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CRYSTAL STRUCTURES OF THE CHALCOPYRITE SERIES*

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ABSTRACT

A comparison of the crystal structures of the minerals chalcopyrite, $CuFeS_2$ (Hall & Stewart 1973), talnakhite, $Cu_9Fe_8S_{16}$ (Hall & Gabe 1972), mooihoekite $Cu_9Fe_9S_{16}$ (Hall & Rowland 1974) and haycockite $Cu_4Fe_5S_8$ (Rowland & Hall 1975) is made. The metal-rich minerals are related to chalcopyrite by additional metal atoms located at interstitial sites, and have structures consistent with stoichiometric compositions. The interstitial metals can be described in terms of metal-coordination octahedra which vary in size according to the packing arrangements.

INTRODUCTION

The crystal structure of chalcopyrite, $CuFeS_2$, was first investigated by Burdick & Ellis in 1917, and has been studied by a number of workers since, most recently by Hall & Stewart (1973). In the last few years three new minerals closely related to chalcopyrite have been discovered. They are talnakhite $Cu_9Fe_8S_{16}$ (Cabri & Harris 1971), mooihoekite $Cu_9Fe_9S_{16}$ and haycockite $Cu_4Fe_5S_8$ (Cabri & Hall 1972). The crystal structures of these minerals have been determined (Hall & Gabe 1972; Hall & Rowland 1974; Rowland & Hall 1975), and this paper summarizes the results of these studies and identifies their relationship to each other.

DISCUSSION

The crystal data for chalcopyrite, talnakhite, mooihoekite and haycockite are summarized in Table 1. For these minerals the relative unit cell volumes V/Z' increase with an increasing metal-to-sulphur ratio. Z' is the number of pseudocubic sphalerite-like cells which form the basic lattice of these minerals. The V/Z' values provided the first indication that the compositions of these minerals were *metal-rich* rather than *sulphur-poor*. They also provided early evidence that the basic structural mechanism for these minerals was based on the addition of metal atoms at the interstitial sites of a sphalerite-like arrangement of sulphur and metals, rather than on metal-substitution or sulphur-removal which are the other two structural mechanisms possible for this type of cubic close-packed arrangement of atoms. On this basis, the compositional data determined by electron-microprobe methods (Table 1) were considered in terms of an integral number of sulphur atoms. The resulting chemical formulae contain an integral number of metal atoms, within the estimated standard deviation of the probe measurements. This was the first evidence that the chemical formulae for these minerals were stoichiometric (Hall 1974).

Interstitial metals

The principal structural aspect common to talnakhite, mooihoekite and haycockite is the presence of extra metal atoms located at interstitial sites of the *ccp* sulphur lattice. Minerals related in this way are sometimes referred to as "stuffed derivatives". In these structures each additional interstitial metal atom has a first-order tetrahedral coordination to sulphur atoms, at interatomic distances of about 2.3Å, and a second-order octahedral coordination to "regular" metal atoms, at about 2.7Å. The proximity of the interstitial metals to the surrounding "regular" metals is significant in view of the fact that the metallic Fe-Fe and Cu-Cu distances are only 2.48 and 2.56Å respectively. Though these distances do not give rise to purely metallic properties for these minerals, the resulting

TABLE 1. CRYSTAL DATA OF CHALCOPYRITE-LIKE MINERALS

	Chalcopyrite	*Talnakhite*	*Mooihoekite*	*Haycockite*
Probe Data				
At. % Cu	25.19(12)	27.19(10)	26.41(10)	23.56(15)
Fe,Ni	29.27(15)	24.74(15)	26.44(14)	29.46(20)
S	49.63(25)	48.16(13)	47.16(20)	46.98(25)
Formula	$Cu_8Fe_8S_{16}$	$Cu_9Fe_8S_{16}$	$Cu_9Fe_9S_{16}$	$Cu_8Fe_{10}S_{16}$
Space Group	$I\bar{4}2d$	$I\bar{4}3m$	$P\bar{4}2m$	$P2_*2_*2_*$
a (Å)	5.289(1)	10.593(3)	10.585(5)	10.705(5)
b	5.289(1)	10.593(3)	10.585(5)	10.734(5)
c	10.423(1)	10.593(3)	5.383(5)	31.630(15)
Z'	2	8	4	24
V/Z' (Å^3)	145.8	148.6	150.8	151.5
Intensity	694 refl.	528 refl.	1614 refl.	2890 refl.
R-value				
all data	0.086	---	0.205	--
"less thans" omitted	0.031	0.051	0.047	0.14

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TABLE 2. SELECTED AVERAGE INTERATOMIC DISTANCES

	Chalcopyrite	*Talnakhite*	*Mooihoekite*	*Haycockite*
$<M{-}{-}M'>$	2.645(1) x,y	2.648(2) x,y,z	2.646(2) x,y	2.636(2) z
	2.606(1) z	--	2.692(2) z	2.680[8] x,y
$<M{-}{-}M^{\circ}>$	2.625[20]	2.574[5]	2.562[5]	2.594[8]
$<M{-}{-}M^{+}>$	--	2.722[18]	2.731[15]	2.720[15]
$<M{-}{-}M^{*}>$	--	--	2.692[3]	2.690[10]
<Cu-S>	2.302(1)	2.31[2]	2.33[5]	2.32[11]
<Fe-S>	2.257(1)	2.27[2]	2.28[2]	2.30[14]

Standard deviations are given in round brackets, r.m.s. values in square brackets. Sites M', M°, M^{+}, and M^{*} occupy what are termed "ideal", "vacant", "isolated" and "linked" metal-octahedra. M is a regular metal site.

second-order metal-octahedra are a most important component in relating the chalcopyrite-like structures. An examination of the metal-octahedra packing in these structures (see Fig. 1) illustrates clearly their fundamental structural character. There are, of course, a number of other structural differences, such as metal-type ordering, but these tend to be of lesser importance. In every structure the presence of an interstitial metal displaces the surrounding six "regular" metals outwards from the positions they occupy when this site is vacant. Distortion of the sphalerite-like lattice due to the addition of interstitial metals is conveniently described in terms of the second-order octahedral coordination surrounding each interstitial metal site or each "potential" interstitial metal site. For the sake of brevity each of the "regular" metal atoms at the vertices of the metal-octahedra is denoted by an M; interstitial sites which are unoccupied, by an M°; occupied interstitial sites which are not adjacent to other interstitial metals, by an M^{+}; and occupied interstitial sites which are adjacent to other interstitial metals, by an M^{*}. For comparative purposes it is also useful to consider one other octahedral site, M' based on the hypothetical position of an interstitial metal in the respective unit cells of the minerals. The $<M{-}M'>$ distance would then be half the length of the pseudo-cubic cells which make up each structure (Z' in Table 1 gives the number of these cells).

The metal-octahedra coordinating each M', M°, M^{+} and M^{*} site are referred to as "ideal", "vacant", "isolated" and "linked", respectively. A summary of the metal-metal distances for the different structures is given in Table 2. The similarity of the $<M{-}M'>$ for the "ideal" metal-octahedra is, of course, consistent with the common structural feature of these minerals, the sphalerite-like arrangement of metals and sulphurs. Metal-occupied octahedra which are isolated in the lattice (*i.e.* coordinated to M^{+}) are significantly larger than those that are

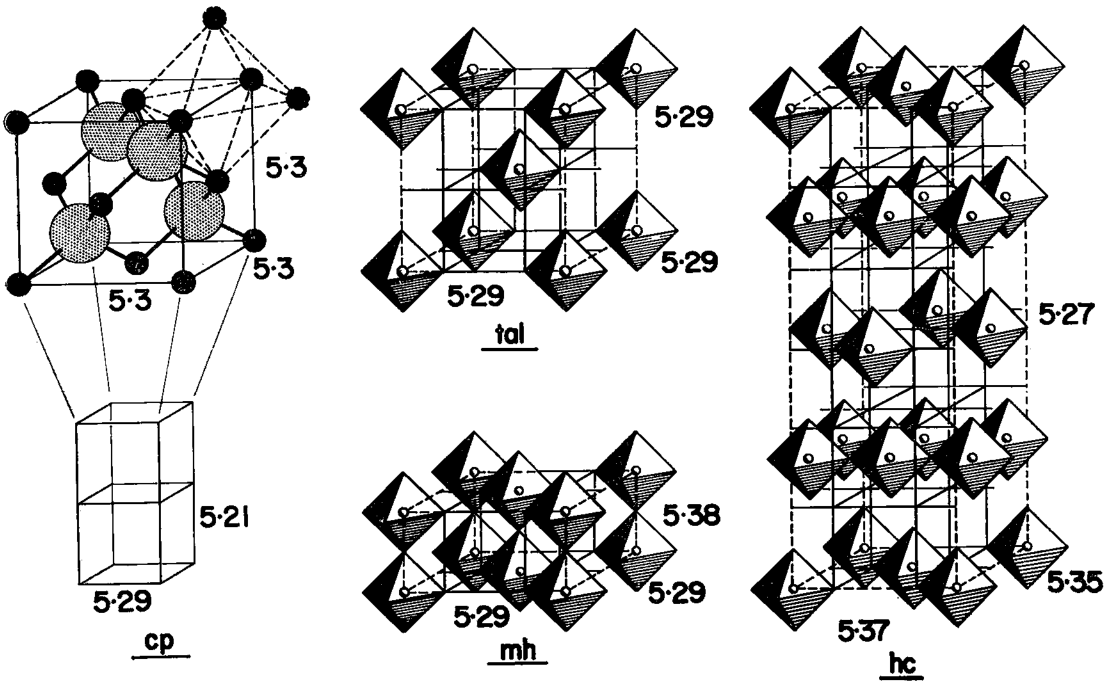

FIG. 1. The crystal structures of chalcopyrite (*cp*), talnakhite (*tal*), mooihoekite (*mh*) and haycockite (*hc*) are shown schematically in terms of sphalerite-type "cubes" of metals and sulphurs (detailed in the upper-left corner), and in terms of interstitial metal-octahedra. The *a*, *b* and *c* dimensions of the "cubes" are given (in angstroms) for each structure.

"linked". That is, $<M–M^{+}>$ are greater than $<M–M^{*}>$ .This is because the addition of the interstitial metal into an "isolated" site is facilitated by an outward movement of the *M*-atoms which is not prevented by an opposing distortion from adjacent occupied metal-octahedra. The contraction of all surrounding "vacant" octahedra is witnessed by the relatively smaller $<M–M^{\circ}>$ distances. For structures containing only isolated metal-octahedra, the contraction of adjacent vacant metal-octahedra enables the repeat unit of the sphalerite-like lattice to remain essentially unchanged. The $<M–M'>$ distances show that this is the case for all lattice directions in talnakhite, the *x* and *y* directions in mooihoekite. and the *z* direction in haycockite. When two "occupied" metal-octahedra are adjacent (*i.e.* "linked") expansion in the direction of the common *M* atom occur without an over-all expansion of lattice in this direction. The increased energy required for lattice expansion results in significantly smaller $<M–M^{*}>$ than $<M–M^{+}>$ distances for these directions. This is the case for the *z* direction of mooihoekite, and the *x* and *y* directions of haycockite. The extent of the lattice expansion due to the adjacent interstitial metals can be gauged by the difference between the two $<M–M'>$ distances for mooihoekite and haycockite.

Magnetic structure

The magnetic structure of chalcopyrite has been established as antiferromagnetic by Donnay *et al.* (1958) using neutron diffraction techniques. Mössbauer and magnetic susceptibility studies of talnakhite and synthetic mooihoekite have shown them to be predominantly antiferromagnetic (Townsend *et al.* 1972). Haycockite has not been extracted in sufficient purity or quantity, nor has it been synthesized to enable magnetic studies.. However, it is expected to have an antiferromagnetic structure from its structural similarity to the other minerals in the series.

The antiferromagnetic $I\bar{4}2d$ structure of chalcopyrite arises from the two Fe(4*b*) atoms being tetrahedrally arranged (with two Cu(4a) atoms) about each sulphur atom and having opposed moments aligned along the *c*-axis. The magnetic coupling between the Fe atoms is via the sulphur atom and is generally referred to as an Anderson superexchange interaction. The sulphur coordination-tetrahedra of two irons and two coppers also form significant portions of the structures of talnakhite and mooihoekite, and this is expected to account for the antiferromagnetic aspect of these minerals.

Thermal motion

The relative magnitude of the thermal motion for the Cu, Fe and S atoms in these minerals is remarkly consistent. The average isotropic temperature factors, <B>, summarized for these atoms in Table 3, show that the thermal motion of the iron atoms is consistently lower than that for copper atoms. This was also found to be the case for cubanite $CuFe_2S_3$ (Szymanski 1974). The relative difference for Fe and Cu atoms may be expected for several reasons: the stronger covalent interaction between iron and sulphur over copper and sulphur, as witnessed by the consistently shorted Fe-S distances over Cu-S (see Table 2); the magnetic exchange interaction between the Fe atoms but not the Cu atoms; and lastly the proposed higher effective charge of Fe atoms over Cu atoms (Hall & Stewart 1973). It should be stressed, however, that while the *x*-ray diffraction analyses provide the relative magnitudes of the thermal motion of these atoms to a reasonable degree of certainty, they provide little insight into the cause. Nevertheless, in the structural study of these minerals

TABLE 3. ATOMIC SITES, AVERAGE TEMPERATURE FACTORS AND COORDINATION

Coordination: T. tetragonal
TBP. trigonal bipyramidal

Qualifier: R. regular
IR. irregular
D. distorted

Chalcopyrite				*Talnakhite*[1]				*Mooihoekite*				*Haycockite*[3]		
$I\bar{4}2d$ Site	Atom Type	<B>	Coordination	$I\bar{4}3m$ Site	Atom Type	<B>	Coordination	$P\bar{4}2m$ Site	Atom Type	<B>	Coordination	P222[2] Site	Atom Type	<B>
M1(4*a*)	Cu	1.48	IR.T.	M1(2*a*)	Fe	0.86	R.T.*	M1(4*a*)	Cu	1.54	IR.T.	M1(1*d*)	Cu	1.58
M2(4*b*)	Fe	0.92.	R.T.	M2(12*e*)	Cu	1.42	IR.T.*	M2(4*l*)	Fe	0.95	IR.T.*	M2(1*l*)	Fe	0.89
S (8*c*)	S	1.00	IR.T.	M3(12*d*)	Fe	0.78	R.T.	M3(4*i*)	Cu	1.41	IR.T.*	M3(2*q*)	Fe	0.73
				M4(8*c*)	Cu	1.54	IR.T.	M4(2*f*)	Fe	0.95	R.T.	M4(2*t*)	Cu	1.87
				S1(4*c*)	S	1.03	D.TBP.	M5(1*c*)	Fe	0.93	R.T.	M5(2*r*)	Fe	0.87
				S2(8*d*)	S	0.95	IR.T.	M6(1*b*)	Cu	1.46	IR.T.*	M6(2*s*)	Cu	1.68
								M7(1*a*)	Fe	0.75	IR.T.*	M7(1*b*)	Cu	1.52
								M8(1*d*)	Fe	0.75	IR.T.*	M8(1*c*)	Fe	0.71
								S1(8*o*)	S	1.04	IR.T.	M9(1*a*)	Fe	0.81
								S2(4*n*)	S	0.78	D.TBP.	M10(1*f*)	Fe	1.24
								S3(4*n*)	S	0.97	D.TBP.	S1(4*u*)	S	1.0
												S2(4*u*)	S	1.16
												S3(4*u*)	S	0.87

[1] A recent refinement of these data involving metal-ordering [2] Small tetragonal pseudo-cell used for site symmetry [3] All coordination polyhedra are irregular and not listed

*Adjacent interstitial metal site

the isotropic temperature factors did provide, along with the "regularity" of the metal coordination polyhedra (see Table 3), an important guide to determine the metal-ordering.

Metal-ordering

The metal-ordering in chalcopyrite is determined unambiguously from electron-density considerations (Hall & Stewart 1973). However, for the more complex structures of mooihoekite, talnakhite and haycockite this is not feasible due to the rapid increase of the ratio of the number of refinable atomic parameters over the diffraction data available. The resulting decrease in electron-density resolution is accentuated by the superstructure nature of these minerals, and their propensity for integral twinning. Both these factors made the measurement of diffraction data relatively difficult and as a consequence, meant that electron-density considerations could not be used alone to identify metal-types. An identification approach evolved in the study of these structures that was based largely on the relative thermal motion of the metals and the regularity of their metal polyhedra. A summary description of the metal tetrahedra for these structures is given in Table 3. This shows that, in general, the iron tetrahedra tend to be "regular" whereas those containing a copper atom are not. The joint agreement of a low $<B>$ value and a "regular" tetrahedron was used in a number of cases to identify iron atoms, though there were exceptions. For this reason it should be stressed that this procedure is largely empirical, and the metal-ordering reported for these structures is by no means unequivocal. There is no question, however, that the metal-ordering proposed for talnakhite and mooihoekite has a high correlation with both structural and magnetic considerations. In the case of haycockite, the lack of magnetic data, the much lower atomic resolution of the x-ray diffraction data, and the general irregularity of the metal tetrahedra makes the assignment of metal types less reliable.

Powder patterns from single-crystal data

The similarity of the x-ray powder patterns of talnakhite, mooihoekite and haycockite to that of chalcopyrite has been discussed by Cabri & Hall (1972). In particular, for mooihoekite and haycockite it is difficult to obtain a characteristic powder pattern due to problems in obtaining sufficient pure material. Because of the considerably higher precision of the single crystal diffraction data, reliable powder patterns for these minerals may be constructed for the measured diffraction maxima. Table 4 gives the d-spacings and intensities determined from the *measured* diffraction data of chalcopyrite (Hall & Stewart 1973), talnakhite (Hall & Gabe 1972), mooihoekite (Hall & Rowland 1973) and haycockite (Rowland & Hall 1975).

TABLE 4. POWDER DIFFRACTION DATA*

Chalcopyrite			*Talnakhite*			*Mooihoekite*			*Haycockite*		
hkl	*d*	*Im*	*hkl*	*d*	*Im*	*hkl*	*d*	*Im*	*hk l*	*d*	*Im*
			110	7.490	1	110	7.485	4	00 4	7.907	1
						001	5.383	1			
			200	5.296	1	200	5.292	2	20 0	5.367	1
									02 2	5.082	1
011	4.717	1							20 2	5.070	1
			112	4.325	1	111	4.370	2	02 4	4.441	3
									00 8	3.954	2
						201	3.774	3			
			220	3.745	2	220	3.742	1	22 2	3.686	1
			310	3.350	1	310	3.347	3			
									02 8	3.182	1
112	3.038	100	222	3.058	100	221	3.073	100	22 6	3.077	100
			312	2.831	1	311	2.843	2			
						002	2.691	6	04 0	2.683	6
200	2.644	9	400	2.648	11	400	2.646	13	40 0	2.676	4
004	2.606	5							0012	2.636	5
						112	2.533	1			
			330	2.497	1				2210	2.428	2
						041	2.375	1			
			332	2.258	1	331	2.264	2	04 8	2.220	1
						222	2.185	1			
			422	2.162	1	421	2.167	1			
			314	2.077	1	312	2.098	1	44 0	1.895	15
						402	1.887	47	0412	1.880	25
220	1.870	20	440	1.873	53	440	1.871	23	4012	1.878	21
204	1.856	36				332	1.830	1			
						223	1.618	12	26 6	1.615	11
312	1.593	29	622	1.597	28	621	1.598	24	62 6	1.612	8
116	1.575	14							2218	1.594	12
						313	1.581	1			
224	1.519	3	444	1.529	3	442	1.536	3	4412	1.539	3
						171	1.442	1			
						004	1.346	3	08 0	1.342	4
400	1.322	6	800	1.324	7	800	1.323	7	80 0	1.338	3
008	1.303	3							0024	1.318	4
						623	1.224	8	66 6	1.229	3
332	1.212	6	662	1.215	12	661	1.215	4	2618	1.221	5
316	1.205	11							6218	1.219	4
420	1.183	1				404	1.200	1	0812	1.196	1
404	1.179	1	804	1.184	2	802	1.187	1	0424	1.183	1
208	1.169	1				480	1.183	1	4024	1.182	1
244	1.077	17	448	1.081	21	444	1.093	9	4812	1.092	9
228	1.069	9				482	1.083	18	8412	1.090	7
									4424	1.082	10
						225	1.035	3	210 6	1.032	4
									102 6	1.030	3
			666	1.019	3	663	1.024	4	6618	1.026	3
512	1.017	9	1022	1.019	9	1021	1.019	7	2230	1.016	4
336	1.013	6									
1110	1.004	5				804	0.943	12	88 0	0.947	5
440	0.935	7	880	0.936	14	880	0.936	6	0824	0.940	7
408	0.928	14							8024	0.939	6

* Powder diffraction data generated from *measured* single crystal intensities using the program POWGEN (Hall & Szymanski 1975). Powder intensities *Im* include $K\alpha_1$ and $K\alpha_2$ components and assume negligible absorption.

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