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Symmetry of Magnetic Structures: Magnetic Structure of Chalcopyrite*

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The transformation properties of magnetic moments under symmetry and antisymmetry operations lead to 1421 possible space groups for ferromagnetic and antiferromagnetic crystal structures. A systematic procedure for magnetic structure determination is proposed, which takes into account the restrictions imposed on spin directions by space groups. This method is applied to chalcopyrite, $CuFeS_2$, which is found to be antiferromagnetic at room temperature: the chemical structure is that proposed by Pauling and Brockway, the space group $I\bar{4}2d$ holds for the magnetic structure, in which the two iron (and possibly also the two copper) atoms tetrahedrally bonded to a common sulfur atom have antiparallel spins directed along the c axis. A value of $3.85\,\mu_B$ is found for the iron moment ($0\pm0.20\,\mu_B$ for copper). The possible existence of a second chalcopyrite modification in nature, suggested by conflicting results on material of Japanese origin, is ruled out, as specimens from both Ugo, Japan and Joplin, Missouri are found to have the same structure.

SYMMETRY CONSIDERATIONS

In the last few years Russian crystallographers and mathematicians[1] have worked out the extension of the 230 symmetry space groups to include the operations of antisymmetry. They enumerated 1651 groups, which they call the Shubnikov groups: 230 uncolored, 1191 black-and-white, and 230 gray. The possible usefulness of these groups in the study of magnetic crystal structures has been mentioned.[2] Dzyaloshinsky[3] has applied point groups of extended symmetry[4] to study the magnetic structures of Cr_2O_3 and α-Fe_2O_3. As far as we know, no actual application of space groups to magnetic structure determinations has been published with the exception of an abstract,[5] which discussed the application of symmetry space groups to Cr_2O_3 and to chalcopyrite.

Structures possessing aligned, but not necessarily collinear, magnetic moments may be described in terms of the 230 uncolored and the 1191 black-and-white space groups; the 230 gray groups are applicable to paramagnetic crystals. The change of color that characterizes an operation of antisymmetry is here replaced by the reversal, R, of spin direction to be combined with the corresponding symmetry operation. The operation, "identity combined with R," is allowed only in the 230 gray groups; it does not occur in black-and-white groups. The transformation properties of magnetic moments differ from those of black and white objects so that the positions available in a given space group may be different for the two cases. Thus, a magnetic atom can be placed on a twofold antiaxis provided its spin is perpendicular to the antiaxis, although such an atom in the corresponding black-and-white space group would be gray. (Not every gray atom can be interpreted as an atom with zero spin.)

The effects of symmetry and antisymmetry operations on magnetic moments are summarized in Fig. 1. Following Belov's convention[1] an element of antisymmetry will be designated by a primed symbol. A magnetic atom can be placed on any rotation axis, provided its spin is directed along the axis, but only on an antiaxis $2'$, in which case the spin must be perpendicular to the antiaxis. Screw axes and screw antiaxes are not subject to such restrictions. A magnetic atom cannot be placed on an anticenter or at the inversion point of an antiaxis of rotatory inversion. A magnetic atom can be placed on such an axis, though not at the inversion point, provided its moment is parallel to the axis. Note that the antiaxis $3'$, of order 6, leads to three atoms with zero spin when it operates on a magnetic atom, so that $3'$ cannot be included as a possible antielement of magnetic groups. (The same restriction applies to black-and-white groups.) Only magnetic atoms in general positions can carry spins that are neither parallel nor perpendicular to symmetry directions. Such atoms will produce generalized ferromagnetic or antiferromagnetic structures, which may contain noncollinear spins.

The problem of placing magnetic moments in a ferromagnetic or antiferromagnetic crystal structure previously determined by x-rays can be attacked in two ways. One can proceed without utilizing the fact that magnetic moments are subject to either symmetry or antisymmetry operations and assume arbitrary spin directions consistent with the macroscopic magnetic

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[1] A. M. Zamorzaev, dissertation, Leningrad, 1953 (unpublished); Belov, Neronova, and Smirnova, Trudy Inst. Krist. Akad. Nauk S.S.S.R. **11**, 33 (1955); Kristallografiya **2**, 315 (1957).

[2] A. L. Mackay, Acta Cryst. **10**, 543 (1957).

[3] I. Dzyaloshinsky, J. Phys. Chem. Solids **4**, 241 (1958).

[4] B. A. Tavger and V. M. Zaitsev, J. Exptl. Theoret. Phys. U.S.S.R. **30**, 564 (1956) [translation: Soviet Phys. JETP **3**, 430 (1956)].

[5] Donnay, Corliss, Hastings, and Donnay, Abstracts of the American Crystallographic Association Meeting, Pittsburgh, Pennsylvania, November 6–8, 1957 (unpublished).

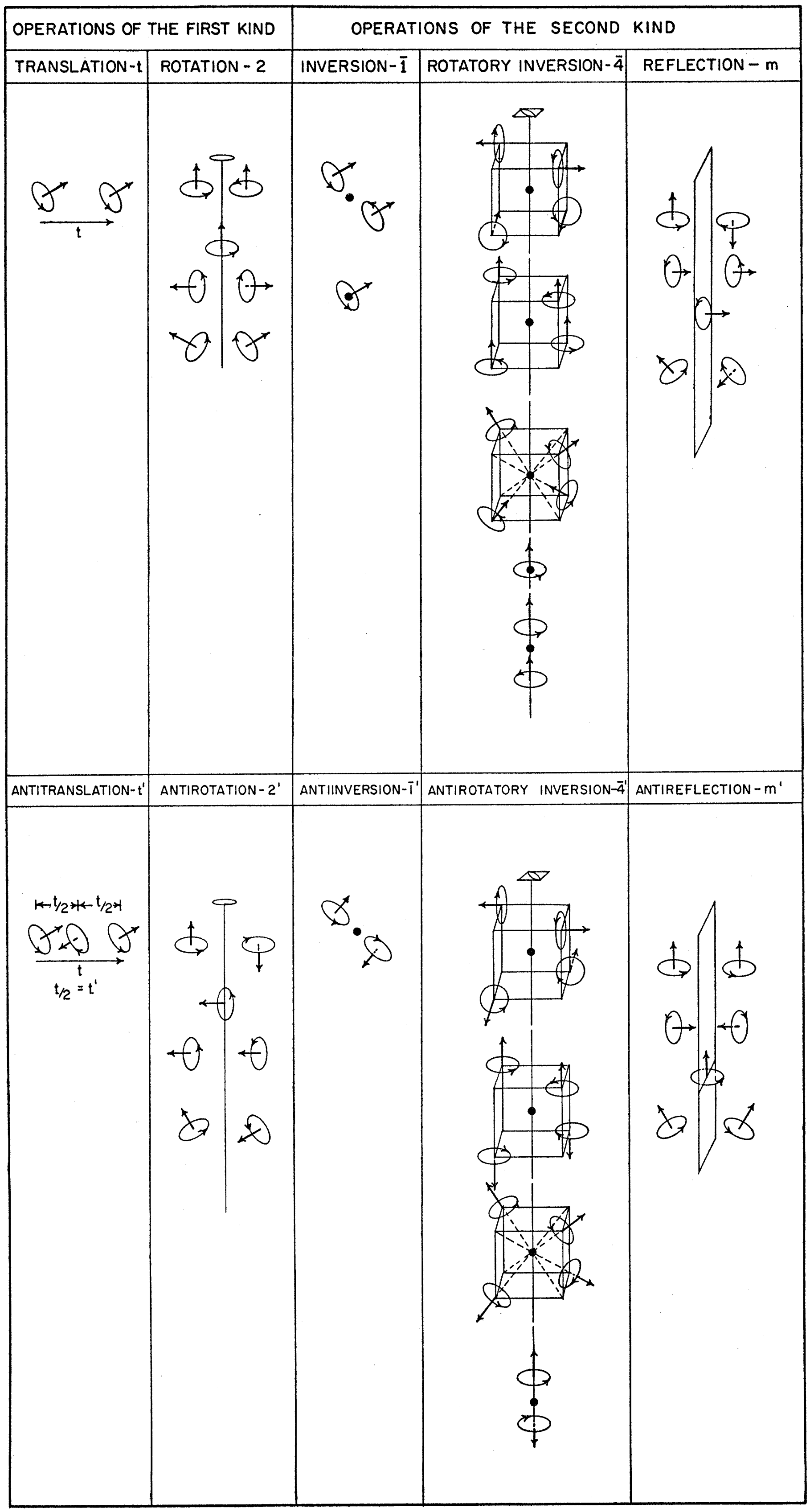

FIG. 1. Effects of symmetry and antisymmetry operations on magnetic moments. A symmetry operation of the first kind transforms a magnetic moment as if it were a polar vector; an operation of the second kind reverses the sense of the vector. An antisymmetry operation requires an additional reversal of sense.

state. It follows (Fig. 1) that all symmetry elements present in the chemical cell are lost, except in the fortuitous case where the spin happens to be exactly parallel or perpendicular to a symmetry direction. The resulting space group of the crystal becomes $P1$. Although the deviations of atomic coordinates from the special values assigned to them in the chemical structure may be so slight as to be undetectable by x-ray diffraction, we must nevertheless rewrite the coordinates so as to indicate that they refer to general onefold positions in space group $P1$. For example, a magnetic atom which appeared to be on a special position in the chemical structure, at $\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{4}$, say, will now have to be considered as lying at $0.25+\Delta x$, $0.25+\Delta y$, $0.25+\Delta z$. For a cell that contains N atoms, $3N$ positional parameters must be refined, quite apart from the directional parameters of the magnetic moments. This procedure is unsatisfactory for complex structures and may even present difficulties in simple structures.

Alternatively one may recognize that magnetic moments are subject to symmetry and antisymmetry operations. It is then possible to follow a systematic procedure in the determination of magnetic structures by starting with a spin distribution that obeys the highest possible symmetry (minimum number of parameters) compatible with the chemical space group and neutron diffraction data. The latter, when differing from the x-ray data, are used to determine the size of the magnetic cell, its symmetry, and its diffraction aspect. In determining the lattice type it should be noted that the Shubnikov groups are based upon 36 lattices: the 14 classical Bravais types and 22 additional lattices containing both translations and antitranslations. The latter always lead to a cell which is a multiple of the x-ray cell and produce additional lattice extinctions depending on the mode of anticentering. Anticentering of an edge (P_s) requires the corresponding index to be odd; anticentering of one face (P_C) introduces the condition that the sum of the appropriate pair of indices be odd; anticentering of the cell (P_I) requires the sum $(h+k+l)$ to be odd. (These indices refer, of course, to the magnetic cell.) The extinction rules needed to derive the remainder of the diffraction aspect are not necessarily the same for magnetic reflections as for nuclear (or x-ray) reflections, since in the case of the former they depend on the relation of spin directions to symmetry directions.

An an example, consider a magnetic atom in general position in the monoclinic space group $P2_1/m$. The x-ray and nuclear reflections $0k0$ with k odd are absent. A pair of magnetic moments related by a twofold screw axis gives rise to scattered intensity[6] proportional to

$$|\mathbf{F}|^2=2(1\pm\boldsymbol{\kappa}_1\cdot\boldsymbol{\kappa}_2)-(\mathbf{e}\cdot\boldsymbol{\kappa}_1\pm\mathbf{e}\cdot\boldsymbol{\kappa}_2)^2,$$

where the + and − signs refer to the conditions k even and k odd, and where $\boldsymbol{\kappa}_1$ and $\boldsymbol{\kappa}_2$ are unit vectors in the direction of the moments and $\mathbf{e}$ is the scattering vector. For the case of $0k0$ reflections and moments perpendicular to the symmetry axis, we have $\mathbf{e}\cdot\boldsymbol{\kappa}_1=0$, $\mathbf{e}\cdot\boldsymbol{\kappa}_2=0$, $\boldsymbol{\kappa}_1=-\boldsymbol{\kappa}_2$. This requires that magnetic reflections vanish only for k even. If, however, the spins are parallel to the symmetry axis, $\boldsymbol{\kappa}_1=\boldsymbol{\kappa}_2$ and $\mathbf{e}\cdot\boldsymbol{\kappa}_1=\mathbf{e}\cdot\boldsymbol{\kappa}_2=1$ and $F^2=0$ for both k even and k odd. Thus, in this case the extinction ($0k0=0$ for k odd) produced by the screw axis is obscured by the more general restriction imposed by the special nature of magnetic scattering; namely, the magnetic intensity vanishes when the moments are directed parallel to the scattering vector.

The chemical space group, or its most symmetrical subgroup, compatible with the magnetic diffraction aspect, is the first space group to try. A look at the point symmetries of sites in this space group, as listed in the *International Tables for X-ray Crystallography*, tells us whether the atoms presumed to be responsible for the magnetic effect, are indeed in positions that can be occupied by magnetic moments. (Only sites whose point symmetry is a subgroup of ∞/m, the symmetry of the axial vector, can accommodate magnetic atoms.[5]) The spin must be directed along the symmetry direction. Thus, provided the magnitudes of the magnetic moments are known, only one or a few magnetic structures have to be tested in the chemical space group.

If the agreement of structure factors is not satisfactory, the next step is to try the antigroups derivable from the chemical space groups[1] and permitted by the magnetic diffraction aspect. (There are as yet no *International Tables* available for these groups, so that they must be worked out individually.) Only after all these possibilities have been ruled out does one proceed to the next lower space group permitted by the diffraction aspect. Additional positional parameters are thus introduced that may be varied to improve the agreement within the limits of accuracy of the x-ray structure determination. We have successfully applied this procedure to the cases of CrN and $CuFeS_2$. The latter is discussed below.

In many cases the crystal structure is known only above a magnetic transition and is therefore almost certain to differ in detail from the structure of the magnetic phase in which one is interested. When the material is available only in powder form, it is often impossible to determine with certainty any change in the lattice and space group of the chemical structure, but the appearance of magnetic reflections may clearly necessitate the enlargement of the cell. In such a case one must consider two possibilities. (1) The chemical cell has remained unchanged and the magnetic space group is based on an antilattice; this space group will be chosen so as to admit atomic positions close to those found above the transition. (2) The chemical cell has become enlarged and is equal to the magnetic cell, so

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[6] This formula is derived from the general expression for magnetic scattering [Corliss, Hastings, and Brockman, Phys. Rev. **90**, 1013 (1953)]: $|\mathbf{F}|^2=|\mathbf{K}|^2-(\mathbf{e}\cdot\mathbf{K})^2$, where $\mathbf{K}=\Sigma\boldsymbol{\kappa}_i e^{2\pi i(hx_i+ky_i+lz_i)}$, by substitution of the coordinates xyz and $\bar{x}$, $y+\frac{1}{2}$, $\bar{z}$.

that the magnetic space group is based on a classical Bravais lattice.

EVIDENCE FOR ANTIFERROMAGNETISM IN CHALCOPYRITE

Previous studies of antiferromagnetic compounds involving tetrahedral coordination of magnetic atoms about an anion have shown that the local magnetic structure is consistent with an indirect exchange coupling mechanism. Additional examples of such structures were sought in order to study the effect of tetrahedral bonding and covalency on the interaction of magnetic atoms. The appearance of antiferromagnetism in the zincblende and wurtzite forms of MnS suggested that chalcopyrite, $CuFeS_2$, might also prove to be antiferromagnetic.

Measurements of the magnetic susceptibility were carried out by the Gouy method. Between 77°K and room temperature the susceptibility was found to be low, with a small positive temperature coefficient. Above room temperature the susceptibility increased more rapidly with increase in temperature, but was not completely reversible. The dependence on thermal history may have been caused by chemical reaction with impurities present in the sample.[7] While the evidence for antiferromagnetism obtained from these measurements is not entirely conclusive, confirmation was obtained from the presence of strong additional reflections in the neutron diffraction powder patterns. This evidence will be detailed in the discussion of diffraction data obtained by neutrons and x-rays.

CHEMICAL STRUCTURE OF CHALCOPYRITE

The crystal structure of chalcopyrite $CuFeS_2$ was first determined in 1917 by Burdick and Ellis.[8] It was the first structure to be determined in the U.S.A. and the first structure of a "complex sulfide." The crystal used came from French Creek, Pennsylvania; it was studied with Pd radiation and gave the cell dimensions: $a=5.228$ kx), $c=5.15$ kx, $c/a=0.985$. On the basis of the seventeen reflections studied, the structure was reported to be of the ZnS (zincblende) type:

$$\text{At } (0,0,0;\tfrac{1}{2},\tfrac{1}{2},0)+$$
$$2\ \text{Cu}: 0,0,0;$$
$$2\ \text{Fe}: 0,\tfrac{1}{2},\tfrac{1}{2};$$
$$4\ \text{S}: \tfrac{1}{4},\tfrac{1}{4},z;\ \tfrac{1}{4},\tfrac{3}{4},\bar{z},$$

in which z was assumed to be $\frac{1}{4}$. The value of z was changed to 0.21 by Gross and Gross,[9] who used data from Laue patterns.

In 1932 Pauling and Brockway,[10] using Mo radiation, studied a crystal from Joplin, Missouri, by Laue and oscillation techniques. The Laue diagrams showed that the c length had to be doubled: $a=5.24$ kx, $c=10.30$ kx, $c/a=1.97$. The space group $I\bar{4}2d$ was uniquely determined from the diffraction aspect $I{*}{*}d$ (hkl only with sum even; hhl only with half-sum even) and the morphological point group $\bar{4}2m$. The atoms were placed as follows:

$$\text{At } (0,0,0;\tfrac{1}{2},\tfrac{1}{2},\tfrac{1}{2})+$$
$$4\ \text{Cu}: 0,0,0;\ 0,\tfrac{1}{2},\tfrac{1}{4};$$
$$4\ \text{Fe}: 0,0,\tfrac{1}{2};\ 0,\tfrac{1}{2},\tfrac{3}{4};$$
$$8\ \text{S}: x,\tfrac{1}{4},\tfrac{1}{8};\ \bar{x},\tfrac{3}{4},\tfrac{1}{8};\ \tfrac{3}{4},x,\tfrac{7}{8};\ \tfrac{1}{4},\bar{x},\tfrac{7}{8};$$

with $x=0.73\pm0.01$. The PB structure[11] (Fig. 2) differs from that of Burdick and Ellis in the arrangement of copper and iron atoms; it also displaces the sulfur atoms slightly from the centers of the metal tetrahedra toward the Fe–Fe edge (Cu–S$=2.32\pm0.03$ A, Fe–S$=2.20\pm0.03$ A).

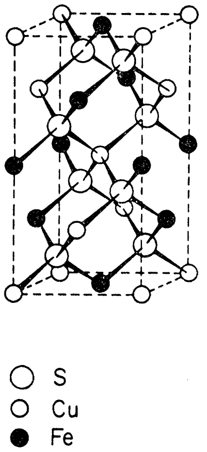

FIG. 2. The crystal structure of $CuFeS_2$ (Pauling and Brockway).

In 1934, Kôzu and Takané[12] studied chalcopyrite from the Arakawa mine, Ugo Province, Japan. They used CuK and MoK radiations to take Laue, oscillation, and rotation patterns. The structure reported was the same as that of Burdick and Ellis, with $a=5.28$ kx, $c=5.22$ kx, $c/a=0.989$, space group $C\bar{4}2m$, and the sulfur parameter z "between 0.25 and 0.26." They state explicitly that they could not confirm the PB structure.

In 1944 Boon[13] re-examined the structure on chalcopyrite from an undisclosed locality. He used CoK

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[7] G. Kullerud (private communication).

[8] C. L. Burdick and J. H. Ellis, Proc. Natl. Acad. Sci. U. S. **3**, 644 (1917); J. Am. Chem. Soc. **39**, 2518 (1917).

[9] R. Gross and N. Gross, Neues Jahrb. Mineral. **48**, 113 (1923).

[10] L. Pauling and L. O. Brockway, Z. Krist. **82**, 188 (1932), hereafter referred to as PB.

[11] The PB structure is here referred to a new set of coordinate axes that can be obtained from the PB axes by the transformation matrix $0\bar{1}0/100/001$. The new axes enable us to use the atomic positions as listed in the *International Tables*. The sulfur parameter $x=0.73$ is related to the PB parameter $u=0.27$ by $x=-u$. In our calculations we set $u=\frac{1}{4}+\epsilon$ so that ϵ indicates the displacement of a sulfur atom from the center of its metal coordination tetrahedron. The value $\epsilon=0.02$ of the PB structure was confirmed by our neutron diffraction work. The matrix $010/\bar{1}00/001$ expresses the PB axes in terms of our axes.

[12] S. Kôzu and K. Takané, Proc. Imp. Acad. Tokyo **10**, 498 (1934).

[13] J. W. Boon, Rec. trav. chim. **63**, 69 (1944).

radiation in order to increase the effective difference in the scattering powers of copper and iron, thereby enhancing the intensities of those reflections to which copper and iron atoms contribute with opposite phases. He confirmed the PB structure.

The conflicting data in the literature left open the possibility that two polymorphic forms of chalcopyrite might be found in nature, especially since Cheriton[14] had claimed the existence of a cubic synthetic high-temperature modification. (The latter has since been confirmed, with $a=5.264\pm0.003$ A, by single-crystal work on $CuFeS_2$ synthesized at 600°C and quenched to room temperature.[15]) X-ray data were therefore obtained on crystals from both localities. A hand specimen from Joplin, Missouri (U. S. National Museum No. R740) was kindly given to us by Dr. George Switzer; the Japanese specimen came from Ugo Province. The cell dimensions, determined from c-axis rotation (CoK radiation) and precession patterns (MoK radiation) are: $a=5.24\pm0.01$ A, $c=10.34\pm0.03$ A for the Joplin crystal and $a=5.32\pm0.01$, $c=10.45\pm0.03$ A for the Ugo crystal, in good agreement with the values previously reported for these localities. Both crystals have diffraction aspect $I{*}{*}d$ and show no significant differences in relative intensities of corresponding reflections. We thus conclude that both localities yield the same form of $CuFeS_2$, the only form found in nature so far, and that the chalcopyrite structure described by Pauling and Brockway is indeed the correct one.

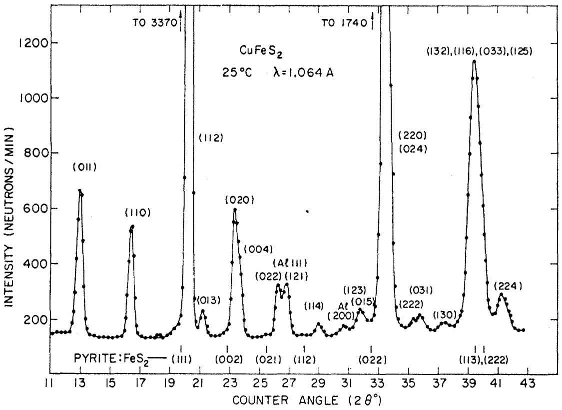

FIG. 3. Neutron diffraction pattern of $CuFeS_2$.

NEUTRON DIFFRACTION DATA

TABLE I. Chalcopyrite from Ugo, Japan. Neutron diffraction data (powder method).

Total I_{obs}	Admixed materials	Chalcopyrite	I_{obs}
987		011	987
676		110	676
5199	$(111)_{pyr}$		140
		112	4903
		013	156
1105	$(002)_{pyr}$		93
		020, 004	1012
825	$(111)_{Al}$		150
	$(021)_{pyr}$		22
		022, 121	569
	$(112)_{pyr}$		21
		114	63
4952	$(200)_{Al}$		87
		123, 015	152
	$(022)_{pyr}$		80
		220, 024	4430
	$(221)_{pyr}$		~ 0
		222, 031	203
4343		130	84
		132, 116, 033, 125	3675
	$(113)_{pyr}$		160
	$(222)_{pyr}$		35
		224	389

Powder patterns were obtained for the Japanese sample of chalcopyrite, which was ground to 200 mesh and packed in a cylindrical aluminum sample holder, 1½ inches in diameter. A typical pattern, taken at room temperature at a wavelength of 1.064 A is shown in Fig. 3. The indexing shown is based upon the chemical cell. Extraneous peaks, besides the aluminum peaks, were recognized as coming from FeS_2 (pyrite). Marcasite was considered and ruled out. The amount of admixed pyrite was determined from a chemical analysis performed by R. Stoenner: S = 35.68, Cu = 33.54, Fe = 30.91, (total 100.13), which leads to the molecular composition $0.95\ CuFeS_2+0.05\ FeS_2$. The observed integrated intensities were corrected for pyrite and aluminum impurity lines as indicated in Table I.

TABLE II. Comparison of calculated and observed structure factors F_{hhl} (single-crystal method).

		F_{obs}	
hhl	F_{calc}[a]	Crystal I (Ugo, Japan)	Crystal II (Joplin, Missouri)
004	220	237	224
008	342	351	348
0.0.12	141	155	157
110[b]	188	184	187
220	397	354	390
330[b]	4	4	0
440	303	295	311
112	393	371	379
224	175	182	175
336	244	236	241
448	295	273	288
222[b]	78	78	
444	144	148	
114[b]	6	6	
228	316	313	315
116	289	298	
2.2.12	142	159	
1.1.10	244	254	
1.1.14	231	246	
226[b]	3	3	
332	260	235	
3.3.10	232	209	

[a] Differences in cell dimensions for the two crystals do not significantly alter the calculated F's.
[b] Purely magnetic reflection.

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[14] C. G. Cheriton, thesis, Harvard University, Cambridge, Massachusetts, 1953 (unpublished).

[15] G. Donnay and G. Kullerud, *Carnegie Institution of Washington Year Book* (Carnegie Institution of Washington, D. C., 1957–1958).

TABLE III. Comparison of calculated and observed intensities I_{hkl} (powder method).

Peaks hkl	$\lvert F\rvert_{\text{calc}}^2$ Nuclear	Magnetic	Total	I_{calc}		kI_{obs} ($k=0.035$)
011	1.3	36.4	37.7	37.7		34.5
110	0	39.8	39.8	24.7		23.7
112	427	0	427	171.8		171.6
013	4.2	9.6	13.8	5.0		5.5
020	78.8	0	78.8	23.7	34.9	35.4
004	38.7	0	38.7	11.2		
022	~0	40.2	40.2	9.5	22.2	19.9
121	9.8	46.8	56.6	12.7		
114	0	14.4	14.4	2.7		2.2
123	4.2	23.5	27.7	4.3	5.3	5.3
015	4.2	2.5	6.7	1.0		
220	345	0	345	48.5	144.7	155.0
024	695	0	695	96.2		
222	0	28.1	28.1	3.5	6.3	7.1
031	8.4	15.2	23.6	2.8		
130	~0	28.1	28.1	3.1		2.9
132	848	0	848	82.8	125.6	128.6
116	427	0	427	40.5		
033	0.1	9.9	10.0	1.0		
125	4.2	10.3	14.5	1.3		
224	160	0	160	13.9		13.6

Single-crystal neutron data were obtained from the same two crystals on which x-ray work was done. Their size was average for neutron work (1–2 mm in largest dimension) but too large for x-ray study so that only a corner of each crystal had been placed in the x-ray beam. The crystals were mounted with $[1\bar{1}0]$ vertical so that the recorded zone includes all the purely magnetic reflections (*hhl* with half-sum odd). Data were obtained at room temperature with a neutron wavelength of 1.07 A (Table II). Enough reflections were recorded with the Joplin crystal to ascertain satisfactory agreement between the data from the two crystals. No reflections within the observable radius happen to be structurally absent. It will be shown below that all magnetic reflections $00l$, $l=4n+2$, have zero F value because of the direction of the magnetic moment.

The tetragonal symmetry of the magnetic structure was checked by mounting the Joplin crystal with [001] vertical and comparing intensities of reflections $hk0$, $\bar{k}h0$, $\bar{h}\bar{k}0$, and $k\bar{h}0$. They were the same within experimental limits of accuracy.

INTERPRETATION OF NEUTRON DIFFRACTION DATA: THE MAGNETIC STRUCTURE

The symmetry of the magnetic structure remains tetragonal as checked by neutron diffraction; all the magnetic reflections can be indexed keeping the cell of the chemical structure; only those *hkl* magnetic reflections are observed for which $(h+k+l)$ is even, and only those *hhl* magnetic reflections for which $(h+\frac{1}{2}l)$ is odd (Tables II and III), so that the diffraction aspect $I{*}{*}d$ of the chemical structure is retained for the magnetic structure. (Note that the *hhl* nuclear reflections obey the x-ray criterion "present only for $(h+\frac{1}{2}l)$ even.") Of the two symmetry space groups compatible with aspect $I{*}{*}d$, namely $I\bar{4}2d$ and $I4md$, the latter is ruled out because it is not isomorphic with point group $\bar{4}2m$, known from morphology, and also because its only fourfold position, which has point symmetry $mm2$, cannot receive a magnetic atom. The antisymmetry space groups compatible with aspect $I{*}{*}d$ are[16]: $I\bar{4}'2'd$ (No. 335), which is ruled out because a magnetic atom cannot be placed at the inversion point of an antiaxis $\bar{4}'$, and $I4'm'd$ (No. 241), which is ruled out both by morphology and because no available positions can accommodate the sulfur atoms. The magnetic space group is thus established as $I\bar{4}2d$.

The Pauling and Brockway structure has only one parameter, that of the nonmagnetic sulfur atoms; it was redetermined to fit the nuclear reflections. As regards the magnetic moments, the point symmetry $\bar{4}$ of the metal sites requires a spin direction parallel with the $\bar{4}$ axis. The glide planes demand that the moments on the four sites occupied by metal atoms of one kind be of the same magnitude and compensate (two must point up, two down). The space group does not tell us which metal carries a magnetic moment: either iron alone, or copper alone, or both, will give antiferromagnetism. The configuration of iron moments relative to the symmetry elements of $I\bar{4}2d$ is shown in Fig. 4.

CALCULATIONS

The intensities of the nuclear reflections were computed for various values of the sulfur parameter, from

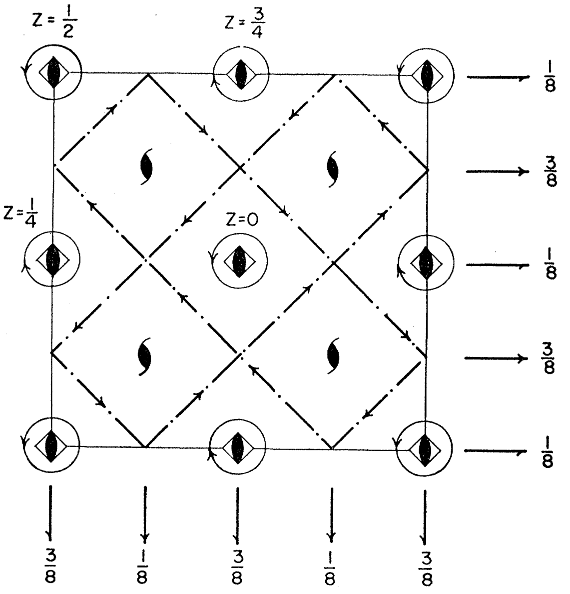

FIG. 4. Relationship of iron moments to symmetry elements of space group $I\bar{4}2d$. Moments, indicated schematically as current loops, are located at the inversion points of the $\bar{4}$ axes and are directed along the c axis. z coordinates give the fractional distances of atoms above the plane of projection. Notation for symmetry elements is that of the *International Tables of Crystallography.*

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[16] Numbers are those of Belov, Neronova, and Smirnova [Kristallografiya 2, 315 (1957)].

$\epsilon=0$ (sulfur atom exactly at the midpoint of the tetrahedron) to $\epsilon=0.040$ in steps of 0.005. The best value of ϵ confirms the PB structure ($\epsilon=0.020$).

The magnetic intensities were first calculated on the assumption that only iron carries a moment. Various values of the iron moment μ_{Fe} were considered, from $5.0\,\mu_B$ to $3.5\,\mu_B$; the best one being $3.85\,\mu_B$. Several f curves were tried and the best agreement was obtained with that for Fe^{3+} on octahedral sites in $\mathrm{ZnFe_2O_4}$, previously published.[17] Integrated intensities were corrected for temperature using the value $B=1.20$.

For the single-crystal data, calculated and observed structure factors $F(hhl)$ are compared in Table II; the residual $R=\sum\big||F_{\mathrm{obs}}|-|F_{\mathrm{calc}}|\big|/\sum|F_{\mathrm{obs}}|$ is 0.044 for the 34 *hhl* reflections. A comparison of calculated and observed intensities for the powder data is given in Table III; the residual, calculated for the intensities rather than the structure factors, is 0.040 for the 13 observed reflections.

If a moment is placed on the copper, two possibilities are open for a given arrangement of iron moments: either the copper moment is positive at $0, 0, 0$; $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ (and consequently negative at $0, \frac{1}{2}, \frac{1}{4}$; $\frac{1}{2}, 0, \frac{3}{4}$) or these signs are reversed. In either case the agreement between calculated and observed values cannot be improved so that, within the limits of accuracy of our neutron diffraction data, it is impossible to prove the existence of a copper moment. On the other hand, the agreement will not be appreciably impaired by the addition of a copper moment provided the latter is $0.2\,\mu_B$ or less.

DISCUSSION OF THE MAGNETIC STRUCTURE

The atoms in $\mathrm{CuFeS_2}$ form a network in which each metal atom is connected through approximately tetrahedral linkages to four sulfur atoms and in which each sulfur atom is similarly bonded to a pair of iron atoms and a pair of copper atoms. The antiferromagnetic structure consists of an arrangement in which the two iron atoms connected to a common sulfur atom have oppositely directed moments. If we admit the possibility of a small moment ($\leq 0.2\,\mu_B$) for the copper, the same magnetic arrangement is obtained for the copper substructure. In its magnetic structure $\mathrm{CuFeS_2}$ closely resembles the zincblende form of MnS. If, in the latter structure, we delete those magnetic moments corresponding to the copper sites in $\mathrm{CuFeS_2}$, we obtain the antiferromagnetic structure observed for $\mathrm{CuFeS_2}$. This relationship is shown in Fig. 5. In MnS each sulfur is tetrahedrally bonded to four metal atoms which are pairwise antiparallel, and one cannot say *a priori* whether the indirect exchange interaction between a pair of metal atoms is ferromagnetic or antiferromagnetic. The evidence provided by the magnetic structure of $\mathrm{CuFeS_2}$ strongly suggests that this interaction is antiferromagnetic.

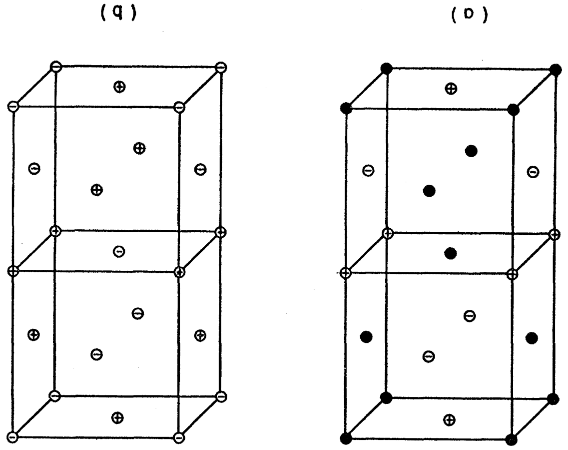

FIG. 5. Magnetic structures of (a) $\mathrm{CuFeS_2}$ and (b) the zincblende form of MnS. Sulfur atoms have been omitted and the relative orientations of magnetic moments have been designated by + and − signs. In (a) the copper atoms are represented by the solid circles. The magnetic moments are directed along the c axis.

Since the results of the structure analysis indicate that the moment for copper is zero or at most $0.2\,\mu_B$, one is led to assume valence one for copper and valence three for iron. These values are consistent with a simple covalent model in which each atom in the structure is bonded to its nearest neighbors by means of four sp^3 hybrid orbitals. The observed iron moment however is $3.85\,\mu_B$, which is less than the $5\,\mu_B$ to be expected for trivalent iron and which therefore cannot be explained by this simple model. The bonding scheme is undoubtedly more complex. Qualitatively we may explain the discrepancy in the iron moment by postulating further participation of the $3d$ electrons of iron in the covalent bonding. This would be expected to decrease the iron moment and at the same time to strengthen the iron-sulfur bonds. This idea is supported by the fact that the sulfur atoms are displaced from the centers of the metal tetrahedra towards the iron atom pairs.

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[17] Brockhouse, Corliss, and Hastings, Phys. Rev. 98, 1721 (1955). See Fig. 7.