INTERNATIONAL ATOMIC WEIGHTS, 1917 (*continued*).

	Symbol.	Atomic weight.		Symbol.	Atomic weight.
Indium	In	114.8	Rubidium	Rb	85.45
Iodine	I	126.92	Ruthenium	Ru	101.7
Iridium	Ir	193.1	Samarium	Sa	150.4
Iron	Fe	55.84	Scandium	Sc	44.1
Krypton	Kr	82.92	Selenium	Se	79.2
Lanthanum	La	139.0	Silicon	Si	28.3
Lead	Pb	207.20	Silver	Ag	107.88
Lithium	Li	6.94	Sodium	Na	23.00
Lutecium	Lu	175.0	Strontium	Sr	87.63
Magnesium	Mg	24.32	Sulfur	S	32.06
Manganese	Mn	54.93	Tantalum	Ta	181.5
Mercury	Hg	200.6	Tellurium	Te	127.5
Molybdenum	Mo	96.0	Terbium	Tb	159.2
Neodymium	Nd	144.3	Thallium	Tl	204.0
Neon	Ne	20.2	Thorium	Th	232.4
Nickel	Ni	58.68	Thulium	Tm	168.5
Niton (radium emanation)	Nt	222.4	Tin	Sn	118.7
Nitrogen	N	14.01	Titanium	Ti	48.1
Osmium	Os	190.9	Tungsten	W	184.0
Oxygen	O	16.00	Uranium	U	238.2
Palladium	Pd	106.7	Vanadium	V	51.0
Phosphorus	P	31.04	Xenon	Xe	130.2
Platinum	Pt	195.2	Ytterbium (Neoytterbium)	Yb	173.5
Potassium	K	39.10	Yttrium	Yt	88.7
Praseodymium	Pr	140.9	Zinc	Zn	65.37
Radium	Ra	226.0	Zirconium	Zr	90.6
Rhodium	Rh	102.9			

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORIES OF THROOP COLLEGE OF TECHNOLOGY, NO. 3.]

THE CRYSTAL STRUCTURE OF CHALCOPYRITE DETERMINED BY X-RAYS.

BY CHARLES L. BURDICK AND JAMES H. ELLIS.

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Introduction.

This investigation of the atomic structure of crystals of chalcopyrite ($CuFeS_2$) was undertaken, as no study of a complex sulfide by the method of X-rays had previously been carried out. Moreover, comparatively few crystals of the tetragonal system in which chalcopyrite crystallizes, have been examined, the only ones being certain oxides (rutile, anatase, cassiterite, zircon) of the formula MO_2 studied by Vegard[1] and by Williams.[2] Yet the determination of the structure of crystals belonging to other than the isometric system is likely to throw most light on the funda-

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[1] *Phil. Mag.*, **32**, 65, 505 (1916).

[2] *Proc. Roy. Soc. London*, **93**, 418 (1917).

mental factors involved, such as the interatomic forces and the size and shape of the atoms themselves.

This research was carried out at the suggestion of A. A. Noyes with the aid of a grant made to him by the Carnegie Institution of Washington, for which we wish to express our indebtedness.

Description of the Apparatus and Procedure.

The method employed was in principle the same as that described by W. H. and W. L. Bragg,[1] but the apparatus was modified in several respects.

The electrical equipment for the X-ray excitation consisted of an interrupterless transformer of 20-kilowatt capacity.[2] Tests of several different types of transformers showed that more steady and satisfactory operation is obtained when the transformer is of large capacity and has to deliver only a fraction of its rated output. From our observations it seems also that the closed-core is more satisfactory than the open-core type.

The X-ray tube was provided with a target of specially purified palladium 2 mm. thick, silver-soldered onto a copper block, whose face was set perpendicular to the direction of the cathode rays. With this arrangement the tube could be operated for considerable periods without overheating or fusing the target, and at loads which can be regarded as heavy for this type of work, that is, with currents of 12 milliamperes passing through the tube. In this way it is possible to measure, with considerable accuracy, reflections from small faces or through moderately large thicknesses of crystal which otherwise might be completely overlooked.

The X-ray spectrometer consisted of three slits, of a graduated circle, and of an ionization chamber like that described by W. H. and W. L. Bragg. The electroscope was one of the double-tilted form devised by Bumstead.[3] This is more sensitive and more convenient than the usual Wilson form. One great advantage of the Bumstead type lies in the fact that the electroscope leaf is vertical, enabling the operator to make a long series of readings without fatigue.

The crystal used in this investigation was selected from a number kindly loaned us by C. H. Warren of the Massachusetts Institute of Technology. The crystal which was from French Creek, Pa. was of the sphenoidal type[4] and was approximately 8 mm. on the edges and with faces strongly etched and striated. None of the planes measured were developed as faces on the crystal. The sharpness and general excellence of the reflections obtained indicated it to be a specimen of high perfection. Numerous

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[1] "X-Rays and Crystal Structure," p. 22 (1915).

[2] Purchased from the Campbell Electric Co., of Lynn, Mass.

[3] *Phil. Mag.*, **22**, 907 (1911).

[4] See Dana's "Mineralogy," 1892, p. 81, Fig. 10.

other specimens, to the eye apparently very perfect tetrahedra, gave unsatisfactory and weak reflections; and no significance was attached to the data obtained with them.

The spectra of the different planes were measured in the usual manner. Practically no stray radiation reached the ionization chamber, owing to the purity of the palladium used for the target and to the perfection of the crystal. The stray radiation was probably also diminished by the fact that the rays were reflected, not from faces, but from planes within the crystal.

In determining the angles corresponding to maximum intensity of reflection the opening of the chamber slit was always 1.0 mm.; and in measuring the relative intensities for the different orders the opening was 2.0 mm. The opening of the slit just in front of the crystal was kept at 3 mm.

The correction 2δ which is to be added to the observed "chamber angle" for the spectrum of any order to correct for the variation of the zero reading was computed by the equation

$$\tan \delta = \frac{\sin \beta - 2 \sin \alpha}{2 \cos \alpha - \cos \beta},$$

in which α and β represent half the chamber angles observed for the first and second orders, respectively. This equation follows immediately from the fundamental equation of reflection $n\lambda = 2d \sin \theta$, by substituting for θ the values $\alpha + \delta$ and $\beta + \delta$, and solving the two equations for δ.

The chamber angles were commonly determined with an accuracy of about 5 minutes of arc.

Summary of the Observations.

The following table summarizes the observations. The significance of the calculated angles and intensities will be described below.

TABLE I.—SUMMARY OF THE OBSERVED AND CALCULATED RESULTS.

Crystal plane.	Order of reflection.	Chamber angle.		Angle of reflection.		Electroscope deflection.	Ratio of intensities.	
		Obs.	Cor.	Obs.	Calc.		Obs.	Calc.
(100)	I	12° 7′	12° 50′	6° 25′	6° 25′[1]	5.5	100	100
	II	25° 7′	25° 50′	12° 55′	12° 55′[1]	9.0	164	217
(001)	I	12° 22′	13° 4′	6° 32′[2]	6° 32′	13.0	100	100
	II	25° 35′	26° 18′	13° 9′	13° 8′	33.5	256	222
(111)	I	10° 37′	11° 4′	5° 32′	5° 35′	40.9	100	100
	II	21° 47′	22° 14′	11° 7′	11° 14′	6.5	13	3
	III	32° 45′	33° 6′	16° 33′	16° 58′	4.0	8	7
$(11\bar{1})$	I	10° 7′	11° 22′	5° 41′	5° 35′	69.0	100	100
	II	21° 37′	22° 52′	11° 26′	11° 14′	10.0	14	3

[1] These values were used to compute the remainder of the calculated values.

[2] The atomic structure which is deduced from these observations in the following section would lead one to expect a reflection of slight intensity (8% calc.) at one-half this angle of reflection, but no reflection could be detected at this angle.

TABLE I (*continued*).

Crystal plane.	Order of reflection.	Chamber angle.		Angle of reflection.		Electroscope deflection.	Ratio of intensities.	
		Obs.	Cor.	Obs.	Calc.		Obs.	Calc.
(110)	I	19° 0′	18° 14′	9° 7′	9° 6′	190.0	100	100
	II	37° 42′	36° 56′	18° 28′	18° 27′	45.0	24	20
	III	56° 30′	55° 44′	27° 52′	28° 19′	11.0	11.6	7
$(1\bar{1}0)$	I	18° 29′	18° 8′	9° 4′	9° 6′	61.0	100	100
	II	37° 8′	36° 46′	18° 23′	18° 27′	29.0	47	20
(101)	I	17° 55′	18° 14′	9° 7′	9° 10′	200.0	100	100
	II	36° 40′	36° 58′	18° 29′	18° 35′	50.0	25	20
	III	56° 30′	56° 50′	28° 25′	28° 32′	9.0	4.5	7

Interpretation of the Results.

In determining the atomic structure of chalcopyrite, we will first attempt to fix the type of lattice on which it is constructed. For approximate purposes its crystals may be regarded as isometric, since the axial ratio $a : c$ (1 : 0.985) is nearly unity.

The interplanar distance d (that is, the distance between like planes of atoms) is by the law of reflection inversely proportional to the sine of the angle of reflection ($\sin \theta$). For the three fundamental planes (100, 101, 111) the angles were 6° 25′, 9° 7′ and 5° 32′. The reciprocals of the sines of these angles stand to one another in the ratio 1 : 0.706 : 1.152. The ratios of the interplanar distances in the three possible types of isometric lattice, known as the cubic, the face-centered, and the cube-centered,[1] are, respectively, 1 : 0.707 : 0.573; 1 : 0.707 : 1.146 and 1 : 1.414 : 0.573. The lattice involved in the chalcopyrite crystal is, therefore, obviously the face-centered type, illustrated by Fig. 1; and we may infer that the heavy atoms, which predominate in determining the reflection, must be the points in this lattice.

Since there is only a small difference in the atomic weights of iron and copper, their reflecting powers, like those of potassium and chlorine in potassium chloride,[2] will not be greatly different. It will, therefore, be true that the atoms of iron and copper will be practically indistinguishable in their diffractive effect on the X-rays. The observations then show that the basic lattice formed by the iron atoms must intersect that formed by the copper atoms in such a way as to form together a single face-centered lattice.

A study with the aid of a model of possible arrangements by which two different kinds of atoms, present in equal numbers, could together form a single face-centered lattice shows that there is only one such arrangement, namely, that shown in Fig. 1. It is evident, moreover, from the

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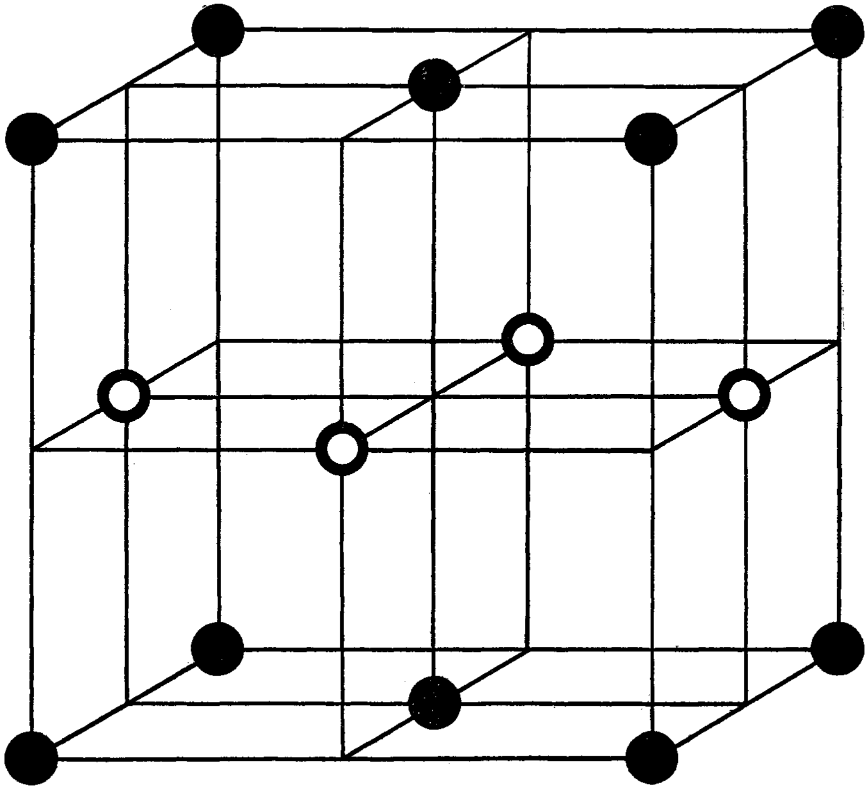
[1] See Tutton's "Crystallography," 1911, p. 501; or Braggs' "X-Rays and Crystal Structure," 1915, p. 91.

[2] Bragg, *Loc. cit.*, p. 94.

symmetries of the atomic arrangements that the vertical axis in the figure corresponds to the tetragonal or *c* axis in the crystal.

These conclusions are corroborated by the fact that the observed angles of reflections agree closely with the "calculated" angles (given in the table), which were computed geometrically from the assumed location of the atoms in the lattice.



COPPER AND IRON ATOMS IN CHALCOPYRITE LATTICE.

Fig. 1.

We may now proceed to determine the location of the sulfur atoms, which can be done with the aid of the intensity measurements. It is known that, when the reflection takes place from only one kind of plane, the first, second, and third order reflections have intensities which stand to one another approximately in the ratios 100 : 20 : 7, commonly called the normal intensity ratios. It is evident, if there be secondary planes of lighter atoms intermediate between the primary planes of heavier atoms giving rise to a given reflection, that the reflection will be diminished or increased in intensity in correspondence with the difference in phase of the two trains of emerging waves. In case the secondary planes of atoms lie midway between the primary planes, there would be a phase-difference of half a wave length for the first order, one wave length for the second order, and $1\,{}^1/_2$ wave lengths for the third order; hence there would result a weakening of the intensity of the first-order and third-order reflections (equal for the two orders) and a strengthening of that of the second order. In case the secondary planes are displaced one-fourth of the distance between the primary planes, there would be a phase-difference of ${}^1/_4$, ${}^1/_2$ and ${}^3/_4$ wave lengths for the three orders, respectively, and, therefore, a small increase in the intensities of the first order and third orders (equal in the two cases) and a relatively large decrease in the second order.

Let us consider now the relative intensities of the different orders for the different planes. We see that for the (100) plane the ratio of the observed intensities of the first and second orders has the value 100 : 164, in place of the normal one 100 : 20. This large relative weakening of the first order and strengthening of the second order shows that planes of sulfur atoms are located not far from midway between the (100) planes of iron and copper atoms. The reflections from the (001) plane show a similar reversal of the normal ratio, and lead to the corresponding conclusion that planes of sulfur atoms are located also not far from midway between the (001) planes of iron and copper atoms. The form and location of the lattice of sulfur atoms becomes thereby fixed, if we consider in addition that the number of sulfur atoms is equal to the number of iron and copper atoms. In Fig. 1 a sulfur atom would be located at the center of each alternate cube (that is, in four of the eight cubes there represented), in the way shown in Fig. 2.

This conclusion is confirmed by the observations of the reflections from the other planes. The geometrical relations show that this location of the sulfur atoms involves that they lie in the (110) and (101) planes of the iron and copper atoms; and that there are planes of sulfur atoms in the (111) position displaced one-fourth of the interplanar distance between the composite planes of iron and copper atoms. Correspondingly, the (110) and (101) planes show the normal ratios of intensities of the reflections for the first, second, and third orders; and the (111) plane shows the required decrease of the second-order reflection, and the expected normal ratio of the first-order and third-order reflections.

The relative intensities of the different orders can be calculated from the principle that the intensity of reflection from a plane of atoms is proportional to the square of the mass per unit area.[1] Thus, the intensity of reflection from the (111) sulfur-atom plane will be to that from the (111) composite iron-copper atom plane as $(2 \times 32)^2 : (56 + 63.6)$,[2] since there are two atoms of sulfur in an area equal to that in which there

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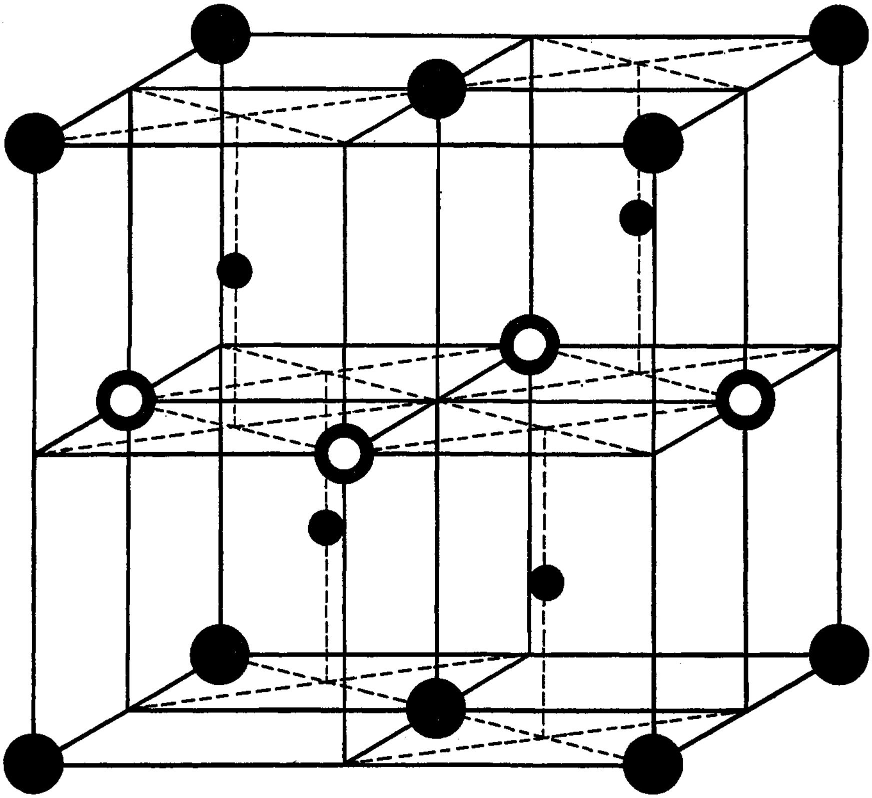
[1] See Bragg, *Loc. cit.*, pp. 120:127.

is one atom of iron and one atom of copper. The intensity of the resultant reflection will evidently be dependent both on the magnitudes of these two-component reflections, and on the difference in phase in which they emerge. The algebraic expression for the resultant intensity I_n of the nth order reflection can be shown to be



SPACE LATTICE OF CHALCOPYRITE.

Fig. 2.

$$I_n = K_n(m_1^2 + m_2^2 + 2m_1m_2 \cos 2\pi nx),$$

in which m_1 and m_2 represent the masses per unit area in the primary and secondary atom planes, x is the fraction of the distance between the primary planes by which the secondary planes are displaced, and K is a constant which has the relative values 100 for the first order, 20 for the second order, and 7 for the third order, these three values corresponding as above stated to the normal ratios of intensities of the three orders (that is, to the ratios when the reflection takes place from a single kind of plane).

The "calculated" ratios of intensities given in the above table were obtained by computing for each plane by this equation the values of I_n for each order, and multiplying their ratio by such a factor as will make the intensity of the first order 100. It will be seen that there is a striking parallelism between the calculated and observed intensities.

Finally we may further test the correctness of the deduced atomic structure of chalcopyrite by calculating the density of the substance and comparing it with the known density. Referring to Fig. 2 it is seen that the space which it represents has associated with it two iron atoms, two copper atoms, and four sulfur atoms, or 2 of the atom groups $CuFeS_2$. Since the mass of the hydrogen atom[1] is 1.64×10^{-24} g., that of these two $CuFeS_2$ groups is, therefore, $2 \times 183.6/1.008$ times as great, or 5.972×10^{-22} g. The volume of the space in question is, however, equal to $8d^3 \times 0.985$, where d represents the distance between the 100 planes of copper-iron atoms (that between the 001 planes being 0.985 d). This distance d may be obtained from the law of reflection $\lambda = 2d \sin \theta$ by substituting for θ the observed angle of reflection (6° 25′) for the (100) plane, and by substituting for λ its value 0.584×10^{-8} cm. as determined by W. L. Bragg for a palladium target.[2] The value of d is thus found to be 2.614×10^{-8} cm., and that of the volume in question 1.407×10^{-22} cm. The calculated density is, therefore, 5.972/1.407, or 4.24. The density of the mineral chalcopyrite according to the best determinations, lies between 4.1 and 4.3. That of the specimen used in this investigation is 4.19.

Summary.

In this article have been presented measurements of the angles of reflection of X-rays from the main planes of a crystal of chalcopyrite ($CuFeS_2$), which belongs to the tetragonal system and has the axial ratios 1 : 1 : 0.985. The results show that the iron and copper atoms are located so that they together form a face-centered tetragonal lattice (as illustrated in Fig. 1), the planes perpendicular to the tetragonal axis being made up alternately of copper atoms alone and of iron atoms alone.

Measurements of the relative intensities of the first, second, and third order reflections were also made, and the results interpreted. They show that the sulfur atoms are located (as shown in Fig. 2) on an exactly similar face-centered lattice with the planes of sulfur atoms lying midway in all three of the axial directions between the planes of iron and copper atoms.

From the weights of the atoms and from the distances between the atom planes derived from the angles of reflection the density of chalcopyrite was calculated, and found to be 4.24; while the densities recorded in the literature lie between 4.1 and 4.3.

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[1] Bragg, *Loc. cit.*, p. 110.

[2] Kaye, "X-Rays," 1917, p. 226.