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A REVIEW OF THE PROPERTIES OF ZINC SULPHIDE

by

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ABSTRACT

The physical and chemical properties of zinc sulphide, as reported in the literature, are reviewed and summarized. The topics covered include crystallography, structure, composition, stability relations, physical properties, optical properties, electronic and magnetic properties, thermodynamic properties, lattice dynamics, and methods of synthesis.

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REVUE DES PROPRIÉTÉS DU SULFURE DE ZINC

par

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RÉSUMÉ

L'auteur passe en revue et résume les propriétés physiques et chimiques du sulfure de zinc, telles qu'elles sont rapportées dans la bibliographie. Ces sujets englobent la cristallographie, la structure, la composition, les rapports de stabilité, les propriétés physiques, optiques, électroniques, magnétiques et thermodynamiques, la dynamique du réseau cristallin et les méthodes de synthèse du sulfure de zinc.

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INTRODUCTION

The sulphide research programme recently initiated in the Mineral Sciences Division, Mines Branch, has as one of its objectives the study of the physical properties of sulphide minerals and their relationships to the basic properties of crystal structure and interatomic bonding. A further objective is the assessment of such fundamental data for potential applications in mineral technology. Sphalerite (ZnS) is one of Canada's most important ore minerals and is currently the subject of intensive research in the Division. This report constitutes a review of the literature on sphalerite and other forms of zinc sulphide.

In undertaking this review, the author was confronted with an embarrassment of riches. The vast amount of literature on zinc sulphide, particularly on its luminescent properties, makes a complete review practically impossible. It has therefore been necessary to exercise judgement in the selection of references and give preference to papers of original, comprehensive or fundamental nature. Although of necessity incomplete, it is hoped that this review will nevertheless serve the twin objectives of illustrating the large number of ways in which information about the physical and chemical properties of a sulphide mineral can be obtained and of providing a useful compilation of data on zinc sulphide itself.

CRYSTALLOGRAPHY AND STRUCTURE

Zinc sulphide has two well-recognized polymorphic forms: the cubic form, which is variously known as β -ZnS, zincblende, blende, or sphalerite, and the hexagonal form, known as α -ZnS or wurtzite. A less familiar polymorph is the rhombohedral form, γ -ZnS.

Sphalerite

Cubic ZnS, which will henceforth be referred to as sphalerite, is face-centred, with space group $F\bar{4}3m$. The structure, according to Bragg (1913), can be described in terms of a unit cube with zinc atoms at the corners and face centres, and with 4 sulphur atoms inside the cube with the following co-ordinates: $(\frac{1}{4} \frac{1}{4} \frac{1}{4})$, $(\frac{3}{4} \frac{3}{4} \frac{1}{4})$, $(\frac{1}{4} \frac{3}{4} \frac{3}{4})$, and $(\frac{3}{4} \frac{1}{4} \frac{3}{4})$. Each sulphur atom lies at the centre of a regular tetrahedral configuration of zinc atoms and each zinc atom is at the centre of a regular sulphur tetrahedron. If the structure is envisaged as a three-dimensional array of sulphur spheres in cubic close-packing, zinc atoms occupy one-half of the

tetrahedral and none of the octahedral interstices. The distance between the centres of neighbouring zinc and sulphur atoms, if the unit-cell parameter is taken as 5.4093 Å (Skinner and Barton, 1960), is 2.342 Å.

Various values for the unit-cell parameter of pure sphalerite have been reported, some of the more recent ones being listed in Table 1.

TABLE 1

Reported Values of the Unit-Cell Parameter of Sphalerite

<u>Unit Cell Edge</u> (Angstroms)	<u>Reference</u>
5.4060	Swanson and Fuyat (1953)
5.4094	Kullerud (1953), corrected by Skinner, Barton and Kullerud (1959)
5.410	Henriques (1957a)
5.4093	Skinner and Barton (1960)

The unit-cell parameter of sphalerite is affected by the substitution of either sulphur or zinc by other elements. The substitution of sulphur by selenium (Klemm, 1961) increases the unit cell edge; the substitution by oxygen (Skinner and Barton, 1960) decreases it. The substitution of zinc by one or more of iron, manganese and cadmium, increases the unit-cell edge linearly (Skinner, 1961); but cobalt, on the other hand, causes a decrease (Hall, 1961). Reports that the variation of unit-cell edge with iron content is not linear (van Aswegen and Verleger, 1960; Krause, 1961) have been criticized by Boyle and Jambor (1963) and Kullerud (1964).

It is generally accepted that cation impurities are incorporated in sphalerite as substitutions for zinc at normal zinc lattice sites (Kullerud, 1953; Skinner and Barton, 1960). According to Wiekliem (1962), the optical absorption spectra of nickel and cobalt in sphalerite confirm this. On the other hand, Curie (1964) presented evidence to show that manganese is not situated in a site of cubic symmetry, i.e. a normal zinc site, or, if it is, the cubic symmetry is distorted in some way.

Because of the sequence of zinc and sulphur planes along the (111) trigonal axis, sphalerite has a polar lattice; i.e., opposite crystal faces on the trigonal axes have different polarities (Bragg, 1913). This polarity is independent of polymorphism, polytypism, twinning, and stacking disorder (Brafman et al, 1964). The two types of surface can be distinguished by etching (Gebhardt, 1933; Warekois et al, 1962; Brafman et al, 1964), by X-ray diffraction (Coster et al, 1930; Gebhardt, 1933; Warekois et al, 1962) and even by visual appearance (Coster et al, 1930; Brafman et al, 1964).

Wurtzite

Hexagonal ZnS, which will henceforth be referred to as wurtzite, belongs to the space group $P6_3mc$ and has a structure that is closely related to that of sphalerite (Bragg, 1920; Aminoff, 1923; Ulrich and Zachariasen, 1925; Fuller, 1929). The unit cell contains 2 atoms of sulphur situated at 000 and $1/3, 2/3, 1/2$, and 2 atoms of zinc at $00u$ and $1/3, 2/3, u+1/2$, with u close to $3/8$. As in sphalerite, each atom is tetrahedrally surrounded by 4 atoms of the other kind, but the arrangement of the tetrahedra is such that a lattice with hexagonal, rather than cubic symmetry, is formed. The relationship is analogous to that between cubic and hexagonal close packing of spheres, i.e., the cubic structure has the repeat pattern ABCABC... etc. along its (111) axis, whereas the hexagonal structure has the repeat pattern ABABAB... etc. along its equivalent (0001) direction. The ideal wurtzite structure can be derived from the sphalerite structure simply by rotating alternate Zn-S layers in sphalerite through 180° around one of the trigonal (111) axes (Aminoff and Broomé, 1931).

The unit-cell parameters of wurtzite, as reported by different investigators, are shown in Table 2. Indexed X-ray powder diffraction data have been published by Short and Stewart (1955).

TABLE 2

The Unit-Cell Parameters of Wurtzite

<u>a</u> (A)	<u>c</u> (A)	c/a	<u>References</u>
3.819*	6.247*	1.636	Fuller (1929)
3.820	6.260	1.639	Swanson and Fuyat (1953)
3.8217	6.2702	1.641	Kullerud (1953), corrected by Skinner and Bethke (1961)
3.8230	6.2565	1.6365	Skinner and Bethke (1961)
3.844*	6.290*	1.636	Ulrich and Zachariasen (1925)

*kX units converted to Angstrom units.

If the wurtzite structure were ideal, i.e. corresponding to the hexagonal close packing of spheres, the c/a ratio would be 1.633. As shown in Table 2, however, all the investigators reported axial ratios larger than that. This indicates a slight elongation of the hexagonal unit cell in the c-direction, hence a deformation of the zinc-sulphur tetrahedra.

The unit-cell parameters of wurtzite, like those of sphalerite, are affected by the incorporation of impurities. Skinner and Bethke (1961) have shown that the a and c parameters increase linearly with the substitution of zinc by iron, manganese, and/or cadmium.

Gamma Zinc Sulphide

A rhombohedral polymorph, designated as γ -ZnS, has been described by Buck and Strock (1955). They interpreted this structure as being derived from that of sphalerite by elongation parallel to one of the (111) directions, the amount of deformation increasing with increasing temperature up to the sphalerite-wurtzite inversion. Rhombohedral zinc sulphide has been interpreted as an intermediate structure in the conversion of sphalerite to wurtzite (Buck and Strock, 1955; Kendall, 1964).

High-Pressure Polymorph

At pressures of 240 to 250 kb, zinc sulphide apparently undergoes a structural transformation (Minomura et al, 1962; Samara and Drickamer, 1962; Rooymans, 1963). Rooymans has suggested that this modification has the rocksalt structure.

ZnS Polytypes

In addition to the polymorphs noted above, a considerable number of wurtzite polytypes formed by systematic variations of layers in the sequence along the (0001) direction have been described (Table 3).

TABLE 3

Wurtzite Polytypes

<u>Symbol</u>	<u>References</u>
2H (normal wurtzite)	
4H	Frondel and Palache (1950)
6H	"
8H	Evans and McKnight (1959)
10H	"
9R	Haussühl and Müller (1963)
12R	"
15R	Frondel and Palache (1950)
21R	Haussühl and Müller (1963)

The polytype symbols, first adopted by Frondel and Palache (1950), follow the terminology introduced by Ramsdell (1947) for silicon carbide polytypes. H and R (Table 3) refer to hexagonal and rhombohedral unit cells, respectively, and the prefixed number indicates the total number of hexagonally closest-packed individual Zn-S layers stacked within the length of the unit cell. Within each polytype there are a number of possible atomic arrangements having the same number of layers but differing in the method of stacking the individual layers. Ramsdell (1947) classified this stacking in SiC on the basis of "zig-zag sequence" on the $11\bar{2}0$ symmetry plane. This terminology has also been applied to wurtzite. Strock and Brophy (1955) introduced a further notation (TB) based on the orientation of Zn-S tetrahedra in adjacent 0001 planes, i.e. whether the tetrahedra are in rotated or parallel sequence. This approach permits an analysis of possible polytypes produced by stacking various rotated and parallel sequences.

In addition to regular stacking sequences, both natural and synthetic wurtzites have frequently been found to possess stacking disorder along the c-axis (Jagodzinski and Laves, 1948; Jagodzinski, 1949; Müller, 1952; Strock and Brophy, 1955). A number of X-ray methods have been devised for determining the degree of disorder and for determining the hexagonal-cubic stacking ratios (Müller, 1952; Smith, 1955; Short and Steward, 1959; Singer and Gashurov, 1963). Czyzak et al (1962) were able to distinguish layers of sphalerite and wurtzite by etching.

Dislocations

Bakradze and Rom-Krichevskaya (1963) concluded, from the number of etch pits developed on the surface of single crystals of zinc sulphide grown by a sublimation method, that the density of dislocations was about 200,000 per square centimetre. Chadderton et al (1963, 1964) suggested that dislocations tend to be localized at the intersection of stacking faults which can be produced by high compressive stresses. Holt (1962, 1964) has discussed the configuration of bonds, dislocation, dissociation, and electronic charge, along grain boundaries in sphalerite.

COMPOSITION AND STABILITY RELATIONS

Compositional Variations

Because all stable forms of zinc sulphide have a zinc-sulphur ratio approximating 1:1, the chemical formula is given as ZnS. There is a considerable amount of evidence, however, that the composition of zinc sulphide can deviate appreciably from strict stoichiometry. Much of this evidence has been gained from a study of its luminescent properties and is discussed in a later section of this paper. Reviews of the chemical analyses of naturally occurring sphalerite indicate that most of them contain a sulphur:metal ratio in excess of 1:1 (Chudoba and Mackowsky, 1939; Krause, 1961; Togari, 1961). Furthermore, Dember effect studies on sphalerite (Morehead, 1963) indicate that the formation of a zinc vacancy is energetically more

favourable than a sulphur vacancy. On the other hand, there is evidence that when zinc sulphide is heated in a zinc atmosphere, excess zinc can be introduced (Baba, 1963). The deviation of sphalerite composition from stoichiometry is not sufficiently great, however, to be detected by X-ray diffraction analysis (Skinner and Barton, 1960).

Both sulphur and zinc can be isomorphously replaced by substantial amounts of other elements. Complete solid solutions have been reported between ZnS and each of ZnSe (Klemm, 1961), CdS (Kröger, 1940), and HgS (Kremheller et al, 1960). Partial solid solutions have been reported with the following sulphides: up to 56 mol % FeS (Barton and Toulmin, 1963), up to 52 mol % MnS (Kröger, 1939), and 35 mol % CoS (Hall, 1961). Oxygen can replace sulphur to an appreciable extent in both sphalerite and wurtzite (Skinner and Barton, 1960).

A number of other elements have been found in naturally occurring sphalerites in relatively small amounts. These include copper, germanium, gallium, tin, indium, and lead (Fryklund and Fletcher, 1956; Mintser, 1964). Lawrence (1963) was able to identify the following mineral phases that had apparently exsolved from sphalerite: argentiferous tetrahedrite, several types of stannite, chalcopyrite, pyrargyrite, pyrrhotite, valeriite, and cubanite. From this he concluded that, at elevated temperatures, the sphalerite lattice can accommodate appreciable amounts of iron, copper, tin, antimony and silver. Mintser (1964) has discussed isomorphism in sphalerite on the basis of co-ordination number, valence angles and bond lengths.

The iron in sphalerite is generally regarded as divalent since, in this state, it contributes as many bonding electrons as the zinc that is being replaced. On the other hand, Mössbauer studies indicate that the iron in sphalerite heated above 600°C is trivalent (Luchner and Dietl, 1963). Ultraviolet illumination has also been found to convert the iron in sphalerite from the divalent to the trivalent state (Räuber and Schneider, 1962).

Kullerud (1953) proposed that the iron content of sphalerite formed in equilibrium with pyrrhotite could be used as an indicator of the temperature of formation. This method, however, has not proven to be successful (Kudenko and Stetsenko, 1964). Toulmin and Barton (1964) have shown that Kullerud's FeS-ZnS solvus was in error and that further calibration, taking account of the deviation of the FeS activity from unity, is required.

Stability

Sphalerite is the stable form of zinc sulphide at room temperature and atmospheric pressure, although Birman (1962) has suggested that in the sphalerite space group there is a configurational instability for almost all degenerate electronic states that tends to distort the entire lattice to a space group of lower symmetry. γ -ZnS appears to be the stable phase between about 600°C and 1020°C (Buck and Stroock, 1955). The lower stability limit of wurtzite, the high-temperature form of ZnS, is generally given as 1020°C (Allen et al, 1912). A later value of 1040°C (Müller, 1952) has not found general acceptance and a suggestion (Addamiano and Aven, 1960) that the correct transition temperature lies above 1150°C has received practically no

support. Shalimova and Morozova (1964a) demonstrated that the composition of the atmosphere has an appreciable effect on the transition temperature. The sphalerite-wurtzite inversion temperature is considerably depressed by the presence of iron (Allen et al, 1912), cadmium, and manganese (Kullerud, 1953).

Reports on the rate of inversion of one polymorphic form to another are somewhat confused by the fact that many investigators have ignored the existence of the intermediate polymorph and have simply reported on the sphalerite-wurtzite inversion (Allen et al, 1912; Kullerud, 1953; Hartman, 1962), which is said to take place rapidly at the inversion temperature. Because of the existence of the rhombohedral polymorph, however, these observations can be taken as applying to the transformation of γ -ZnS to wurtzite. The reverse reaction is much more sluggish (Allen et al, 1912; Müller, 1952; Hartman, 1962). According to Buerger (1951), such a transition, which can be described as a reconstructive transformation of secondary coordination, is typically sluggish. Kendall (1964) reported that the transformation from γ -ZnS to sphalerite is more sluggish still.

Although unstable at room temperatures, wurtzite can nevertheless persist metastably for an indefinite period. Shearing stress, such as that produced by grinding, can, however, convert either wurtzite (Bridgman, 1939; Wecker, 1942; Kullerud, 1953) or γ -ZnS (Buck and Stroock, 1955) to sphalerite.

The melting point of wurtzite has been reported as 1840°C (Kullerud, 1953). In air, sphalerite decomposes into ZnO₂ and SO₂ at about 850°C (Maurel, 1964). The sublimation temperatures of sphalerite and wurtzite at 0.01 mm Hg have been reported at 854°C and 1182°C, respectively (Rossini et al, 1952).

PHYSICAL PROPERTIES

Specific Gravity

The theoretical specific gravity of sphalerite, based on a unit cell of $a = 5.4093$ (Skinner and Barton, 1960), is 4.089. The experimental values reported by Allen et al (1912) and Berlincourt et al (1963), viz. 4.090 and 4.088, respectively, are in very close agreement. Substitution of zinc by iron reduces the specific gravity (Allen et al 1912; Krause, 1961).

The theoretical specific gravity of wurtzite, based on a unit cell with $a = 3.8230$ and $c = 6.2565$ (Skinner and Bethke, 1961), is 4.086. This is in good agreement with the experimental values of 4.087 and 4.09 reported by Frondel and Palache (1950).

Hardness

The hardness of sphalerite varies with crystallographic orientation. The Vickers hardness values of oriented sections of sphalerite, reported by Henriques (1957b), are as follows: (001) - VHN 165; (011) - VHN 187; (111) - VHN 193. These hardness values are in the ratio 1 : 1.13 : 1.17. The

theoretical ratio of hardness in these three planes, based on the number of bonds per unit surface area, is 1 : 1.41 : 1.73 (Henriques, 1957b). Therefore, although the measured hardness values are in the correct relative order, the ratios depart appreciably from theory.

Henriques (1957b) found that the hardness of naturally occurring sphalerite increases linearly with the logarithm of the iron content. Young and Millman (1964), on the other hand, reported an initially rapid increase of hardness with increasing iron content up to 1.2% Fe, followed by a moderate decrease with progressively higher iron contents.

According to Ramdohr (1960), the hardness of wurtzite is similar to that of sphalerite. Cline and Kahn (1963) obtained Knoop hardness values of 158 and 246 for the (11 $\bar{2}$ 0) and (0001) planes, respectively. Although Knoop hardness values are slightly higher than the Vickers Hardness Numbers, the hardness anisotropism indicated by these values is considerably greater than that of sphalerite. Cline and Kahn (1963) considered the hardness anisotropism of wurtzite to be a true reflection of the differential bonding.

Cleavage

In a face-centred cubic lattice, such as that of sphalerite, adjoining (111) planes are connected by fewer bonds per unit area than any other principal planes (Winkler, 1955). Consequently, in minerals having this structure, the (111) cleavage should predominate, as is the case in diamond. Sphalerite, however, exhibits perfect cleavage parallel to the (011) direction (Palache et al, 1944; Wolff and Broder, 1959). Tertsch (1921) has shown that, if the lattice is occupied by atoms of different charge, the resultant of the attractive and repulsive forces causes the atoms normal to (110) to be less tightly bound than in the other directions, including (111). Wolff and Broder (1959) have therefore taken the sphalerite cleavage as indicating predominantly ionic bonding.

There are conflicting reports on the cleavage in wurtzite. According to Shôji (1931) and Wolff and Broder (1959), the principal cleavage is (10 $\bar{1}$ 0); the former gave the (0001) cleavage as weak, whereas the latter reported it as being prominent. On the other hand, Palache et al (1944) and Fréchette and Cline (1963) reported the best cleavage to be parallel to (11 $\bar{2}$ 0); according to the latter, the (0001) and (10 $\bar{1}$ 0) cleavages are poor.

Morphology

Sphalerite most often crystallizes in tetrahedra or modified tetrahedra, although many other crystal forms have also been noted (Gebhardt, 1933; Palache et al, 1944). Wurtzite crystals usually occur as hemimorphic pyramids or as hexagonal prisms (Palache et al, 1944).

Thermal Expansion

The thermal expansion of sphalerite between room temperature and 900°C was measured by Skinner (1962), using a high-temperature X-ray diffractometer. His derived expression for the molar volume (in cc/mol) of

sphalerite with respect to temperature is as follows:

$$V = \frac{24.427}{T} + 23.552 + (0.6865 \times 10^{-3}T) + (0.0084 \times 10^{-7}T^2)$$

No mention was made of the anisotropic expansion implicit in the existence of the rhombohedral polymorph above 600°C (Buck and Stock, 1955). The thermal expansion of sphalerite between 0°C and -258°C was measured by Adenstedt (1936).

The expression for the molar volume of wurtzite with respect to temperature, as determined by Skinner (1962), is as follows:

$$V = \frac{11.407}{T} + 23.659 + (0.4946 \times 10^{-3}T) + (1.4501 \times 10^{-7}T^2)$$

Thermal Conductivity

The thermal conductivity of zinc sulphide was measured by Chizhikov and Khirik (1963), who reported values ranging from 0.115 at 200°C to 0.039 at 800°C.

OPTICAL PROPERTIES

Absorption Spectrum

Throughout the visible range (approximately 4000 to 7500 Å), pure sphalerite and wurtzite exhibit very little absorption (Coogan, 1957; Piper et al, 1958; Vlasenko, 1959) and are consequently clear and colourless in transmitted light. Impurities, however, cause rather profound changes in the absorption spectrum. Low and Weger (1960) found that iron in sphalerite causes 3 absorption peaks in the neighbourhood of 7000 Å. McClure (1963) and Ryskin et al (1964) noted that the presence of manganese results in a number of pronounced absorption peaks in the 3900 - 5000 Å region. Cobalt and nickel each produce a number of absorption peaks in the neighbourhood of 7000 Å and 8000 Å, respectively (Weakliem, 1962). These and possibly other absorption effects are responsible for the wide variation in colour exhibited by zinc sulphide. According to Deer et al (1962), spectrographic analyses suggest that a green colour may be associated with cobalt and iron; red with tin, indium, silver, and molybdenum; and yellow with germanium, calcium, copper, mercury, and cadmium. Kröger (1939) reported that ZnS-MnS solid solutions have an orange colour. Togari (1961) proposed that the colour of sphalerite can be attributed primarily to excess sulphur.

Below about 4500 Å, the absorption of both ZnS polymorphs begins to increase, culminating in what is commonly referred to as the fundamental absorption edge. The transition from low to high absorption is a gradual one, the steepness of the absorption curve depending on the state of aggregation (Coogan, 1957; Vlasenko, 1959). This makes the assignment of a

particular wavelength somewhat arbitrary. Values in the neighbourhood of 3400 Å for the absorption edge of sphalerite are generally accepted (Kröger and Hellingman, 1948; Beun and Goldsmith, 1961). The absorption edge of wurtzite is at a slightly shorter wavelength (Kroeger and Hellingman, 1948; see also references in Table 4).

TABLE 4

Position of the Optical Absorption Edge in Wurtzite

<u>Temperature</u>	<u>Parallel to c-Axis</u>		<u>Normal to c-Axis</u>		<u>References</u>
	<u>Å</u>	<u>eV</u>	<u>Å</u>	<u>eV</u>	
Room	3310	3.75	3340	3.71	Piper et al (1958)
Temp.	3320	3.73	3360	3.69	Beun and Goldsmith (1961)
4° K	3200	3.87	--	--	Piper et al (1959)
	3200	3.87	3320	3.84	Gross et al (1960)

Table 4 shows that the absorption edge of wurtzite irradiated with polarized light vibrating parallel to the *c* crystallographic axis (extraordinary ray) is at a slightly shorter wavelength, i.e. greater energy, than when irradiated with light vibrating normal to this axis (ordinary ray).

The position of the absorption edge is affected by temperature (see Table 4; also Van Doorn, 1954), pressure (Piper et al, 1958; Edwards et al, 1959), and strong electric fields (Damašková and Pátek, 1962). Foreign elements in solid solution also appear to influence the position of the absorption edge, pronounced shifts to longer wavelengths having been noted for cadmium, manganese, and mercury (Bube, 1953; Gisolf, 1939; Kremheller et al, 1960).

The value of the photon energy (in electron volts) of the absorption edge in zinc sulphide is generally taken as a measure of the forbidden energy gap separating the valence and conduction bands in semiconductor band theory (Piper, 1953; Bube, 1953; Hall, 1956; Beun and Goldsmith, 1961, etc.), although Curie (1963) stressed that this is only strictly the case if the transition is vertical, i.e., no phonons are involved.

At low temperatures, structure in the form of narrow absorption bands can be detected at the absorption edge (Piper et al, 1959; Gross et al, 1960; Shalimova and Morozova, 1964b). According to Shalimova and Morozova (1964b), sphalerite shows three absorption bands, at 3210 Å, 3273 Å, and 3290 Å. Wurtzite, on the other hand, exhibits a different and more complex spectrum, with three bands at 3090 Å, 3127 Å and 3164 Å, two intense lines at 3190 Å and 3217 Å, and one weak band at 3224 Å. They also reported that the absorption spectrum of polycrystalline material corresponds to that of single crystals, except that the former exhibit a small shift toward longer wavelengths. Gross et al (1960) showed that, in strained crystals, the absorption maxima are also shifted toward longer wavelengths.

Below the absorption edge, the absorption spectrum can be derived from reflectivity measurements by means of a Kramers-Kronig analysis. Such an analysis, performed by Cardona and Harbeke (1965), shows a number of maxima between 3,000 and 1,000 Å.

The absorption of ZnS in the infrared portion of the spectrum is very low up to about 14 microns (Deutsch, 1962). At longer wavelengths the absorption spectrum becomes very complex. The general configurations of the absorption curves of sphalerite and wurtzite are similar (Balkanski et al, 1964), both containing six well-defined absorption maxima between 14 and 30 microns (Deutsch, 1962; Balkanski et al, 1964) and then rising to a maximum in the neighbourhood of 30 microns. The wurtzite spectrum contains an additional number of deflections of a minor nature. Marshall and Mitra (1964), for example, recorded no less than twenty-seven absorption maxima between 13 and 33 microns. The strong absorption peak at about 30 microns can be attributed to the primary lattice vibrations; the peaks at lower wavelengths to resonance frequencies, i.e. multiphonon combinations (Marshall and Mitra, 1964; Balkanski et al, 1964).

The state of aggregation of the zinc sulphide appears to influence the position of the strong absorption band. Mitsuishi et al (1958), for example, obtained wavelength values of 33 and 36 microns with samples of powdered and evaporated wurtzite, respectively.

The presence of impurities produces profound changes in the near infrared portion of the absorption spectrum. Low and Weger (1960) found that as little as 0.03% iron in sphalerite results in a strong absorption band at 3 microns. Cobalt produces an absorption maximum at 1.5 microns (Weakliem, 1962), and nickel, maxima at about 1 and 2 microns (Weakliem, 1962).

Reflectivity Spectrum

The specular reflectivity of ZnS in the visible part of the spectrum is lower than that of almost all other sulphides. Gray and Millman (1962) reported that the reflectivity of sphalerite varies from 16.0% at a wavelength of 7000 Å to 19.2% at 4700 Å. The values for these wavelengths, calculated from the well-known Fresnel equation for non-absorbing minerals,

viz. $R (\%) = \frac{100 (n - 1)^2}{(n + 1)^2}$, using the values of n given in another section,

are 16.1% and 17.5%, respectively. The values for wurtzite given by Gray and Millman (1962) are similar at the longer wavelength, but appreciably higher at shorter wavelengths. Ramdohr (1960) stated that the reflectivities of sphalerite and wurtzite are identical.

Some sharp deflections have been noted in the reflectivity spectra of sphalerite and wurtzite in the vicinity of the fundamental absorption edge. Sphalerite exhibits two reflection maxima between 3200 and 3300 Å (Birman et al, 1961; Shalimova and Morozova, 1964a). Wurtzite has been credited with three (Birman et al, 1961) or four (Shalimova and Morozova, 1964a) maxima in this region. Reflectivity maxima in the region of the fundamental absorption edge have been attributed to exciton formation, i.e., an electron-

hole pair bound together by mutual coulomb attraction (Birman et al, 1961).

The reflectivity spectra of sphalerite and wurtzite below the fundamental absorption edge have been reported by a number of workers (Cox et al, 1959; Robin-Kandará et al, 1963; Cardona, 1963a, b; Walker and Ostanowski, 1963; and Cardona and Harbeke, 1965). Although there is some disagreement as to the exact positions of the reflectivity maxima, it appears that the spectra for sphalerite and wurtzite are very similar (Cardona and Harbeke, 1965). Assignment of the maxima to electronic transitions between energy levels has been attempted by the more recent authors cited above. Robin-Kandará et al (1963) approached this problem from the point of view of orbital energies; Cardona and Harbeke (1965), on the other hand, from the Brillouin zone concept.

The principal feature of the infrared portion of the reflectivity spectrum of ZnS is at the reststrahlen frequency -- the abrupt increase in reflectivity in the vicinity of 30 microns, which corresponds to the absorption maximum in this region. Yoshinaga (1955) reported the reflectivity maximum at 25.5 microns, but did not specify whether his material was sphalerite or wurtzite. Deutsch (1962) reported the reflectivity maximum of wurtzite at 30.8 microns. Balkanski et al (1964) were able to resolve two reflectivity peaks in wurtzite: 30.3 and 36.5 microns, which they attributed to longitudinal and transverse lattice vibrations, respectively. At longer wavelengths, the reflectivity curve is completely flat up to at least 200 microns (Yoshinaga, 1955).

Refractive Index

The refractive index of sphalerite in the visible portion of the spectrum increases from 2.320 at 7670 Å to 2.679 at 3650 Å (Brun, 1930; DeVore, 1951); consequently, sphalerite has normal dispersion throughout this region. The refractive index continues to rise into the near ultraviolet, after which it passes through a series of maxima and minima (Hall, 1956; Cole and Oppenheimer, 1962; Cardona and Harbeke, 1965). The maximum index reported is 3.6 at 2140 Å (Hall, 1956), and the minimum, 0.66 at 900 Å (Cole and Oppenheimer, 1962). Coogan (1957) noted anomalous dispersion between 3700 and 2800 Å, which he attributed to an absorption band peculiar to evaporated layers.

The refractive indices of wurtzite have been measured throughout the visible range and into the near infrared region by Bieniewski and Czyzak (1963). In the visible range they correspond very closely to that of sphalerite, and are in fair agreement with the values given for two wavelengths of light by Allen et al (1912). The birefringence ($n_x - n_w$) of wurtzite reported by Bieniewski and Czyzak (1963) viz. 0.004, is much lower than the value of 0.020 reported by Allen et al (1912). The suggestion by Singer (1963) that the variable birefringence observed in polycrystalline wurtzite is due to structural heterogeneities may perhaps explain this discrepancy.

Iron in sphalerite increases both the refractive index and dispersion in the visible region of the spectrum (Allen et al, 1912).

In the near infrared portion of the spectrum, the refractive index of ZnS (measured on a mixture of sphalerite and wurtzite) continues to decline with increasing wavelength (Hall and Ferguson, 1955), reaching the value of 2.15 at 4 microns. The same trend was noted by Piper et al (1958) who, however, did not detect an appreciable decrease in refractive index beyond 4 microns, at which wavelength they obtained a value of 2.26. At the reststrahlen frequency, in the neighbourhood of 30 microns, the refractive index rises precipitously (Balkanski et al, 1964).

Luminescence

Zinc sulphide can be made to luminesce by means of suitable excitation, including light (photoluminescence), heat (thermoluminescence), or electric current (electroluminescence). The emission spectra depend on a variety of factors, the principal ones being the composition of the zinc sulphide and the excitation conditions. A comprehensive survey of the extensive literature on luminescence is given in a recent book by Curie (1963).

It is generally agreed that zinc sulphide fluoresces only when its composition departs from ideality, either by the presence of impurities or vacant lattice sites, or both (Hopfield, 1959; Curie, 1963; Uchida, 1964). Zinc sulphide with cation impurities that give rise to luminescence is termed "activated". If the luminescence is not due to the presence of cation impurities, the material is called "self-activated".

It has been proposed that the fluorescence of self-activated ZnS can be attributed to a deficiency either of the cation or anion (Kröger and Vink, 1954; Uchida, 1964), with the wavelength of the fluorescence being different for the two cases. Other workers (Kasai and Otomo, 1962; Koda and Shionoya, 1964) have suggested that when the luminescence is due to a zinc vacancy, this vacancy must be associated with an acceptor ion, such as chlorine, that replaces one of the adjoining sulphur atoms. In the excited state, an electron is excited from one of the sulphur ions surrounding the vacancy and is transferred to the $4s$ orbital of the chlorine ion. The resulting hole rotates among the three equivalent sulphur atoms due to resonance among the three bond orbitals, forming an electric dipole oriented along the tetrahedral bond direction.

Zinc sulphide can be activated by a number of elements. The most common elements used in luminescence work (Shionoya et al, 1964) are the activators from Group Ib of the periodic table (Cu, Ag, Au), co-activators from Group IIIb (Al, Ga, In), and acceptors from group VIIb (Cl, Br, I). Although manganese is also sometimes termed an activator, its effect is different from that of the normal activators (Curie, 1963, p. 122). Other elements, such as iron, cobalt and nickel, "kill" luminescence (Jaffe and Banks, 1964).

In photoluminescence, the excitation is provided by radiation with a wavelength close to that of the fundamental absorption edge (Hopfield, 1959); at low temperatures, there is an additional excitation frequency at a longer wavelength (Koda and Shionoya, 1964). The emission always occurs at a longer wavelength than that of the exciting radiation, and is most often observed

in the visible region of the spectrum. Infrared luminescence has been discussed in detail by Schulz (1963).

Electroluminescence has been described in recent reviews by Matossi and Gutjahr (1963) and Henisch (1964).

The intensity of luminescence is increased by an applied electric field (Bar et al, 1964), and is reduced by infrared (Kramer and Turner, 1963; Koda and Shionoya, 1964) and visible (Kasai and Otomo, 1962) radiation.

The various theories proposed to explain luminescence are listed by Razbirin and Ioffe (1964), who observed that there is as yet no complete agreement as to its exact nature. In terms of band theory, the luminescence phenomena in activated ZnS are attributed to "luminescence centres" that form intermediate energy bands between the normal valence and conduction bands. Luminescence occurs when an electron that has been excited into a higher energy level drops to a lower level, and thereby emits energy in the form of visible light. Shionoya et al (1964) recognized five distinct luminescence phenomena in ZnS, which they interpreted on the basis of three different types of transitions: 1) electron transition from the conduction band to a luminescent centre lying above the valence band; 2) electron transition from a luminescent centre below the conduction band to the valence band; and 3) electron transition from the excited or ground state of the donor to the ground state of the acceptor, both states lying between the valence and conduction bands.

Although Curie (1963, p. 107) states that there is very little difference in the luminescence spectra of sphalerite and wurtzite, polymorphism (Wecker, 1942) and polytypism (Hartman, 1963) have been shown to exert an influence on the intensity of the luminescence. According to Kendall (1964), the best ZnS phosphors are mixtures of cubic and hexagonal forms. Kendall's explanation for this is that, in "single crystals", a transition from cubic to hexagonal form gives rise to quasi p-n junctions along the cubic (111) direction, which may be a source of traps, impurity concentrations, and electric fields.

ELECTRONIC AND MAGNETIC PROPERTIES

Magnetic Susceptibility

Pure zinc sulphide is diamagnetic. The theoretical specific magnetic susceptibility, calculated from the susceptibilities of the zinc and sulphur ions (Int. Crit. Tables, 1929), is -0.30×10^{-6} e.m.u./g. The measured specific magnetic susceptibilities of sphalerite and wurtzite are -0.262 and -0.290 , respectively (Larach and Turkevich, 1955). These values are in good agreement with those of Voigt and Kinoshita (cited in Int. Crit. Tables, 1929), although not with the value of -0.463×10^{-6} (converted from a molar susceptibility of -45.1×10^{-6}) reported by Matyas (1962). According to Larach and Turkevich (1955), the magnetic susceptibility depends on the

method of preparation, well crystallized samples being less diamagnetic than fine-grained precipitates. They attribute this to the decrease in surface area where the electrons have a greater orbital radius than in the bulk.

The presence of impurities, particularly iron (Stutzer et al, 1918; Spokes and Mitchell, 1958) and manganese (Brummage et al, 1964), has a pronounced effect on the magnetic susceptibility of sphalerite, both elements rendering the mineral paramagnetic. Brummage et al (1964) noted that ZnS containing substantial amounts of manganese departs from Curie behaviour at temperatures above 77°K. They attributed this to antiferromagnetic coupling between adjacent manganese ions.

Electron Paramagnetic Resonance (EPR)

The Landé spectroscopic splitting factor, g , for self-activated zinc sulphide has been found to be greater than the free spin value of 2.0023 (Schneider et al, 1963a). These authors suggested that at very low temperatures their results are consistent with a hole trapped at a S^{-2} ion that is situated in various crystalline fields. These fields are thought to arise from an adjacent zinc vacancy, the associated group III or group VII impurity, the non-cubic symmetry of the wurtzite structure, and from stacking faults. At higher temperatures, the hole hops rapidly among the three equivalent sulphur ions adjacent to the zinc vacancy.

Müller and Schneider (1963) investigated the EPR spectrum of sphalerite doped with chlorine, bromine, iodine, and aluminum-zinc. They reported that, in all cases, the resonance lines had g -values smaller than the free spin value, and showed no hyperfine structure. Variations in g -value were attributed to the doping agent and to intrinsic lattice properties. Wurtzite doped with chlorine was found to have an anisotropic g -value that is higher than that of sphalerite, but still smaller than the free electron value. Müller and Schneider (1963) interpreted their results as indicating mobile electrons in the conduction band and/or shallow donor bands.

The paramagnetic resonance parameters of different cations in sphalerite are shown in Table 5.

The foreign ions incorporated in sphalerite are generally divalent, and it is necessary to illuminate the crystal with ultraviolet light to convert the Cr^{+2} and Fe^{+2} to the Cr^{+1} and Fe^{+3} valence states (Matossi et al, 1963). The presence of doping agents also appears to have a profound effect, the conversion being promoted by those elements that produce p-type conductivity (Matossi et al, 1963).

TABLE 5

Paramagnetic Resonance Parameters for Certain Ions in Sphalerite

<u>Ion</u>	<u>g-factor</u>	<u>Hyperfine Structure Constant A (10⁴ cm⁻¹)</u>	<u>Cubic Field Splitting Parameter a (10⁴ cm⁻¹)</u>	<u>References</u>
Cr ⁺¹	1.9995	13.4	3.9	Title (1963)
Mn ⁺²	2.0021 2.0024	63.73 64.0	7.97 7.87	Title (1963) Schneider et al (1963b)
Fe ⁺²	2.25	--	--	Low and Weger (1960)
Fe ⁺³	2.019 2.0194	7.69 7.8	127.4 128	Title (1963) Räuber and Schneider (1962)

The Cr⁺¹, Mn⁺², and Fe⁺³ ions all have the 3d⁵ electron configuration in the d-shell, giving the ion spherical symmetry. Consequently these ions should have no orbital angular momentum, so that the g-factor should correspond to the free-spin value of 2.0023 (Title, 1963; Watanabe, 1964). The values of g for these ions, shown in Table 5, are similar to the free spin value. The small negative shifts exhibited by Cr⁺¹ and Mn⁺² have been explained by an admixture of other states of the d² configuration into the ground state (Watanabe, 1964). The positive g-shift for Fe⁺³ has been attributed to electron transfer to Fe⁺³ from the surrounding sulphur ligands through spin-orbit interaction.

Because of the spherical symmetry of the Cr⁺¹, Mn⁺², and Fe⁺³ ions, they should not show any hyperfine structure due to interaction with the magnetic moment of the nucleus (Van Wieringen, 1955; Title, 1963). The anomalous hyperfine structure observed (Table 5) has been attributed to the partially covalent nature of the bonding in ZnS (Title, 1963). Van Wieringen (1955) showed that the hyperfine splitting shown by Mn⁺² is decreased when the manganese content becomes sufficiently high for exchange interaction to occur between neighbouring manganese ions.

The cubic field splitting parameter a is larger than predicted by calculations based on an ionic model. This has also been taken as indicating an appreciable proportion of covalent bonding (Title, 1963).

The structure and state of aggregation of the sample have an important effect on the EPR spectrum of zinc sulphide. Hershberger and Leifer (1952) found that the EPR spectra of manganese-containing sphalerite and wurtzite are markedly different. Schneider et al (1963b) reported values of g, A, and a for manganese in wurtzite that are only slightly different

from those for sphalerite. R uber and Schneider (1962) noted the appearance of a second line in the EPR spectrum of iron-bearing sphalerite after their sample had been pulverized in a mortar, and also after the annealing of single crystals. Twinning in sphalerite results in doubled peaks, except when the magnetic field is parallel to (111) or (110) (R uber and Schneider, 1962).

Electrical Conductivity

Zinc sulphide is a semi-conductor. Under normal conditions of temperature and pressure it is non-conducting, but when a suitable amount of energy is added to the electrons, it becomes conducting. In terms of band theory, electrons are transferred from the valence to the conduction band. The energy difference between an electron in its valence and conduction states is generally referred to as the forbidden energy gap, and is expressed in terms of electron volts (eV).

Photoconductivity measurements on sphalerite (Gudden and Pohl, 1922) and on wurtzite (Piper, 1953; Cheroff and Keller, 1958) have shown that these minerals both have a photoconductivity peak between 3350 and 3400 Å, which corresponds to a photon energy of 3.70 to 3.65 eV. This is in agreement with values of the wavelength of the fundamental absorption edge given in the section "Optical Properties". On the other hand, Fok (1963) claimed that the thermal energy gap is nearer 3.9 eV. The temperature coefficient of the optical band gap energy of wurtzite is 3×10^{-4} eV/°K (Piper, 1953). Photoconductivity at longer wavelengths has been attributed to the presence of foreign elements (Cheroff and Keller, 1958).

The thermal energy gap, measured on polycrystalline zinc sulphide, has been reported as 3.2 eV (Fok, 1963), which is considerably lower than the optical energy gap. This discrepancy has been attributed to the partially covalent bonding (Fok, 1963).

Pressure reduces the forbidden energy gap of zinc sulphide (Edwards et al, 1959). Samara and Drickamer (1962) reported that sphalerite becomes electrically conducting at very high pressures (240-245 kilobars). This has been interpreted by Rooymans (1963) as a structural transformation of zinc sulphide to a rocksalt structure with large numbers of defects.

Mixed-structure zinc sulphide shows a very high anomalous photo-voltaic effect. This has been attributed to high electrical field gradients at the borders between different structural arrangements (Brafman et al, 1965).

Piezoelectricity

As a consequence of their polar lattices, both sphalerite and wurtzite are piezoelectric (Cady, 1946), i.e., they develop positive and negative electrical charges at opposite ends of their trigonal axes when subjected to pressure normal to these axes. The piezoelectric constant d_{14} of sphalerite has been variously reported as -9.08×10^{-8} (Coster et al, 1930), -9.7×10^{-8} (Cady, 1946), and -9.53×10^{-8} cgs units (Berlincourt et al, 1963). Merten (1962) reported that piezoelectric and elastic constants

calculated from lattice energies, assuming only Coulomb attraction, give values that are too high by a factor of 5, and that electron polarization effects, i.e., covalency, must therefore be taken into account in such calculations.

The piezo-optic constant Π_{44} has been reported as -3.16×10^{-13} cm²/dyn. (Bechman, 1960).

Pyroelectricity

Pyroelectricity, the ability of a substance to develop opposite charges at the ends of its polar axes when heated, is exhibited by wurtzite (Cady, 1946; Berlincourt et al, 1963). Reports that sphalerite is also pyroelectric (Friedel, 1879) have been discredited on crystallographic grounds (Cady, 1946; Berlincourt et al, 1963). Landauer (1960) pointed out that false observations of pyroelectricity have been made because of surface pyroelectric effects.

Dielectric and Electro-Optic Constants

The static dielectric constant of sphalerite measured at room temperature has been reported as 8.78 (Sharma and Gupta, 1963), 8.73 (Berlincourt et al, 1963), 8.5 (Chopra, 1965), 8.3 (Piper et al, 1958) and 7.5 (Deutsch, 1962). The high-frequency (optical) dielectric constant has been variously reported as 4.7 (Deutsch, 1962), 5.07 (Curie, 1963), and 5.2 (Piper et al, 1958). Hascaylo and Feldman (1962) demonstrated that anomalous results can be obtained by measurements of thin films, probably due to depositional stresses and the piezoelectric nature of zinc sulphide. Chopra (1965), however, did not obtain anomalous values on thin films thicker than about 1,000 Å.

The electro-optic constant r_{41} of sphalerite has been reported as 3.4×10^{-8} cm.stat. V⁻¹ at 4040 Å and 6.2×10^{-8} at 6440 Å (Bechman, 1960).

Bonding

The spatial arrangement of the atoms in the sphalerite lattice can be interpreted both in terms of an ionic and a covalent model. In the case of the ionic model, the structure can be envisioned as an array of divalent, closely packed, negatively charged sulphur ions with divalent, positively charged zinc ions in one set of tetrahedral interstices. In the covalent model, both the zinc and sulphur atoms participate in forming tetrahedrally directed hybrid sp³ electron-pair bonds.

In sphalerite, the zinc-sulphur distance (2.342 Å) is considerably less than the sum of the ionic radii of Zn⁺² (0.74 Å) and S⁻² (1.84 Å), which indicates that the bonding is not purely ionic. On the other hand, purely covalent bonds can only be formed between elements with the same electronegativities, any difference in electronegativity leading to a partially ionic character (Pauling, 1960). From Pauling's suggested relationship between electronegativity and bonding ratio, the zinc-sulphur bonding in sphalerite should be 82% covalent and 18% ionic. The concept of mixed

bonding in sphalerite is generally accepted, but there is a lack of agreement about the relative contributions of the two types of bonding. Evidence that the bonding is largely covalent has been obtained from calculation of elastic constants (Rajagopal and Srinivasan, 1960), the difference between optical and thermal energy gaps (Fok, 1963), and from an evaluation of piezoelectric data (Merten, 1962).

On the other hand, Saksena (1951) and Berlincourt et al (1963) were able to interpret their piezoelectric data on the basis of predominantly ionic bonding. Other evidence supporting the view that the bonding is chiefly ionic has been obtained from the wavelength of the sulphur K_{α} doublet (Faessler and Goehring, 1955), the reststrahlen frequency and dielectric constant (Vasileff, 1955), electron density mapping (Jumpertz, 1955), cohesive energy (Asano and Tomishima, 1956), paramagnetic resonance (Title, 1963), and Mössbauer studies (Luchner and Dietl, 1963). Goodman (1955) reached the same conclusion from the relationship of energy gap, bond length and electron mobility; and Poulet (1953), from vibration frequency, dielectric constant, and refractive index. Wolff and Broder (1959) suggested that the (011) cleavage in sphalerite indicates predominantly ionic bonding between zinc and sulphur atoms. In reviewing the various lines of evidence, Birman (1958) and Curie (1963) gave estimates of 67% and 75%, respectively, for the degree of ionic bonding. This implies effective charges of approximately 1 and -1 on the zinc and sulphur atoms, respectively, although Mooser and Pearson (1961) have warned against the calculation of effective charges from formal bond ionicities.

In addition to ionic-covalent bonding between zinc and sulphur atoms, Jumpertz (1955) found evidence of electron bridging between neighbouring zinc atoms, which he interpreted as a degree of metallic bonding.

Because the nearest-neighbour environment of the zinc and sulphur atoms in sphalerite and wurtzite is similar, the type of bonding in these two modifications would also be expected to be similar. Jeffrey et al (1956), Birman (1959), and Berlincourt et al (1963), however, are in agreement that bonds in the wurtzite-type structure probably have a greater degree of ionicity than in the sphalerite structure.

Energy Band Structure

Band theory has proven to be successful in explaining the electronic properties of many semiconductors. Efforts to elucidate the energy band structure of sphalerite and wurtzite have been made through the application of group theory (Parmenter, 1955; Dresselhaus, 1955; Casella, 1959, Cardona, 1963c), by linear combination of atomic orbitals (Shakin and Birman, 1958; Birman, 1959), and by an orthogonalized plane wave procedure (Bassani and Celli, 1961).

The Brillouin Zone of sphalerite is envisioned as a truncated octahedron (Birman, 1959) and corresponds to the reduced zone (Dresselhaus, 1955; Birman, 1959). The Brillouin Zone of wurtzite is a hexagonal prism (Birman, 1959), and has twice the volume of the reduced zone. Electron transitions are generally referred to vectors in k-space related to points of symmetry in the Brillouin Zone. According to Shakin and Birman (1958), the valence and conduction band edges are at $k = (0,0,0)$. Neglecting spin-orbit

splitting of energy states, there is eight-fold degeneracy of states in sphalerite along (111) in k-space (Cardona, 1963c). In wurtzite, the (1000) direction can be regarded as a perturbed sphalerite (111) state, the perturbation depending on the difference in bond type and departure of the wurtzite structure from ideality (Birman, 1959; Cardona, 1963c). The perturbation results in a splitting of the degeneracy in wurtzite.

According to Hopfield (1959) and Birman et al (1961), spin-orbit coupling splits the valence band in sphalerite into two closely spaced bands. Birman et al (1961) estimated the energy difference to be 0.068 eV. In wurtzite, uniaxial crystal field splitting is added to the spin-orbit splitting, resulting in three closely spaced energy levels in the valence band (Shakin and Birman, 1959; Birman et al, 1961; Sandomirskii, 1964). The energy differences between these bands have been reported as 0.027 and 0.084 eV (Birman et al, 1961). Adler (1962) found that, by expressing the crystal field and spin-orbit parameters in terms of the matrix elements of the wurtzite and sphalerite Hamiltonians, two-parameter formulae could be derived, which gave values for the valence band splittings in these two minerals that were very close to the experimental ones reported by Birman et al (1961). In general, crystal field theory has been shown to be successful in explaining electronic transitions and resultant absorption spectra in sphalerite and wurtzite (Allen, 1962).

It is generally agreed (Hopfield, 1959; Birman et al, 1961; Curie, 1963) that the conduction bands are s or s-like bands, that the valence bands are p or p-like, and that these bands possess extrema at or near $k = (0,0,0)$. Curie (1963) stated that the conduction band can be attributed to the zinc orbitals, and the valence band to the sulphur orbitals. If the effective charges on the zinc and sulphur atoms are +1 and -1, respectively, then the zinc atoms have one occupied and one unoccupied orbital s-state, and the sulphur atoms have five occupied and one unoccupied p-states. Hopfield (1959) suggested that the lowest energy electron and hole states probably correspond to a return to a configuration nearer free atoms, i.e., two s-electrons for zinc and four p-electrons for sulphur.

THERMODYNAMICS AND LATTICE DYNAMICS

Thermodynamic Values

Selected thermodynamic values for sphalerite at 298°K, with solid sulphur and zinc as standard reference states, have been given by Rossini et al (1952) as follows:

Heat of formation	48.5 Kcal/mole
Free energy of formation	47.4 Kcal/mole
Logarithm of equilibrium constant of formation	34.74
Entropy	13.8 cal/deg mole
Heat capacity	10.8 cal/deg mole

Richardson and Jeffes (1952), using diatomic sulphur gas as the standard reference state, reported a value of 107.6 Kcal/mole as the free energy of formation of sphalerite.

The heat of formation of wurtzite has been reported at 45.3 Kcal/mole (Rossini et al, 1952), i.e., 3.5 Kcal/mole lower than that of sphalerite. Richardson and Jeffes (1952), however, considered so large a difference between the heats of formation of the two modifications to be improbable.

Rossini et al (1952) reported that the heat of sublimation of sphalerite at 854°C and 0.01 mm Hg is 64.3 Kcal/mole, and the entropy of sublimation is 57.1 cal/deg mole. They also reported that the sublimation temperature of wurtzite is 1182°C at atmospheric pressure.

Elastic Constants

Values for the elastic constants of sphalerite, obtained by a variety of methods, are shown in Table 6.

TABLE 6

Elastic Constants of Sphalerite

(All values given in units of 10^{11} dynes/cm²)

<u>Method of Determination</u>	C_{11}	C_{12}	C_{44}	<u>References</u>
Static	9.43	5.68	4.37	Voigt (1963), quoted by Zarembovitch (1963)
Piezoelectric properties	10.78	7.23	4.12	Bhagavantam and Suryanarayana (1944), quoted by Zarembovitch (1963)
Thermal diffuse X-ray scattering	10	6.5	3.4	Prince and Wooster (1951)
Ultrasonic	9.76	5.96	4.51	Einspruch and Manning (1963)
"	10.32	6.46	4.62	Zarembovitch (1963)

Lattice Vibrations and Lattice Energy

The lattice vibration frequency of zinc sulphide is indicated by the wavelength of the strong optical absorption peak and the reststrahlen wavelength in the vicinity of 30 microns. According to Tsuboi (1964), group theoretical considerations show that for sphalerite there should be only one fundamental lattice vibration, which is triply degenerate and is active in both Raman effect and infrared absorption. For wurtzite, on the other hand, there should be six fundamental lattice vibrations, two of which are inactive, two of which are Raman and infrared active, and two of which are Raman active.

Mitsuishi et al (1958) reported an absorption band in sphalerite at 32 microns, and were able to detect only one absorption band in wurtzite, at 33 microns. Deutsch (1962) recorded the reststrahlen wavelength of sphalerite at 30.8 microns. Balkanski et al (1964) were able to resolve two reflectivity maxima in wurtzite at 36.5 and 30.3 microns, which they attributed to transverse and longitudinal optical modes, respectively. Raman spectra indicate vibration frequency values corresponding to wavelengths of 36.5 and 28.6 microns for the two optical modes (Couture-Mathieu and Mathieu, 1953).

Calculations of the cohesive or lattice energy of sphalerite have resulted in values of 911 (Asano and Tomishima, 1956), 866 (George and McLure, 1959), and 876 Kcal/mole (Sharma and Gupta, 1963). These values are in fair agreement with the lattice energy of 853 Kcal/mole obtained from the infrared absorption spectrum (Plendl, 1961).

The force constants of sphalerite and wurtzite calculated from the infrared vibration frequencies reported by Mitsuishi et al (1958) are 1.217 and 1.140 mdyn/A, respectively (Tsuboi, 1964).

Kaplan and Sullivan (1963) and Sullivan (1964) have developed expressions for the long-wavelength properties of the lattice vibration spectrum of the sphalerite and wurtzite structures, utilizing the elastic, piezoelectric and dielectric constants, the reststrahlen frequency, and the four phonon frequencies at the Brillouin zone boundaries in the (100) direction. Even using simplifying approximations, however, they were unable to make a unique determination of the parameters of the model.

Characteristic Temperature

The characteristic (Debye) temperature of sphalerite has been variously reported as 315°K (Martin, 1955), 357°K (Zarembovitch, 1963), and 450°K (Plendl and Gielisse, 1963). The latter value corresponds to a characteristic frequency of 32 microns (Plendl and Gielisse, 1963), which is in good agreement with the observed lattice vibration frequency of sphalerite.

SYNTHESIS OF ZINC SULPHIDE

Zinc sulphide can be prepared either by a direct reaction of zinc with sulphur, or by passing a sulphuretting agent such as hydrogen sulphide or sodium thiosulphate through a solution of a zinc salt (Curie, 1963). Hydrogen sulphide yields ZnS directly, although the product generally contains free sulphur (Baba, 1963). Sodium thiosulphate forms ZnS_2 which is unstable and decomposes to ZnS at high temperatures. Allen and Crenshaw (1914) reported that the ZnS precipitated from solution can be either sphalerite or wurtzite, the determining factor being the pH of the solution. This was confirmed by Müller (1952). Corey (1953), on the other hand, was able to show by X-ray diffraction analysis that sphalerite is precipitated over a wide range of conditions varying from strongly alkaline to acidic.

Single crystals may be grown from the melt, from vapour, and from solution.

A good summary of vapour phase methods is given by Reynolds (in Gilman, 1963). These can be classified as either static or dynamic. In the static method, zinc sulphide crystals grow directly on the powder. In general, the crystals produced by this method are not truly single crystals, but rather intergrowths and mixed-layer crystals of sphalerite and wurtzite (Kovács and Szabó, 1962; Räuber and Schneider, 1962). The microcline-like twinning frequently exhibited by ZnS between crossed nicols has been attributed to such intergrowths (Kovács and Szabó, 1962).

In the dynamic method, the zinc sulphide is vapourized in the hot portion of a chamber and is precipitated in a cooler part. Various atmospheres have been used as media, including iodine (Nitsche, 1960), chlorine (Birman et al, 1961), hydrogen sulphide (Samelson and Brophy, 1961), and various mixtures (Kovács and Szabó, 1962). The zinc sulphide produced by this method is generally of the mixed-layer type, although Samelson and Brophy (1961) reported the production of "crystallographically pure" sphalerite. Birman et al (1961) reported the production of purely cubic and purely hexagonal modifications by the addition of additives. Thin films of evaporated ZnS tend to be polycrystalline (Bourg, 1962; Kostylev and Sherstyak, 1963; Aggarwal and Goswami, 1963). Shalimova et al (1963) showed that the structure of ZnS films depends on the composition and temperature of the substrate and on the composition of the atmosphere, but is independent of the structure of the starting material and the evaporation temperature. The effect of the carrier gas on the crystal morphology has been discussed by Hartmann (1962).

The growth of zinc sulphide crystals directly from molten ZnS has been accomplished by a number of investigators. Koda and Shionaya (1963) reported the production of cubic crystals with abundant stacking disorders by this method. Addamiano and Aven (1960) obtained wurtzite under controlled cooling conditions and under pressure of an inert atmosphere. Bean et al (1962) reported the growth of large "monocrystals" from the melt, but did not

specify the crystallographic modification. Sphalerite crystals have also been grown from a variety of molten fluxes (Mita, 1962; Linares, 1962; Malur, 1964; Ryskin et al, 1964). In this type of method, however, some of the flux material remains trapped in the crystals. Mita (1962), for example, reported from 0.1 to 0.4 atomic per cent potassium in wurtzite grown from a KCl flux.

Crystallization of zinc sulphide from aqueous solutions is usually done at low temperatures, generally between 250°C and 400°C (Laudise and Ballman, 1960; Kremheller et al, 1960). The resulting product is sphalerite, but X-ray diffraction analysis has shown that the crystals have stacking faults (Laudise and Ballman, 1960).

The possibility of converting wurtzite crystals to sphalerite has been demonstrated by Müller (1952) and Rauber and Schneider (1962). Hartmann (1962), on the other hand, was not able to get complete inversion. Shalimova and Morozova (1965) showed that the inversion temperature is profoundly affected by the presence of a zinc or sulphur atmosphere during annealing.

Impurities can be introduced into zinc sulphide by the addition of a salt of the impurity to the starting material (Curie, 1963), or by vapour phase diffusion (Weakliem, 1962).

The diffusion rate of zinc from the vapour phase into single crystals of wurtzite was measured by Secco (1958, 1961) at temperatures between 927°C and 1095°C. The diffusion coefficient was found to vary between 1.11×10^{-9} and 2.60×10^{-12} cm²/sec. Secco opined that the sphalerite-wurtzite transition does not play a significant role in the rate of diffusion, since both forms have identical diffusion paths. Strictly speaking, however, the diffusion paths are not identical, wurtzite having linear channels parallel to the c-axis, whereas sphalerite does not.

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