{aligned} D &= D_0 e^{-E/kT} \\ &= a^2 \nu e^{-E/kT} \end{aligned}$$

where  $a$  is the jump distance,  $\nu$  is the vibration frequency of the particle making the jump, and  $E$  is an activation energy. Making use of the Einstein relation (Heikes & Johnston 1957),

$$(2) \quad \mu = \frac{e}{kT} a^2 \nu e^{-E/kT}$$

One consequence of this type of conduction is a very small value for the mobility of the charge carriers. This is to be expected as the model to be proposed suggests that the carriers hop from atom to atom rather than flow "freely" through the crystal, as is the case for electrons in metals and conduction electrons in the usual semiconductors. In low mobility materials, the number of carriers per unit volume cannot be determined by measuring the Hall coefficient and it is necessary to resort to a measurement of the thermoelectric power.

The thermoelectric power results from the application of a temperature difference across a specimen which in turn causes a difference in potential to develop. The thermoelectric power is the difference in potential divided by the temperature gradient and is expressed as microvolts per degree C. One very useful application of the thermoelectric power is in the determination of the sign of the charge carriers. Since conduction can occur through the migration of either electrons or holes, any description of the behaviour of the charge carriers should include a statement of the type present. If the charge carriers are electrons, a temperature gradient applied to a specimen causes the hot side to become positive and the cold side negative. The reverse holds true in hole conduction. This can be explained qualitatively by noting that the carriers at the hot side have more energy than those at the cold, and hence migrate down the temperature gradient causing an unequal distribution of charge within the sample. The above conclusions regarding the sign of the carriers follow directly from this argument.

Quantitatively, the thermoelectric power (Ioffe, 1957), is given by

$$(3) \quad \alpha = \pm \frac{k}{e} \left[ A + E/kT \right]$$

where  $A$  is a transport parameter of order unity. The minus sign results from electron conduction and the positive sign from hole conduction.

*Magnetic susceptibility equations*

The magnetic susceptibility is defined as:

$$\chi = M/H$$

where  $\chi$  is the susceptibility,  $M$  is the magnetization per unit volume, which is equal to the product of the number of atoms per unit volume, and their average atomic moment  $\mu_{\text{eff}}$ , parallel to the applied magnetic field  $H$ . The susceptibility of free atoms is either paramagnetic, giving a positive value for  $\mu_{\text{eff}}$ , or diamagnetic giving a negative value. The former results from the alignment of permanent moments of the atoms and the latter from Lenz's Law. The temperature variation of paramagnetism follows the Curie law

$$(4) \quad \chi = C/T$$

where  $C$  is a constant equal to  $N\mu_{\text{eff}}^2/3k$  and  $T$  is the absolute temperature. Diamagnetism is temperature independent.

The formation of a solid from free atoms introduces the possibility of a spontaneous alignment of the magnet moments. A substance that has a spontaneous moment at low temperatures is termed ferromagnetic. Special cases do occur frequently, where the coupling between atoms causes a magnetic ordering resulting in antiferromagnetism or ferrimagnetism. These situations arise when adjacent atoms have their moments aligned antiparallel in the presence of an external field. In ferrimagnetism, there is a large difference between moments of atoms whose spins are parallel to the field and the moments of those whose spins are antiparallel. Antiferromagnetism is characterized by a net moment corresponding more closely in magnitude to that associated with paramagnetism.

The type of magnetism of a substance can be determined by observing the temperature variation of the susceptibility. For ferromagnetism and antiferromagnetism, there is a well defined temperature above which

$$(5) \quad \chi = \frac{C}{T \pm \theta}$$

where the  $-$  refers to ferromagnetism and the  $+$  to antiferromagnetism, and  $\theta$  is a constant characteristic of the material. The transition temperatures are known as the Curie and the Néel temperatures respectively. The susceptibility of a ferrimagnet is a somewhat more complicated function of temperature and is not discussed in the present work.

#### EXPERIMENTAL PROCEDURE

*Sample preparation*

All the synthetic specimens employed in the magnetic susceptibility

experiments were made in the manner described by Kullerud (1953), in clear silica-glass tubes evacuated at room temperature to a pressure less than 0.1 mm mercury. They were equilibrated in horizontal electric furnaces (with temperature electronically controlled using platinum thermocouples as sensors). The temperatures are considered accurate to  $\pm 5^{\circ}\text{C}$  and the thermocouples were checked at temperature against a calibrated Pt-PtRh 10% thermocouple.

High-purity elements were used to make ZnS and FeS (the Fe being carefully reduced with dry hydrogen). The ZnS was prepared in the same manner as reported by Skinner & Barton (1960), the excess sulphur being removed by distillation in a long evacuated tube over a gradient. The FeS was prepared in the manner reported by Toulmin & Barton (1964). Binary sulphides were made up in 8 to 10-gram lots and the ternary sulphides consisted of 1 to 2-gram lots. Both binary sulphides were checked by *x*-ray diffraction and the (102) reflection of FeS was measured to ensure stoichiometry using the method and value reported by Toulmin & Barton (1964). The iron-bearing zinc sulphides were then prepared from carefully weighed portions of FeS and ZnS which were mixed by grinding in a mortar under acetone and then heated in evacuated tubes for periods ranging from five to fifteen weeks at temperatures of  $800^{\circ}\text{C}$  or  $900^{\circ}\text{C}$ . Usually at least one regrinding operation was performed during the equilibration period.

The identity of quenched charges were then checked by *x*-ray diffraction and a small amount was examined for homogeneity under the electron-probe microanalyser and the ore microscope. The iron, zinc and sulphur contents were found to have standard deviations less than the reproducibility of the counting rate and the sphalerites are thus considered homogeneous within the limits of accuracy of the electron-probe microanalyser. Quantitatively, they are considered homogeneous to within 2.5 and 1.3 wt % of the amount of iron and zinc present, respectively. The standard deviations were calculated from fifteen individual ten-second counts accumulated on different grains selected at random in each sample.

Well-formed natural crystals containing iron in amounts varying from 0.03 atom per cent to 12.4 atom per cent were obtained from Santander, Spain; Timmins, Ontario; Gaspé, Quebec and Chihuahua, Mexico. The Timmins and Chihuahua samples were kindly given by the Royal Ontario Museum (ROM M22550 and M22377 respectively) and the Santander sample by the Geological Survey of Canada. Magnetic susceptibility measurements were performed on all samples and the highest iron-containing specimen was used for electrical measurements.

After the magnetic measurements, the Gaspé, Timmins and Chihuahua samples were mounted in epoxy resin, and were examined under the



ore microscope in polished sections and with the electron-probe micro-analyser with the results given in Table 1.

TABLE 1. SPHALERITE: ANALYSES IN WEIGHT PER CENT\*

	Sample No.	Fe	Zn	Mn	Other phases present†
Gaspé	C-1	1.30	63.50	n.d.†	3 small chalcopyrite inclusions
	C-2	1.60	62.80	n.d.	none
	C-3	4.00	61.85	n.d.	numerous chalcopyrite inclusions
Timmins (M22550)	F-1	3.90	61.60	n.d.	none
	F-2	5.00	60.95	n.d.	one 3 $\mu$ inclusion of chalcopyrite
	F-3	5.00	59.85	n.d.	4 small chalcopyrite inclusions, <5 $\mu$
Chihuahua (M22377)	A-1	14.90	49.35	<.40	numerous chalcopyrite inclusions all <2 $\mu$
	A-2	14.80	49.45	<.40	numerous chalcopyrite inclusions all <2 $\mu$
	A-3	14.40	47.35	<.40	numerous chalcopyrite inclusions all <2 $\mu$
	A-4	14.35	48.50	<.40	numerous chalcopyrite inclusions all <2 $\mu$

\*Cd could not be determined (detection limit  $\sim 1\%$ ). Each value is based on ten spots and each sample was found to be homogeneous using a series of synthetic sphalerites as standards.

†Not detected.

‡In all cases the total inclusions present were estimated to be less 1%.

The microprobe results compared favourably with the wet chemical and spectrographic analyses of portions of two of these specimens reported by Manning (1967).

### MEASURING TECHNIQUES

Magnetic susceptibility was measured by the Faraday method using a Cahn electrobalance. The apparatus will be described in detail at a later date. Electrical conductivity measurements were made by the van der Pauw method using a grounded electrometer circuit that has been described elsewhere (Baleshta & Keys 1968). Thermoelectric power measurements were made in a specially designed device that permitted one side of the specimen to be held at a fixed temperature and the other to be heated at a uniform rate. The thermoelectric force and the temperature difference were plotted on an X-Y recorder and the thermoelectric power was obtained from the slope of the resulting curve.

### MAGNETIC SUSCEPTIBILITY

The results of room temperature magnetic susceptibility measurements for both synthetic and natural specimens containing varying

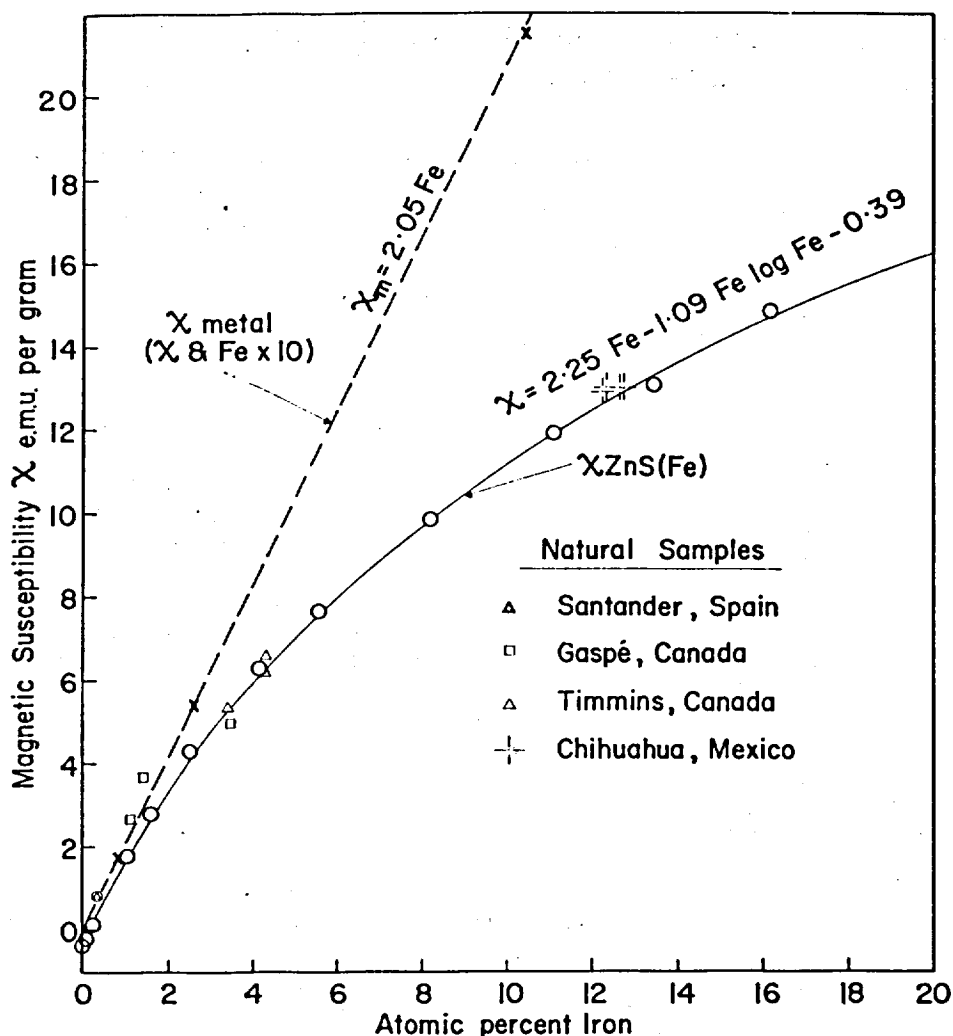


FIG. 1. Curves for magnetic susceptibility versus atomic per cent iron for iron-bearing sphalerites. Values on the ordinate must be multiplied by  $10^{-6}$ . Dotted curve is linear and represents a scale expanded by a factor of 10. The diamagnetism due to ZnS has been subtracted from this curve to give a zero origin. Crosses represent synthetic sphalerites on the expanded linear curve and open circles represent synthetic sphalerites on the other curve. The latter curve includes the diamagnetism due to ZnS.

amounts of iron are shown in Figure 1. Curve fitting has shown that the susceptibility is related to the iron content by the equation  $\chi = 2.25 \text{ Fe} - 1.09 \text{ Fe} \log \text{ Fe} - 0.39$ , for increasingly iron-enriched sphalerites, where Fe is atom per cent iron. The equation for the iron-poor (dilute) sphalerites is given by  $\chi_m = 2.05 \text{ Fe}$ , the value for the diamagnetism due to ZnS having been subtracted in this case.

In the most dilute natural sample (0.03 atom per cent Fe from Santander), the measured moment was equivalent to 5.2 Bohr magnetons. The theoretical value for  $\text{Fe}^{2+}$  is 4.90 and for  $\text{Fe}^{3+}$  is 5.92 Bohr magnetons (Selwood 1956, p. 159). This shows that the observed value obtained from the Santander sample, though considerably lower than that associated with  $\text{Fe}^{3+}$ , is somewhat higher than the theoretical value



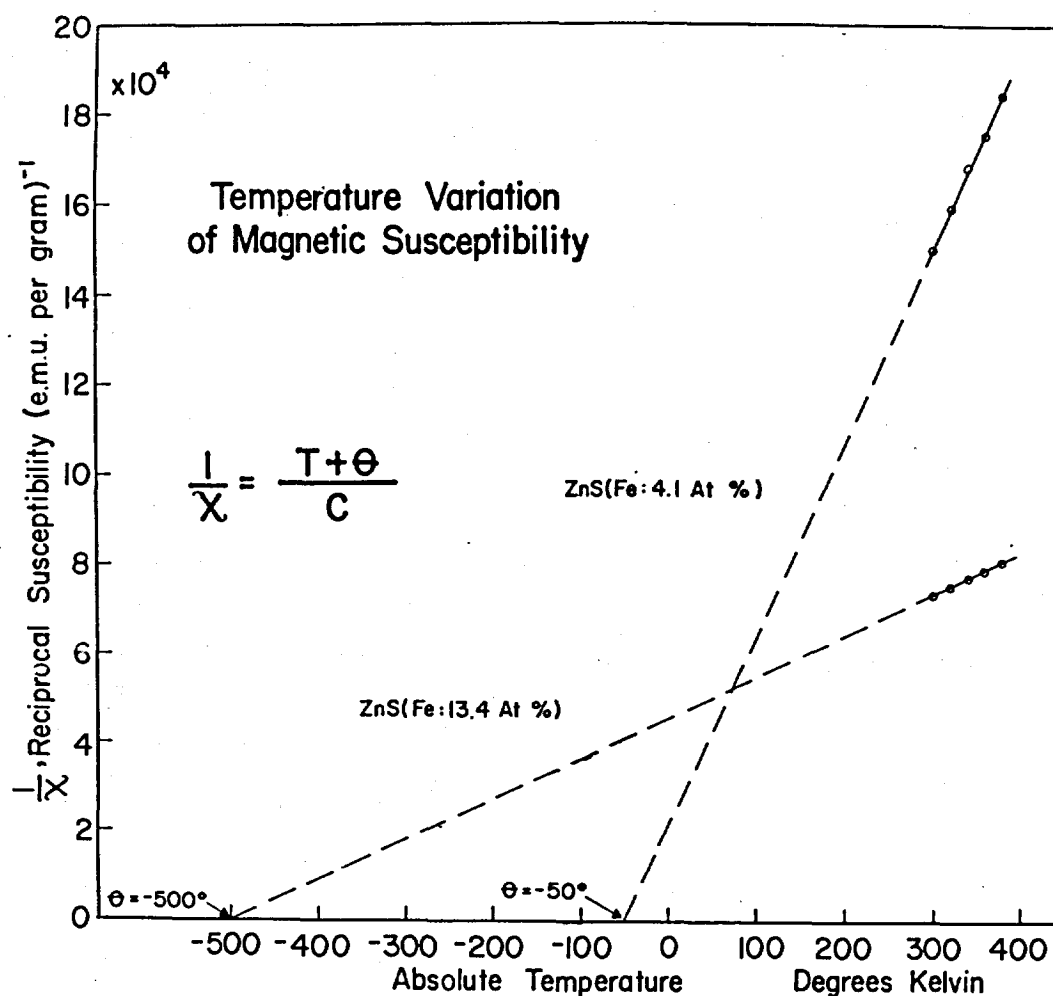


FIG. 2. Curves showing temperature variation of magnetic susceptibility for two synthetic iron-bearing sphalerites.

for  $\text{Fe}^{2+}$ . Selwood, however, quotes a range of effective (observed) values for  $\text{Fe}^{2+}$  (5.0 to 5.5) and for  $\text{Fe}^{3+}$  (5.2 to 6.0). This suggests that our observed value may be due to one of two different situations. Either the contribution to the magnetic moment is due solely to  $\text{Fe}^{2+}$ , or, alternatively there may be a contribution from some  $\text{Fe}^{3+}$ .

The temperature variation of the magnetic susceptibility for two synthetic samples is shown in Figure 2. For the sphalerite of lower iron content the susceptibility is not very different from that associated with paramagnetism i.e.  $\chi = C/T$ .

As the iron content is increased, however, antiferromagnetic coupling occurs and the susceptibility follows the relation:

$$\chi = \frac{C}{T + \theta}.$$

Some form of iron-iron interaction is also indicated by the shape of the curve in Fig. 1.

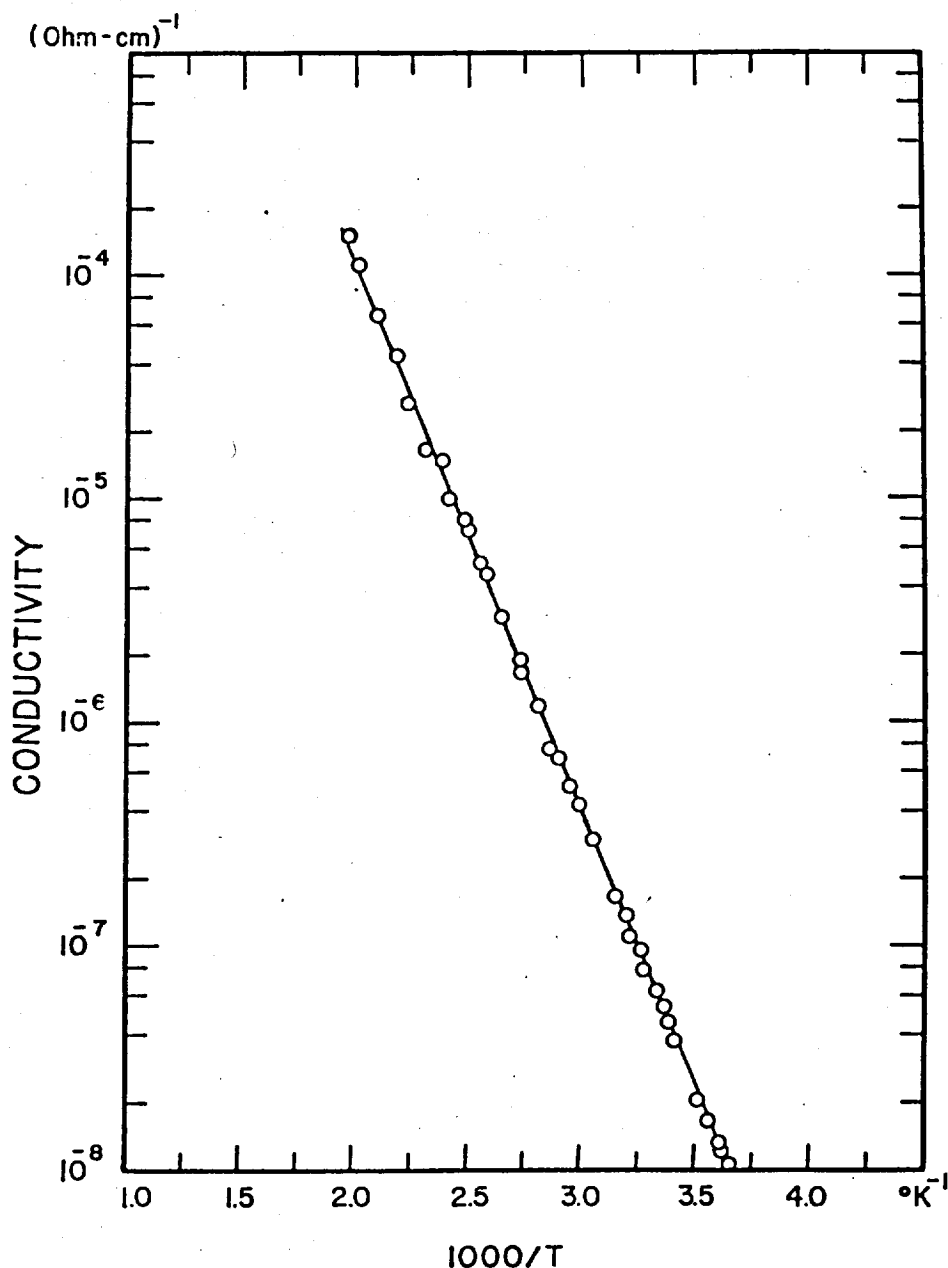


FIG. 3. Electrical conductivity of sphalerite with 12.4 atom per cent iron plotted as a function of temperature. The activation energy of 0.49 eV is obtained from the slope of the curve.

#### ELECTRICAL MEASUREMENTS

Figure 3 shows the electrical conductivity as a function of temperature for a natural crystal containing 12.4 atom per cent iron. The behaviour is typical of a semiconductor and an activation energy of 0.49 eV is obtained from the slope of the conductivity curve. The absence of a measurable Hall effect and the positive sign for the thermoelectric power, suggest that iron-doped zinc sulphide is a *d*-band semiconductor. We have assumed that these results have not been affected by the impurities present which were found to total less than 1% by spectroscopic analysis and microscopic observation.



Thermoelectric power measurements were made on the same sample in the temperature range 300°K to 600°K. However, at the lower temperatures the high resistivity of the sample coupled with the difficulty of making good electrical contacts resulted in a lack of reproducibility. At the higher temperatures, the thermoelectric power decreases as would be expected when electrons become available in significant numbers to add to the conductivity. For the above reasons, the electrical measurements are interpreted for the temperature range 400°K to 500°K where the assumptions upon which the theory is based are considered to be valid.

The results of conductivity and thermoelectric power measurements are given in Table 2.

TABLE 2. RESULTS OF TRANSPORT MEASUREMENTS ON SPHALERITE CONTAINING 12.4 ATOM PER CENT IRON

Temperature deg K	Conductivity (ohm-cm) <sup>-1</sup>	Thermoelectric Power microvolt/deg C	Mobility cm <sup>2</sup> /volt sec	
			Conductivity	Diffusion
400	$7 \times 10^{-6}$	660	$6 \times 10^{-6}$	$5.5 \times 10^{-6}$
500	$10^{-4}$	660	$9 \times 10^{-5}$	$7.6 \times 10^{-5}$

## DISCUSSION

### *Magnetic measurements*

The magnetic measurements can be interpreted in terms of existing theories of antiferromagnetism. Assuming that the main magnetic interactions are between substitutional iron atoms, a comparison can be drawn between the iron-containing zinc sulphide and  $\beta$ -MnS, both tetrahedrally coordinated compounds. The magnetic structure of the latter has been investigated by Corliss *et al.* (1956), and has been shown to be antiferromagnetic, with magnetic ordering of the third kind. The criteria for distinguishing between the various forms of magnetic ordering have been summarized by Goodenough (1963). In both cases the cations form a face-centered cubic sub-lattice and it is reasonable to suppose that the magnetic interactions are similar. The concept of antiferromagnetic coupling has also been successfully used to explain the magnetic susceptibility of a series of Mn-bearing synthetic sphalerites (Brumage *et al.* 1964).

The results shown in Fig. 2 indicate the manner in which the magnetic interaction shifts from essentially paramagnetic at low iron concentrations to antiferromagnetic at higher concentrations. The Néel point does not appear within the studied temperature range and is assumed to be below 100°K. This also is not inconsistent with the values for MnS which lie in the neighbourhood of 100°K (Corliss *et al.* 1956).

*Electrical measurements*

The low electrical conductivity, low mobility and the constant value of the thermoelectric power over the temperature range considered indicate that the conductivity results from a hopping of charge carriers from atom to atom throughout the lattice. The sign of the thermoelectric power shows that the hopping carriers are holes rather than electrons.

We will test the validity of the above conclusions by comparing mobilities calculated by two different methods (a) from conductivity and thermoelectric data; and (b) from a diffusion model based on the jump distance and vibration frequency.

The Chihuahua sample contains 12.4 atom per cent iron and we shall assume that 90% of these iron atoms are on substitutional sites and are in fact the host atoms in the conduction process (Manning 1967). This assumption is based on the optical absorption data but the calculations would not be seriously affected by a substantial percentage increase of substitutional iron atoms. The calculation yields a value of  $5.6 \times 10^{21} \text{ cm}^{-3}$ .

(a) The number of carriers responsible for conduction may be calculated by combining Equation 3 with the number of transition metal atoms providing the carriers. For the so-called "tight binding" or Heitler-London model proposed,  $E/kT$  in Equation 3 is equal to  $\ln(N - n)/n$ , where  $N$  is  $5.6 \times 10^{21} \text{ cm}^{-3}$  and  $n$  is the number of charge carriers. Using the above with Table 2 data we obtain a value for  $n$  of  $7 \times 10^{18} \text{ cm}^{-3}$ .

Applying Equation 1, using  $n$  obtained above, and the conductivity values from Table 2, the mobilities of the holes at 400°K and 500°K are as follows:

$$\mu_{400} = 6 \times 10^{-6} \text{ cm}^2 \text{ per volt-sec.}$$

$$\mu_{500} = 9 \times 10^{-5} \text{ cm}^2 \text{ per volt-sec.}$$

(b) In order to calculate the mobility from Equation 2 it is necessary to know the jump distance  $a$  and the vibration frequency  $\nu$ . Since there are  $5.6 \times 10^{21} \text{ cm}^{-3}$  substitutional iron atoms dispersed uniformly throughout the lattice,  $a$  is equal to  $7.2 \times 10^{-8} \text{ cm}$ . The vibration frequency varies between  $10^{11}$  and  $10^{14}$  per sec. for various materials, and it is not unreasonable to assume a value of  $10^{14}$  per sec.

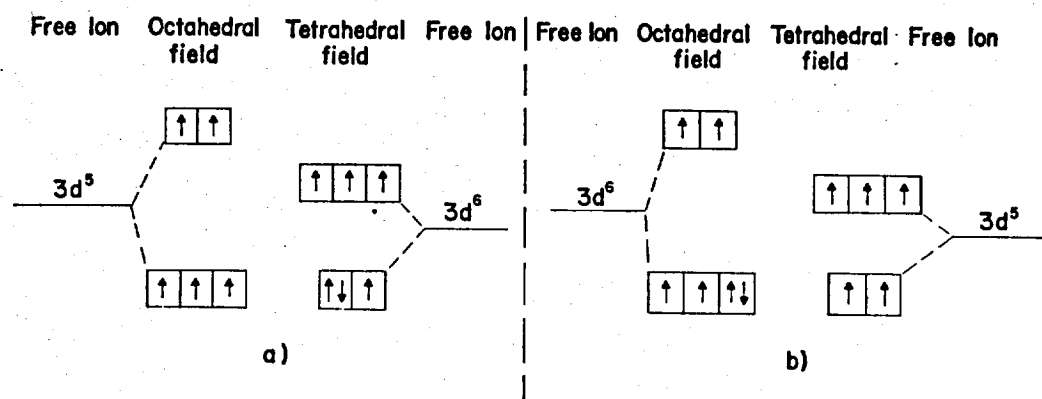
Inserting the above values in Equation 2 together with the activation energy of 0.49 eV (Fig. 3) yields the following mobilities at 400°K and 500°K:

$$\mu'_{400} = 5.5 \times 10^{-6} \text{ cm}^2 \text{ per volt-sec.}$$

$$\mu'_{500} = 7.6 \times 10^{-5} \text{ cm}^2 \text{ per volt-sec.}$$

The values of mobility obtained from the two methods of calculation agree well. Such close agreement may be fortuitous considering the assumptions implicit in the formulations, or it may be tentatively





Octahedral and tetrahedral splittings for iron in ZnS. a) indicates stable configuration and b) proposed model for creation of acceptor state associated with tetrahedral, substitutional iron.

FIG. 4. Schematic representation of octahedral and tetrahedral splittings for iron in ZnS. Arrows represent electrons for a natural 12.4 atom per cent iron sphalerite.

concluded that the model proposed for the conduction process is correct.

In order for a  $d$ -hole to hop from one substitutional iron atom to another, it is necessary that space be available in orbitals of the receiving atom. If all the substitutional atoms have the electronic configuration  $3d^6$  (which is the case for divalent iron), the required space would not be present. However,  $\text{Fe}^{3+}$  has the electronic configuration  $3d^5$  and thus has one less electron in the  $d$ -orbitals than  $\text{Fe}^{2+}$ . It is suggested that  $\text{Fe}^{3+}$  could lie in either a tetrahedral or in an octahedral environment. The interaction visualized is such that a small fraction of the  $\text{Fe}^{2+}$  iron atoms have given up an electron to an  $\text{Fe}^{3+}$  iron atom leaving a hole. This hole could then migrate to other  $d$ -orbitals of other  $\text{Fe}^{2+}$  iron atoms. The number of holes involved in the conduction process can be accounted for provided one in 800 of the  $\text{Fe}^{2+}$  iron atoms relinquishes an electron in the manner described.

A tetrahedral or octahedral ligand field acting on  $d$ -orbitals removes the five-fold energy degeneracy present in the free atom. The new arrangement consists of  $e_g$  orbitals, two-fold degenerate, separated in energy from  $t_{2g}$  orbitals, which are three-fold degenerate. The splitting and electron distribution for each case is shown in Fig. 4. The distinction between the normal electron distribution and that proposed in the hopping mode is made in 4a and 4b. The other possibility for hopping would be between  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ , both in tetrahedral sites.

Since optical absorption measurements have indicated the presence of interstitial  $\text{Fe}^{3+}$  and the electrical measurements can also be explained on the basis of interstitial  $\text{Fe}^{3+}$ , we are left with the question of what has become of the liberated electrons. These electrons must be formed in such a manner that the activation energy to place them in the conduction band is considerably greater than 0.49 eV. The mobility of electrons in the

conduction band for ZnS has been found to be of the order of  $200 \text{ cm}^2 \text{ volt}^{-1} \text{ sec}^{-1}$  (Aven & Mead 1965). Therefore, the presence of a relatively small number of these electrons in the conduction band would change the material from the observed *p*-type to *n*-type. We are therefore led to the conclusion that the electrons are tightly bound in a manner yet to be defined.

### CONCLUSIONS

The magnetic susceptibility of iron-containing zinc sulphide indicates that magnetic interaction occurs between iron atoms and that it is of an antiferromagnetic nature similar to that described for Mn-bearing sphalerite. The magnetic structure is identical to that of  $\beta$ -MnS and is identified as magnetic ordering of the third kind.

It appears to be possible to synthesize specimens with a wide range of iron content which suggests that iron-iron interactions involving dilute solutions in a tetrahedral structure can be studied conveniently in this system. It is also worth noting that bornite falls on the curve in Fig. 1 at the point corresponding to its formula iron content.

The results of the electrical measurements shed some light on the nature of the iron in sphalerite. A hopping process is described which requires both divalent and trivalent iron, but the trivalent iron may be in either tetrahedral or octahedral sites. Since this hopping process can take place with as little as one in 800  $\text{Fe}^{3+}$  iron atoms, the limits for sphalerite stoichiometry as estimated by Barton & Toulmin (1966) are not transgressed. Additional information may be obtained through techniques such as electron-density mapping and Mössbauer effect experiments.

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