CRYSTALLOGRAPHY AND CHEMICAL BONDING OF SULFIDE MINERALS

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Abstract

The sulfur atom in sulfide minerals may have an argononic structure, with the sum of the covalent bonds and unshared pairs equal to 4 (with use of four sp^3 orbitals), or a transargononic structure, with this sum greater than 4 (with use also of one or more $3d$ orbitals). Conclusions about the nature of the bonds and the structure of the sulfur atom can be drawn from the experimentally determined ligancies, bond lengths, and bond angles. A detailed discussion of realgar, orpiment, cinnabar, molybdenite, proustite, pyrargyrite, pyrostilpnite, sphalerite, wurtzite, greenockite, metacinnabarite, galena, baumhauerite, gratonite, binnite, covellite, sulvanite, mackinawite, pyrite, and marcasite leads to the conclusion that the principal structures of sulfur in these minerals are argononic with covalence 2, 3, or 4, and transargononic with covalence 4, 5, or 6. In some cases the structure is an argononic-transargononic hybrid. Fractional bonds (ligancy greater than co-valence) are found in some minerals, such as galena.

Introduction

The principles determining the structure of the sulfide minerals have not as yet been formulated in a comprehensive way. The bonds between the sulfur atoms and the surrounding atoms in these minerals are covalent bonds, usually with only a rather small amount of ionic character. The metallic properties of many of the sulfide minerals, such as luster and electronic conductivity, show that the bonds resonate among alternative positions, and that some of the atoms have a metallic orbital, as in metals (Pauling, 1938, 1948a,b). The observed values of ligancy, bond lengths, and bond angles of sulfur show that the sulfur atom has transargononic structures in some minerals.
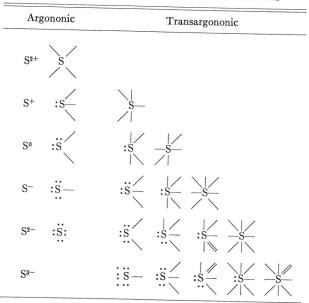
The discussion of chemical bonding of the sulfide minerals in the following pages is for the most part based on the general principles described in my book *The Nature of the Chemical Bond* (Pauling, 1960).

Types of Sulfur Atoms

It is convenient to base the discussion on the 20 types of sulfur atoms shown in Table 1. The horizontal rows correspond to different formal charges of the sulfur atom, from $2+$ to $3-$. (The formal charge is calculated by assigning all unshared electrons and one electron for each covalent bond to the atom.) The five argononic structures involve use of the $3s$ orbital and the three $3p$ orbitals for covalent-bond formation or occupancy by unshared electron pairs. (I use the word argononic to mean having the same number of electron pairs, shared or unshared, as in an argonon atom; that is, a noble-gas atom, and transargononic to mean having a larger number (Pauling, 1964).) The 15 transargononic structures make use also of one or more of the five $3d$ orbitals.

The properties of some sulfide minerals can be discussed in a reasonably satisfactory way by assigning one or another of the structures of Table I to the sulfur atoms. For some minerals the ligancy of the sulfur atom is equal to its covalence, and for others it is greater, the bonds then having fractional bond numbers. It is often necessary to assign a hybrid structure to the sulfur atoms. I shall assume that the covalent bonds indicated in Table I always have the normal amount of covalent character, as given by the

Table I. Electronic Structures of Sulfur Atoms

Argononic	Transargononic				
S^{2+}					
S^{+}					
S^{0}					
S^{-}					
S^{2-}					
S^{3-}					

difference in electronegativity of the metal atom and the sulfur atom.

The Covalent Radius of Sulfur

I shall use the value 1.030 Å for the normal single-bond covalent radius of sulfur, instead of the value 1.04 Å that has been accepted for a long time (Goldschmidt, 1926; Pauling and Huggins, 1934). This value is half the sulfur-sulfur distance 2.060 ± 0.003 Å in the S_8 molecule in orthorhombic sulfur, as determined by Caron and Donohue (1965). The value $S-S = 2.048 \pm 0.006$ Å has been reported by van de Grampel and Vos (1969) in $S_6(NH)_2$. The value 1.030 Å may be used for sulfur with other argononic structures. A somewhat larger value, about 1.07 to 1.10 Å, is indicated for transargononic sulfur.

Interatomic Distances

The length of a single covalent bond A—S may be taken as

$$D(1) = R_A + R_S - 0.060 \text{ Å } (x_A - x_S) \qquad (1)$$

in which x_A is the electronegativity of A and x_S is that of sulfur (Schomaker and Stevenson, 1941; Pauling, 1960, p 228). For formal charge zero the customary values of x are used (2.5 for S°). For S⁺ the value 2.7 is estimated, and for S²⁺, with 25 percent s character to the bond orbitals, the value 3.2. Because of the contribution of the $3d$ orbitals, which have a smaller value of the ionization energy than $3p$, a smaller value of x is expected for transargononic sulfur.

For other elements the same dependence of electronegativity will be assumed; that is, a change by 0.2 z for electric charge z, increase by 0.3 for sp^3 bond orbitals (relative to p bonds), and an equal decrease for d character in transargononic bonds.

To within the reliability of the Schomaker-Stevenson correction, the value of Δx may be taken as that for the atoms with resultant charges $\pm 1/2$, in case that the formal charges are ± 1. For larger formal charges the electronegativity of each atom may be taken as corresponding to the resultant charge when each bond except the one under consideration has the amount of ionic character that for all bonds would reduce the charge to ± 1.

For example, for quadricovalent Cu³⁻ (sp^3 bonds) the charge on the copper atom becomes -1 for 50 percent ionic character of the four bonds. This amount of ionic character for three bonds leads to Cu¹·⁵⁻, for which $x = 1.9 - (1.5 \times 0.2) = 1.6$.

BOND LENGTH AND BOND NUMBER

Metals and alloys can be treated as involving covalent bonds that resonate among alternative positions (Pauling, 1938). Extra orbitals (metallic orbitals), usually 0.7 per atom, are needed for the unsynchronized resonance that gives rise to metallic properties (Pauling, 1948a,b). The value of an interatomic distance (bond length) corresponding to a fractional bond number n is given by the equation (Pauling, 1947)

$$D(n) = D(1) - 0.600 \log n \qquad (2)$$

$D(1)$ is the sum of the single-bond radii of the two atoms plus the correction for the difference in electronegativity. I assume that this equation holds for the sulfide minerals, and also that a metallic orbital is needed for metallic properties.

THE ELECTRONEUTRALITY PRINCIPLE

The electroneutrality principle (Pauling, 1960, p. 172) states that for stable structures the electric charge on each atom is close to zero. The charge is calculated by correcting the formal charges of the atoms by the charges transferred to the atoms by the partial ionic character of the bonds, as given by equation 3 (Pauling, 1960, p. 98):

$$\text{Ionic character } i = 1 - \exp\left[-(x_A - x_B)^2/4\right] \qquad (3)$$

In applying this equation to a multicovalent atom, it should be used for each stage of formal charge, with the corresponding values of the electronegativity. The use of the electroneutrality principle is illustrated in several of the following discussions of sulfide structures.

MINERALS CONTAINING BICOVALENT ARGONONIC SULFUR

The normal valence (normal covalence) of sulfur, corresponding to its position in the periodic table, is 2. The electronic structure of the normal bicovalent sulfur atom is the argononic structure :S̈⟨ with bond orbitals about 93 percent $3p$ and 7 percent $3s$, bond angle between 92° and 108°. Orthorhombic sulfur, realgar, orpiment, and cinnabar may serve as examples of minerals containing this sort of sulfur atom.

The bond angle in orthorhombic sulfur equals 108.0° $\pm 0.1°$.

In realgar there are molecules As₄S₄. Each sulfur atom is bonded to two arsenic atoms, at 2.243 Å (average of eight nonequivalent values, from 2.19 Å to 2.28 Å; Ito, Morimoto and Sadanaga, 1952). The As—S bond length in the As₄S₄ gas molecule is 2.23 ± 0.02 Å (Lu and Donohue, 1944). The average values of the As—S—As bond angle are 101.5° for realgar and 100° for As₄S₄(g).

Orpiment, As₂S₃, has a layer structure in which each sulfur atom is bonded to two arsenic atoms and each arsenic atom to three sulfur atoms. The average bond length and average bond angle in orpiment and in As₄S₆(g) have nearly the same values as for realgar and As₄S₄(g); the bond lengths are 2.25 ± 0.02 Å in both orpiment and As₄S₆(g).

The observed bond angles and bond lengths in realgar and orpiment support the assignment of normal-valence structures to them. The single-bond covalent radius of arsenic is taken to be 1.25 Å, from the observed bond length 2.50 Å in As(c). (The value 2.49 Å is reported for the As—As bonds in realgar.) The expected value for the normal As—S bond length is $1.25 + 1.03 = 2.28$ Å minus the correction for the difference in electronegativity of arsenic and sulfur. This correction, the Schomaker-Stevenson correction (Equation 1), is $-\Delta x \times 0.060$ Å for a bond between sulfur and a more electronegative atom not of the first row in the periodic table (Pauling, 1960, p. 229). The quantity Δx is the difference in electronegativity of sulfur ($x = 2.5$) and the atom to which it is bonded ($x = 2.0$ for arsenic). With this correction, -0.030 Å, the expected value for the As—S bond length is 2.25 Å, in agreement with the realgar-orpiment value.

In realgar the short non-bonding contact distances are 3.3 Å for sulfur-sulfur, 3.6 Å for sulfur-arsenic, and 3.5 Å for arsenic-arsenic. They are accordingly about 1.2 Å greater than the corresponding single-bond lengths, as found in other crystals.

In cinnabar, HgS, the sulfur atom has a normal-valence structure, in which it forms two bonds with mercury atoms. The Hg—S—Hg bond angle is 105°. The mercury atom may be described as forming two oppositely directed bonds with use of two sp hybrid bond orbitals; the value of the S—Hg—S angle is 172°. The bond length, 2.36 Å, leads,

with $R = 1.03$ Å for sulfur and the Δx correction ($x = 1.9$ for mercury), to the value 1.36 Å for the mercury single-bond radius. This value may be compared with that of the metallic single-bond radius of mercury, 1.386 Å, which however, corresponds to metallic valence 4.56 (Pauling, 1960, p. 403).

MINERALS CONTAINING TERCOVALENT ARGONONIC SULFUR

The symbol $[:\overset{..}{S}{\overset{\textstyle=}{}}]^+$ represents tercovalent argononic sulfur. Like $:\overset{..}{S}{<}$, it is argononic in that, counting shared as well as unshared electron pairs, it has four pairs in its outer shell, giving it the electron number of argon. A tercovalent argononic sulfur atom resembles a normal (neutral) tercovalent phosphorus atom. The bond orbitals of $:\overset{..}{S}{\overset{\textstyle=}{}}^+$ are similar to those of $:\overset{..}{S}{<}$.

Molybdenite, MoS_2, has a layer structure in which each sulfur atom has three molybdenum atom neighbors at 2.417 Å. If we assume that the bonds are single covalent bonds, with tercovalent argononic sulfur, the molybdenum atom is given the formal charge -2, which might seem to be incompatible with the electroneutrality principle. It is found, however, as shown below, that the amount of ionic character of the bonds is great enough to make the structure acceptable.

To calculate the amounts of ionic character we use the electronegativity values 1.8 for Mo^0, 1.4 for Mo^{2-}, 2.7 for S^+, 2.5 for S^0, and so on. To simplify the calculation we may assume a value of the average charge of the molybdenum atom, and use the corresponding average value of x, in calculating the ratios of S^+, S^0, S^-, and S^{2-}. Trial shows $Mo^{0.75-}$, with $x = 1.65$, to be consistent with the amounts of partial ionic character and the number of structures (1 for each tercovalent S^+ and zerocovalent S^{2-}, 3 each for bicovalent S^0 and unicovalent S^-). The values of partial ionic character of the bonds of S^+, S^0, and S^- are 24, 17, and 10 percent, respectively, and the contributions of S^+, S^0, S^-, and S^{2-} to the structure are 47, 44, 9, and 0.3 percent, respectively, leading to the average charge $+0.37$ on sulfur and -0.74 on molybdenum. A similar calculation with use of an average value of x for sulfur, 2.57 (corresponding to average charge $+0.37$), leads to the contributions 18, 45, 30, 7 percent for Mo^{2-}, Mo^-, Mo^0, and Mo^+, respectively, average charge -0.74 for molybdenum. The agreement indicates that the approximate calculations involve little error. With the Schomaker-Stevenson correction of -0.042 Å in the bond length and the radius 1.030 Å for sulfur, the observed Mo—S distance 2.417 Å leads to 1.43 Å for the single-bond covalent radius of sexicovalent Mo^{2-}. The increase over the metallic radius 1.296 Å of neutral molybdenum (metallic valence 6) is reasonable as the effect of the unshared electron pair in the valence shell of Mo^{2-}.

Molybdenite was the first substance found to contain a trigonal prism as ligation polyhedron for ligancy 6, instead of the more common octahedron (Dickinson and Pauling, 1923). An acceptable explanation of the stability of the molybdenite structure, rather than the cadmium iodide structure, which is a closely similar layer structure but with octahedral ligation about the metal atom, has been advanced (Pauling, 1960, p. 175). The molybdenum bond orbitals are dsp hybrids. The best dsp bond orbitals correspond to the values 73.15° and 133.62° for the unstrained bond angles. These values are much closer to the observed values for the angles S—Mo—S in molybdenite, 82° and 136°, than to those for the cadmium iodide structure, 90° and 180°.

Proustite, Ag_3AsS_3, is another good example of a mineral containing $:S{\overset{\textstyle=}{}}^+$. It consists of two interpenetrating frameworks. Each sulfur atom is bonded to 1 As and 2 Ag, the bond angles having values close to 90° (83° for Ag—S—Ag, 100° and 107° for As—S—Ag). The observed As—S bond length has the expected value, 2.25 Å (as in enargite); Harker (1936) found 2.25 Å, and Engel and Nowacki (1966) found 2.254 Å.

The Ag-S bond length is 2.44 Å. This value is also found in pyrargyrite and pyrostilpnite, both of which have the formula Ag_3SbS_3 and contain bicovalent silver and tercovalent argononic sulfur. It leads to 1.45 Å for R for bicovalent silver with formal charge -1, which may be compared with the values 1.396 Å and 1.528 Å for silver with metallic valence 3 and 1, respectively (Pauling, 1960, p. 420).

QUADRICOVALENT ARGONONIC SULFUR

Huggins (1922) was the first investigator to assign structures to sphalerite, wurtzite, chalcopyrite, pyrite, marcasite, arsenopyrite, and other sulfide minerals in which each sulfur atom forms four tetrahedrally directed covalent bonds with surrounding atoms. These structures would be described as involving quadricovalent argononic S^{2+}.

For sphalerite and wurtzite, for example, the discussion of partial ionic character as described above for molydenite leads to the resultant average charges $+0.67$ for sulfur and -0.67 for zinc. The distribution of the sulfur atoms is calculated to be 12% S^{2+} (quadricovalent), 50 percent S^+, 32 percent S^0, 6 percent S^-, 0.2% S^{2-}. The observed bond length 2.34 Å with the sulfur radius 1.03 Å and the Schomaker-Stevenson correction 0.05 Å leads to $R_i = 1.36$ Å for zinc (quadricovalent Zn^{2-}). The increase by 0.05 Å over the value 1.309 Å for sp^3 bonds of Zn^0 is reasonable as the result of screening of the nucleus by the extra electrons.

The Cd-S distance 2.53 Å in greenockite and the Hg-S distance 2.54 Å in metacinnabar similarly lead to the values $R = 1.55$ Å for Cd^{2-} and 1.55 Å for Hg^{2-}, 0.06 Å larger than the sp^3 radii of the neutral atoms, 1.485 Å and 1.490 Å, respectively (Pauling, 1960, p. 420).

The above results for ZnS, CdS, and HgS indicate that an additional electron in a transition-metal atom increases its radius by 0.03 Å.

SULFIDE MINERALS CONTAINING RESONATING BONDS

Galena, PbS, has the sodium chloride structure, with ligancy 6 for each atom. The Pb-S distance is 2.968 Å. A possible structure is that based on the normal sulfur atom

(bicovalent argononic sulfur), with the two single bonds resonating among the six positions, giving $n=1/3$. Another reasonable structure is that based on the tercovalent argononic atoms :Pb≡⁻ and :S≡⁺, with three bonds resonating among the six positions. This structure makes use of all of the outer orbitals of the lead atom and the sulfur atom, and with its greater number of bonds may be expected to correspond to a lower energy value than the structure with bicovalent atoms, which, in fact, represents its partial ionic character.

Treatment of the tercovalent structure as given above for molybdenite leads to 51 percent S^+ (Pb^-), 42 percent S^0 (Pb^0), 7 percent S^- (Pb^+), and 0.2 percent S^{2-} (Pb^{2+}), average charges $+0.43$ for S, -0.43 for Pb. The observed Pb—S distance with the bond-number correction 0.181 Å, Schomaker-Stevenson term -0.042 Å, and sulfur radius 1.030 Å gives 1.80 Å for the single-bond radius of lead in this crystal. This value is 0.26 Å larger than the p-bond radius of neutral bicovalent lead. Of this amount, 0.03 Å can be attributed to the screening effect of the extra electron in Pb^- and 0.20 Å to the repulsion of the outer unshared pairs of both lead and sulfur for the surrounding atoms.

The Lead Sulfarsenites and Related Minerals

It is likely that the lead and sulfur atoms in most of the lead sulfarsenites and related minerals have the tercovalent argonic structures :Pb≡⁻ and :S≡⁺, as in galena. Nowacki (1969) has published a valuable summary of results of structural studies of the so-called sulfosalt minerals, in relation to a system of classification of the structures that he has developed. Many structures of sulfide minerals have been determined by him and his coworkers.

In the sulfarsenite minerals arsenic has ligancy 3, with S—As—S bond angles usually between 95° and 105°, as expected for tercovalent arsenic, :As≡. In binnite, $Cu_{12}As_4S_{13}$, for example (Pauling and Neumann, 1934; Wuensch, Takeuchi, and Nowacki, 1966), the S—As—S bond angle is 98.4° and the As—S bond length is 2.246 Å, in agreement with the argononic structure. Lead is usually found with ligancy 6, 7, 8, or 9. In baumhauerite, $Pb_{11.6}As_{15.7}Ag_{0.6}S_{36}$ (Engel and Nowacki, 1969), there are 12 kinds of lead atoms, eight of which are surrounded by nine sulfur atoms, which lie approximately at the corners of a trigonal prism and out from the centers of its rectangular faces. The Pb—S distances for these atoms range from 2.73 Å to 3.70 Å, with averages about 3.2 Å.

I think that the average bond length has little significance. A more significant quantity, which might be generally adopted, is the *valence-average bond length*. Let us consider Engel and Nowacki's lead atom Pb(12), with 9S at 2.91, 3.00, 3.01, 3.02, 3.22, 3.28, 3.32, 3.47 and 3.53. The average of these values is 3.20 Å. The valence-average bond length is calculated by use of equation 2; it is the bond length for the assumed ligancy that corresponds to the same valence for lead and equal Pb—S distances. For the Pb(12) atom its value is 3.121 Å, and for the others it is

3.095, 3.084, 3.120, 3.107, 3.121, 3.124 and 3.116. The average for all eight is 3.111 ± 0.013 Å, which is 0.14 Å greater than for galena. The expected increase from ligancy 6 to ligancy 9, for the same covalence of lead (3), is 0.60 log $1.5=0.11$ Å. Hence the bond lengths in baumhauerite agree with those in galena to within 0.03 Å.

As another example I take gratonite, $Pb_9As_4S_{15}$, in which there are two kinds of lead atoms, each with ligancy 7 (Ribar and Nowacki, 1969). For the two kinds of lead atoms the averages of the seven Pb—S bond lengths are 3.03 Å and 3.09 Å, differing by 0.06 Å, whereas the valence-average bond lengths are 3.000 Å and 2.996 Å, in excellent agreement with one another. The expected value, calculated from the value 2.968 Å for galena by subtracting the term 0.600 log 6/7 for change in ligancy of lead from 6 to 7, without change in valence, is 3.008 Å.

In gratonite, as in galena, baumhauerite, and other minerals with ligancy 5 or more for sulfur and 6 or more for lead, the valence-average bond lengths agree with the values calculated from the single-bond value 2.79 Å by applying the bond-number correction of equation 2, with the covalence of lead taken to be 3.

Transargononic Sulfur

A transargononic structure for sulfur, with six bonds formed by sp^3d^2 hybrid orbitals, was suggested for sulfur in the octahedral molecule SF_6 long ago, and also for one of the sulfur atoms, with ligancy 6, in binnite (Pauling and Neuman, 1934). Some transargononic structures of metal sulfides have been proposed recently by Franzen (1966).

In F_5S—SF_5 the S—S distance is 2.21 Å, which indicates the value 1.105 Å for the single-bond covalent radius of transargononic sulfur. Support for this value is provided by the reported S—S bond lengths 2.209 ± 0.002 Å in potassium pyrosulfite, $K_2S_2O_5$, and 2.16 ± 0.02 Å in sodium dithionate dihydrate, $Na_2S_2O_6\cdot2H_2O$, and potassium dithionate, $K_2S_2O_6$. The sulfur-oxygen double bonds in these complexes make the sulfur atoms transargononic. Values from 2.10 to 2.14 Å, average 2.13 Å, are reported also for the argononic-transargononic —S—SO_3^- bond length in $Na_2S_4O_6\cdot2H_2O$, $BaS_4O_6\cdot2H_2O$, $BaS_5O_6\cdot2H_2O$, $BaS_5O_6\cdot H_2O\cdot(CH_3)_2CO$, $BeSeS_4O_6\cdot2H_2O$, $BaTeS_4O_6\cdot2H_2O$, and $(NH_4)_2TeS_4O_6$. This average corresponds to 2.10 Å for transargononic sulfur.

If we assume that the increase of R over the value 1.030 Å is proportional to the amount of d character of the bond orbitals, we obtain the values 1.10 Å for sp^3d^2 bonds, 1.07 Å for sp^3d bonds, and 1.08 Å for p^3d bonds (:S≡⁺).

Sexicovalent Transargononic Sulfer

In binnite, $Cu_{12}As_4S_{13}$, one of the 13 sulfur atoms is ligated to six copper atoms, which lie at the corners of an octahedron about it (Pauling and Neuman, 1934). The other sulfur atoms have tetrahedral ligation, and are presumably argononic (as in sphalerite, chalcopyrite, and other tetrahedral sulfides). These six copper atoms have

ligancy 3; the bonds from them to the transargononic sulfur atom have length 2.29 Å, which is 0.06 Å greater than that of the bonds from them to the tetrahedral sulfur atoms. Hence the single-bond radius for sexicovalent transargononic sulfur in bonding to metal atoms is 1.09 Å, 0.06 Å greater than for argononic sulfur, in agreement with the value from S_2F_{10} and the polythionic acid ions.

QUINQUECOVALENT TRANSARGONONIC SULFUR

In covellite, $CuCu_2SS_2$, the disulfide sulfur atoms have a tetrahedral quadricovalent argononic structure, with S—S = 2.09 Å and S—Cu(I) = 2.30 Å. The sulfide sulfur atom has ligancy 5, with the bonds directed toward the corners of a trigonal bipyramid, as expected for S^+ with dsp^3 bonds (analogous to P in PCl_5).

The values of R for Cu(I) with sp^3 bonds and Cu(II) with dsp bonds are 1.352 Å and 1.185 Å, respectively (Pauling, 1960, p. 420), and those for quadricovalent S^{2+} and quinquecovalent S^+ are 1.030 Å and 1.075 Å. The respective values of x for use in the Schomaker-Stevenson correction term are 1.6, 1.8, 2.95 and 2.6. The calculated and observed bond lengths are Cu(I)—S_2 = 2.36 (2.34 observed), Cu(I)—S = 2.31 (2.30), and Cu(II)—S = 2.20 (2.19 Å), in excellent agreement.

QUADRICOVALENT TRANSARGONONIC SULFUR

The configurations expected for quadricovalent transargononic sulfur, with nonresonating bonds, :S$\lessgtr$, are those in which the bonds are directed toward four of the five corners of a trigonal bipyramid or a tetragonal pyramid, with the unshared pair occupying a larger solid angle than a shared pair.

Ever since its discovery (Pauling and Hultgren, 1933; also Trojer, 1966), the structure of sulvanite, Cu_3VS_4, has constituted a puzzle. The sulfur atoms form four bonds, directed to one side of the atom; three to copper, at 2.29 Å, and one to vanadium, at 2.21 Å. The angles Cu—S—Cu and V—S—Cu have the values 110° and 72°, respectively. I have pointed out (1965) that there are weak bonds between copper and vanadium atoms in this crystal, as an explanation of its unusual structure, and that the bond lengths calculated for argononic sulfur (Cu—S = 2.37 Å, V—S = 2.27 Å) are larger than those observed. This discrepancy is eliminated by assigning the quadricovalent transargononic structure to the sulfur atom, with R = 1.08 Å. The V—Cu bonds have bond number 1/3 (from equation 2), leading to covalence 6 for V(V^-, R = 1.186 Å) and 4 2/3 for Cu(R = 1.192 Å), and to calculated bond lengths Cu—S = 2.24 Å, V—S = 1.21 Å. The observed values indicate some contribution also of the argononic structure. For a crystal of this sort, for which two alternative structures have about the same stability, a hybrid structure that gives nearly zero charge to the atoms is to be expected. The structure based on tercovalent S^+ leads, with consideration of the ionic character of the bonds, to the charge +0.4 on the sulfur atom, and that based on quadricovalent transargononic S^0 to −0.4; accordingly, the two structures may be expected to make about equal contributions.

Structures in which the sulfur atom is tetraligated and one-sided (bonds in one hemisphere, leaving room for the unshared electron pair of :S$\lessgtr^+$) have been reported for only a few sulfide minerals. One example, in addition to sulvanite, is mackinawite, FeS (Berner, 1962). The tetragonal mineral has been assigned the B10 (anti-PbO) structure, in which there are layers SFeS, iron having tetrahedral ligation to sulfur and sulfur having square pyramidal ligation, appropriate to transargononic quadricovalent S^0. As for sulvanite, we may expect about equal contributions of this structure and the structure based on tercovalent argononic S^+. The calculated values of the Fe—S bond length for the two structures (R for iron 1.170 Å; Fe also forms four Fe-Fe bonds with length 2.60 Å, bond number 0.37) are 2.21 Å and 2.22 Å; the reported bond length is 2.23 Å.

Structures for many sulfides that do not occur as minerals have been reported in which sulfur forms four bonds directed to one side, leaving room for the unshared pair of the sulfur atom. There is little doubt that these sulfides, too, have transargononic structures, as suggested by Franzen (1966).

PYRITE AND MARCASITE

From among the many other sulfide minerals that might be discussed I select pyrite and marcasite.

The structure of pyrite, including a rough determination of the sulfur parameter, was first described by W. L. Bragg (1914), in the paper in which the structures of hauerite, sphalerite, fluorite, calcite, rhodochrosite, chalybite, and soda niter were also reported. The sulfur parameter was then accurately determined, by the comparison of the relative intensities of reflections hkl and khl on symmetric Laue photographs, by Ewald and Friedrich (1914). Their parameter value leads to the bond lengths S—S = 2.10 ± 0.01 Å and Fe—S = 2.27 ± 0.01 Å. Later investigators have reported approximately the same values. The iron atom has ligancy 6, and each sulfur atom has ligancy 4 (one S and 3 Fe). Marcasite has an orthorhombic structure in which the ligancies are the same as in pyrite.

Huggins (1922) assigned argononic structures to pyrite and marcasite (sexicovalent Fe^{4-} and quadricovalent S^{2+}). It is evident, however, that this assignment has to be revised, as has been pointed out long ago by Buerger (1937).

I take this opportunity to extend a belated apology to Professor M. J. Buerger, in which Dr. Maurice L. Huggins also joins. Long ago (Pauling and Huggins, 1934) we attempted to extend and refine a set of covalent radii that had been formulated by Huggins (1926). We were led to accept 2.08 Å for the S—S single-bond length, and in a table we listed the value 2.25 Å reported by Buerger (1931) for marcasite with the comment "Parameters probably inaccurate." Professor Buerger, to whom we are all indebted for his structure determinations of many sulfide minerals as well as other important contributions to min-

eralogy, was more skeptical about simple theoretical arguments than we were; he carried out a second careful investigation of marcasite, with very nearly the same result: he found S—S = 2.210 Å. I agree that this value shows clearly that the sulfur atom does not have an argononic structure in marcasite.

The increase in the S—S bond length over the argononic value 2.06 Å indicates a transargononic structure. A structure based on quadricovalent transargononic S^0 and sexicovalent Fe^0 is reasonable, in that the iron atom in metallic iron is sexicovalent and neutral. The radius 1.08 Å that we have assigned to quadricovalent S^0 is a little smaller than that indicated by the S—S bond length in marcasite. It is likely, as has been suggested for other crystals (Pauling and Soldate, 1948), that the amount of d character of the sulfur bond orbitals is different for the S—S bond and the S—Fe bonds.

For both pyrite and marcasite a hybrid structure is to be assigned, with more argononic character for pyrite and more transargononic character for marcasite. This difference in hybrid character is correlated with the larger amount of room for the unshared electron pair of transargononic sulfur in marcasite. Bond lengths greater than the argononic values are also found for As—S, Sb—S, As—As, and other complexes in minerals with the marcasite structure, showing that in these minerals the electronegative atoms have some transargononic character.

CONCLUSION

The foregoing discussion of the structures of some sulfide minerals, especially the observed bond lengths and bond angles, leads to the conclusion that the sulfur atom may have either an argononic or a transargononic structure with formal charge 0, +1, or (argononic only) +2, sometimes with resonance between two structures. Ligancy 2 and bond angle 100° to 110° indicate bicovalent argononic S^0, and ligancy 3 and angles 100° to 110° indicate tercovalent argononic S^+. Ligancy 4 indicates argononic S^{2+} if the bonds are tetrahedrally directed, and transargononic S^0 if they are one-sided (leaving room for the unshared electron pair). Quinquecovalent S^+ (trigonal bipyramid) and sexicovalent S^0 (octahedron, trigonal prism) are also found. In some minerals the bond lengths resonate among alternative positions, as in metals, leading to bond numbers less than 1, and to bond lengths greater than expected for single covalent bonds. A positive formal charge for sulfur is stabilized by the back transfer of negative charge corresponding to the partial ionic character of the bonds to the metal atoms, which have smaller electronegativity than the sulfur atom. For argononic sulfur the chemical formula of the mineral corresponds to the normal valences (As_2S_3, Cu_3AsS_3, PbS, etc.), whereas for transargononic sulfur it may show deviations ($Cu_{12}As_4S_{13}$, etc.).

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