Canadian Mineralogist
Vol. 23, pp. 61-76 (1985)

THE RELATIONSHIP BETWEEN CRYSTAL STRUCTURE, BONDING AND CELL DIMENSIONS IN THE COPPER SULFIDES

RONALD J. GOBLE
Department of Geology, University of Nebraska-Lincoln,
433 Morrill Hall, Lincoln, Nebraska 68588-0340, U.S.A.

ABSTRACT

Copper and copper-iron sulfides can be classified into three general groups: (1) anilite, digenite, geerite, cubanite, chalcopyrite, haycockite, talnakhite, mooihoekite and bornite with structures based upon approximate cubic close-packing of the sulfur atoms; (2) djurleite and chalcocite with structures based upon approximate hexagonal close-packing of the sulfur atoms; (3) covelline, yarrowite, spionkopite and idaite with a combination of hexagonal close-packing and covalent bonding of the sulfur atoms. The average spacing D between layers in all groups can be expressed as $D = 2.063 + 0.654$ (Cu:S) + 1.183 (Fe:S). The ionic radius R of sulfur for group-1 minerals is $R_1 = D/(2\sqrt{2/3})$, where D is from the previous expression; for group-2 minerals, $R_2 = 1.856 + 0.060$ (Cu:S) + 0.023 (Fe:S); for group-3 minerals, $R_3 = 1.857 + 0.039$ (Cu:S) - 0.020 (Fe:S). Consideration of bond lengths in coordination polyhedra of known copper sulfide structures indicates that major portions of the yarrowite and spionkopite structures will resemble the covelline structure, with probable statistical site-occupancy. Attempts at the determination of the spionkopite structure were hampered by the imperfection of the crystals and the partial occupancy of most structural positions of copper. The geerite structure is rhombohedral ($R\bar{3}m$?) with a 15.77 Å, α 13°56′, $Z = 1$, and will probably resemble the digenite structure.

Keywords: yarrowite, spionkopite, geerite, copper sulfides, copper–iron sulfides, *blaubleibender* covelline, crystal structure, bonding.

SOMMAIRE

On peut regrouper les sulfures de cuivre et de cuivre + fer en trois grandes familles: 1) anilite, digénite, geerite, cubanite, chalcopyrite, haycockite, talnakhite, mooihoekite et bornite, dont la structure contient un empilement approximativement cubique compact des atomes de soufre; 2) djurléite et chalcocite, dont la structure montre un empilement hexagonal compact (*grosso modo*) des atomes de soufre, et 3) covelline, yarrowite, spionkopite et idaïte, qui montrent une combinaison de l'agencement hexagonal compact des atomes de soufre avec liaisons covalentes. Pour les trois groupes, la séparation moyenne D des couches est égale à l'expression 2.063 + 0.654 (Cu:S) + 1.183 (Fe:S). Le rayon ionique R du soufre dans les minéraux du premier groupe est égal à $D/2\sqrt{2/3}$. Pour les minéraux du deuxième groupe, on a $R_2 = 1.856 + 0.060$ (Cu:S) + 0.023 (Fe:S), et pour ceux du troisième groupe, $R_3 = 1.857 + 0.039$ (Cu:S) - 0.020 (Fe:S). Les longueurs de liaisons dans les polyèdres de coordination des sulfures de cuivre de structure connue indiquent que la structure de la yarrowite et celle de la spionkopite ressembleraient sur plusieurs points à celle de la covelline, mais on doit considérer comme probable une occupation statistique des sites. Les tentatives de détermination de la structure de la spionkopite ont été entravées par l'imperfection des cristaux et le grand nombre de sites de cuivre vacants. La structure de la geerite est rhomboédrique ($R\bar{3}m$?), a 15.77 Å, α 13°56′, $Z = 1$, et ressemblerait à celle de la digénite.

(Traduit par la Rédaction)

Mots-clés: yarrowite, spionkopite, geerite, sulfures de cuivre, sulfures de cuivre et fer, covelline *blaubleibender*, structure cristalline, liaisons.

INTRODUCTION

Eight copper-sulfide minerals have been identified to date: covelline $Cu_{1.00}S$, yarrowite $Cu_{1.12}S$, spionkopite $Cu_{1.40}S$, geerite $Cu_{1.60}S$, anilite $Cu_{1.75}S$, digenite $Cu_{1.80}S$, djurleite $Cu_{1.97}S$ and chalcocite $Cu_{2.00}S$. Partial or complete structural determinations have been carried out for covelline (Oftedal 1932, Berry 1954, Kalbskopf *et al.* 1975, Evans & Konnert 1976), anilite (Koto & Morimoto 1970), digenite (Donnay *et al.* 1958, Morimoto & Kullerud 1963), djurleite (Takeda *et al.* 1967a,b, Evans 1979), and chalcocite (Sadanaga *et al.* 1965, Evans 1971). The structures of yarrowite, spionkopite and geerite have not been determined. Yarrowite and spionkopite, two of the *blaubleibender* or "blue-remaining" covellines, were for many years described in terms of the hexagonal unit-cell of covelline, based upon similarities of X-ray powder patterns (*e.g.*, Frenzel 1959, Moh 1971, Rickard 1972, Putnis *et al.* 1977). However, Goble (1980) has shown that the unit cells of yarrowite and spionkopite are not the same as that of covelline. Geerite is a pseudocubic copper sulfide that has only recently been reported (Goble & Robinson 1980).

The known structures can be divided into three general groups based upon the nature of packing of the sulfur atoms: (1) anilite and digenite, with structures based upon approximate cubic close-packing, (2) djurleite and chalcocite, with structures based upon approximate hexagonal close-packing, and (3) covelline, with a combination of hexagonal close-packing and covalent bonding of the sulfur atoms.

The resemblance between the well-developed yarrowite and spionkopite subcells and the covelline unit-cell (Goble 1980) suggests that these minerals belong to group 3; the pseudocubic nature and resemblance of the geerite unit-cell to a structure produced by the leaching of anilite (Goble 1981) suggest that geerite belongs to group 1. Single-crystal X-ray studies provide a method of examining the structures of yarrowite, spionkopite and geerite and of determining the true relationship between these structures and those already known for other copper sulfides.

PROCEDURES

Cleavage fragments of yarrowite, spionkopite and geerite from the studies of Goble (1980) and Goble & Robinson (1980) were used for all single-crystal patterns. Precession, Weissenberg and integrated Weissenberg photographs were prepared for selected orientations of the yarrowite and spionkopite reciprocal lattices. Precession photographs of covelline in the equivalent orientations were also prepared in order to check the supposed structural similarity of the *blaubleibender* covellines to this mineral. For geerite, only precession photographs were prepared. Filtered Cu-radiation was used for all Weissenberg films and Mo radiation for all precession films. The fragments of yarrowite, spionkopite and geerite used measure approximately 0.14 × 0.08 × 0.03, 0.25 × 0.08 × 0.08 and 0.07 × 0.06 × 0.02 mm, respectively.

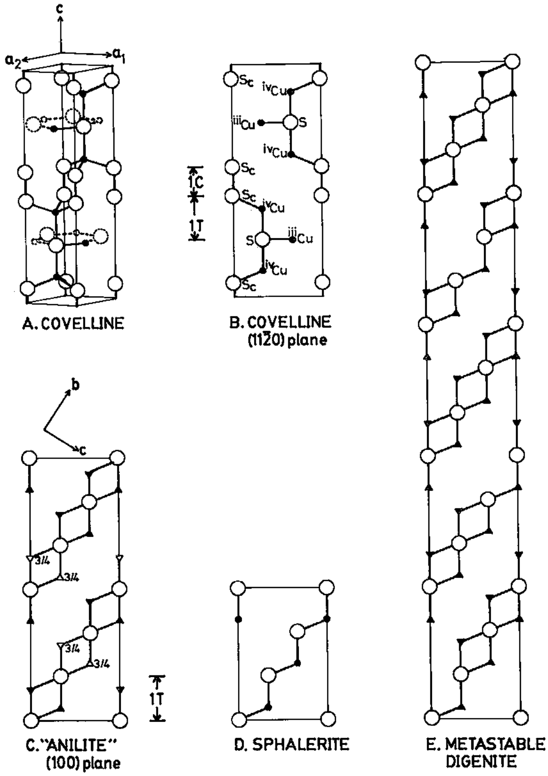

FIG. 1. The crystal structure of covelline (after Wuensch 1974), "anilite", sphalerite and metastable digenite. The "anilite" structure is an idealized version (see text). In B ^{iii}Cu and ^{iv}Cu indicate copper atoms in triangular and tetrahedral co-ordination polyhedra, respectively; S$_c$ indicates covalently bonded sulfur; $1C$ and $1T$ represent the spacings of one covalently bonded and one tetrahedral (ionically bonded) layer, respectively. Filled circles in A, B and D indicate fully occupied triangular co-ordination polyhedra; filled and open triangles in C and E indicate fully and partly occupied tetrahedral co-ordination polyhedra, respectively, with atomic displacement toward the four surrounding triangular faces.

For intensity determinations, 0-, 1- and 2-level integrated Weissenberg photographs (rotation axis *a*), were taken of the yarrowite and spionkopite fragments. Exposure times for all levels were on the order of 200 hours using a Philips fine-focus Cu X-ray tube (point-focus port) with a Philips PW 1008/85 self-rectified high-voltage power supply operating at 40 kV and 12 mA. Three-film packs were used, the films being separated by one sheet of black paper. Individual films of each pack were scaled using the "film factor" of Morimoto & Uyeda (1963). Different levels were scaled by a comparison of reflections present on two or more of the levels, with the assumption that the unit cells are approximately hexagonal.

Intensities were estimated by visual comparison with the {110} reflection of covelline on standard-scale films prepared from multiple exposures. Unobserved reflections were assigned maximum intensities of one-half the minimum observable intensity at that point on the film. Raw intensity-data were corrected for Lorentz and polarization effects and, in the case of spionkopite, for the presence of minor ($\simeq$ 15%) intergrown oriented yarrowite; absorption corrections were not applied. Wilson plots (Wilson 1942) show overall temperature-factors of 0.45 Å^2 and 0.75 Å^2 for yarrowite and spionkopite, respectively.

STRUCTURAL DATA

The crystal structure of covelline, a group-3 mineral, is shown in Figure 1a (after Wuensch 1974); equivalent sites for all atoms lie on the (110) plane, and the structure can be represented by a section through the unit cell on this plane as shown in Figure 1b. The crystal structure of anilite, a group-1 mineral, can be represented in a similar fashion if the structural data of Koto & Morimoto (1970) are transformed into an idealized cubic close-packed unit-cell. Copper atoms in triangularly co-ordinated sites are assigned to the tetrahedra of which these

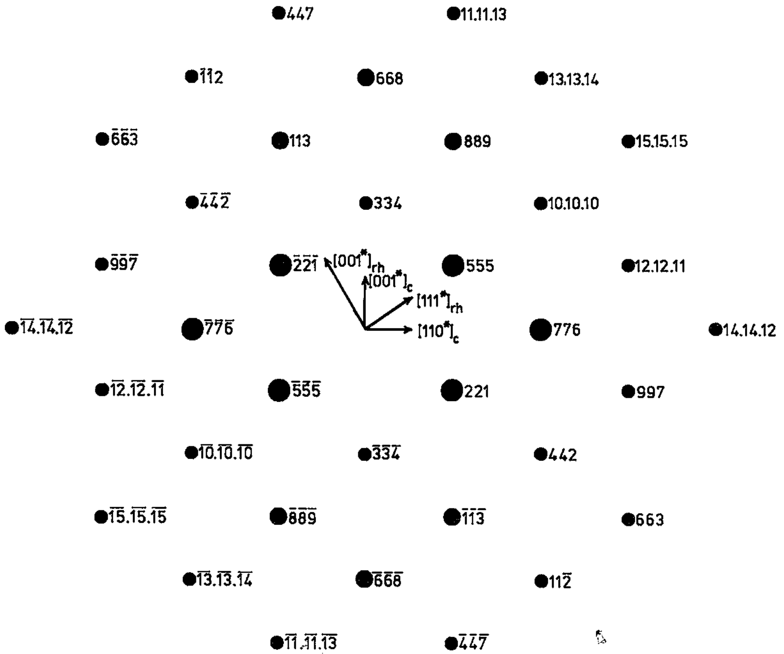

FIG. 2. The reciprocal lattice of geerite with rhombohedral indices. Both rhombohedral and cubic crystallographic axes are indicated.

sites form a face, and displacement of the copper atoms from these tetrahedrally co-ordinated positions are ignored. A section through this "idealized" structure of anilite perpendicular to the close-packed layers of sulfur is shown in Figure 1c; reduction of the cell dimensions necessitates averaging full and empty tetrahedra and results in partial (¾) occupancy by copper for some tetrahedra. The structure of metastable digenite (Morimoto & Kullerud 1963) in the equivalent orientation is shown in Figure 1e. The crystal structures of djurleite and chalcocite, group-2 minerals, involve extensive triangular co-ordination of Cu and cannot readily be represented on sections such as 1b, 1c and 1e. Because of the strong resemblance between the X-ray patterns of geerite and sphalerite, a section through the sphalerite unit-cell in this orientation is represented in Figure 1d.

Goble (1980, Figs. 1, 2) showed that the reciprocal lattices of yarrowite and spionkopite are similar to but distinct from that of covelline. Yarrowite X-ray data were indexed on a hexagonal cell with *a* 3.800, *c* 67.26 Å; spionkopite was shown to be hexagonal, with *a* 22.962 Å (*i.e.*, 6 × 3.827 Å), *c* 41.429 Å. Well-developed subcells with the approximate dimensions of the covelline unit-cell (*a* 3.796, *c* 16.36 Å) were noted. Tables 1 and 2, which list the observed structure-factors for yarrowite and spionkopite, have been submitted to the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2. For yarrowite, 117 nonequivalent reflections were observed, 623 were unobserved (only $|F_{hkl}|$ values are listed in Table 1, $|F_{hk\bar{l}}| \simeq |F_{hkl}|$). For spionkopite, 147 nonequivalent reflections were observed, 406 were unobserved; all supercell reflections of the type hkl with h or $k \neq 6n$ were ignored (*i.e.*, the $a' = a/6 = 3.827$ Å subcell was used). Examination of the structure factors indicates that the space group for both yarrowite and spionkopite is one of $P\bar{3}m1$, $P3m1$, $P321$, $P\bar{3}1m$, $P31m$ or $P312$.

Geerite was described by Goble & Robinson (1980) as being pseudocubic (possibly orthorhombic), space group $F\bar{4}3m$. Careful re-examination of precession photographs shows that geerite can be assigned consistent indices based upon a rhombohedral unit-cell similar to that proposed for digenite by Donnay *et*

TABLE 3. RHOMBOHEDRAL AND CUBIC INDICES FOR THE GEERITE POWDER DATA

d (Å)	I/I_1	Rhombohedral Indices	Cubic Indices
3.128	100	221, 555	111
2.712	10	334	200
1.918	50	776	220
1.870*	10		
1.683*	10		
1.637	30	113, 889	311
1.576	10	442, 10.10.10	222
1.247	10	997, 15.15.15	331
1.109	20	112, 13.13.14	422

*reflection not observed on single-crystal patterns

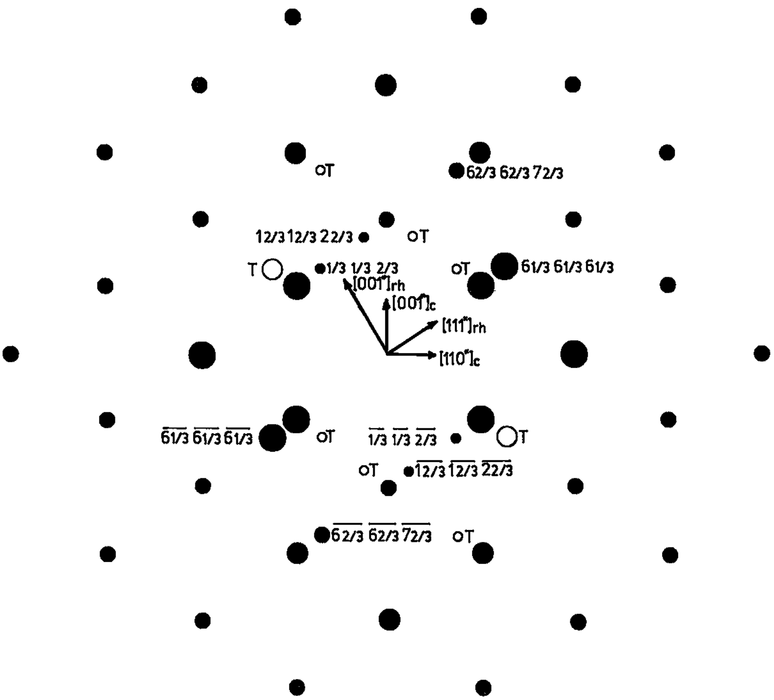

FIG. 3. The reciprocal lattice of anilite after leaching in ferric sulfate solution for twelve hours. Rhombohedral indices consistent with the geerite unit-cell are shown. Open circles labeled T represent reflections attributed to the second individual of a twin.

al. (1958). The geerite reciprocal lattice, indexed on this basis, is reproduced in Figure 2; the X-ray powder pattern with both pseudocubic and rhombohedral indexing is given in Table 3. Geerite is rhombohedral Cu_8S_5 (diffraction aspect $R**$) with a 15.77 Å, α 13°56′, $Z = 1$, space group $R\bar{3}m$, $R3m$, or $R32$. These data are consistent with the weak bireflectance and moderate anisotropism observed by Goble & Robinson (1980).

The choice of the rhombohedral cell for geerite is substantiated by the leaching experiments conducted by Goble (1981), which produced a structure similar to that of geerite. The reciprocal lattice of this material is shown in Figure 3; indices refer to the geerite rhombohedral cell. Fractional indices indicate that the leached phase has approximately three times the a dimension of geerite (a_{rh} 47.12 Å, α 4°40′). Careful re-examination of reflection intensities on precession films of leached anilite shows that reflections indicated by open circles in Figure 3 are produced by twinning about $[001^*]_c$ or $[110^*]_c$. Converting the rhombohedral cell to a hexagonal cell produces a length c_{hex} of 141.2 Å, approximately twice that in yarrowite (67.26 Å), thus explaining the resemblance of the two phases on X-ray powder patterns, as noted by Goble (1981).

Relationship between structure and composition

The five known copper sulfide structures have either approximately cubic or hexagonal close-packed layers of sulfur or, in the case of covelline, a combination of hexagonal close-packed with covalently bonded layers of sulfur. In an ideal close-packed network the distance D between layers is equal to $2R\sqrt{2/3}$, where R is the radius of the sulfur atoms. In copper sulfides such as covelline, with

TABLE 4. AVERAGE DISTANCE BETWEEN SULFUR LAYERS (D) AND RADIUS OF SULFUR ATOMS WITHIN SULFUR LAYERS (R) IN COPPER SULFIDES

mineral	D (Å)	hkℓ	R (Å)	hkℓ	data source
covelline	2.735	006	1.8971	110	Potter & Evans (1976)
yarrowite	2.796	0.0.24	1.899	110	Goble (1980)
spionkopite	2.964	0.0.14	1.910	660	Goble (1980)
geerite	3.128	555	1.918	776	Table 3
anilite	3.208	202,022	1.963	040,400, 224	Potter & Evans (1976)
digenite	3.216	555	1.969	10.10.0	Morimoto & Kullerud (1963)
	3.200		1.959		Donnay et al. (1958)
djurleite	3.362	800	1.9556	046	Potter & Evans (1976)
chalcocite	3.373	$\bar{2}04$	1.9746	630	Potter & Evans (1976)

For anilite D is taken on the average of the four nonparallel {111} planes in the pseudocubic cell, that is, the orthorhombic {022} and {202} planes with spacings of 3.198 Å and 3.218 Å, respectively; R is taken as the weighted average of the six non-parallel {440} pseudocubic planes, that is, the orthorhombic {400}, {040}, and {224} planes with spacings of 1.977Å, 1.953Å, and 1.962 Å, respectively.

layers of covalently bonded sulfur, D will be an average of the covalent, C, and close-packed or tetrahedral, T, interlayer spacings, weighted as to the relative number of each (see, for example, Fig. 1). As noted by Goble (1981), planes with spacings corresponding to R and D are readily identifiable in the copper sulfides; these are listed in Table 4 and shown as functions of composition in Figure 4. The ideal relationship, $D = 2R\sqrt{2/3}$, is also shown in Figure 4. For spionkopite and geerite, the compositions $Cu_{1.40}S$ and $Cu_{1.60}S$ better fit the data of Figure 4 than the compositions $Cu_{1.32}S$ and $Cu_{1.53}S$ determined from the microprobe data of Goble & Smith (1973), Goble (1980) and Goble & Robinson (1980). Digenite D and djurleite R values are anomalous with respect to the data of Figure 4.

Figure 4 confirms that geerite has approximate close-packing of sulfur atoms, whereas yarrowite and spionkopite have structures with a combination of close-packing and covalent bonding of the sulfur atoms. In Table 5 the spacing between close-packed layers, $D' = 2R\sqrt{2/3}$, has been calculated from the R values of Table 4 and combined with the spacing between layers of covalently bonded sulfur in covelline, 2.071 Å (Evans & Konnert 1976), in order to determine the number of each type of layer parallel to the c axes of yarrowite and spionkopite. Comparable data are presented for covelline, geerite and anilite. The geerite and anilite data are consistent with pseudocubic unit-cells containing three and six layers of close-packed sulfur, respectively; the yarrowite and spionkopite data are consistent with a number of different combinations of covalently bonded and close-packed layers corresponding to different unit-cell contents.

Because of the small sample-size, the presence of impurities and the scarcity of yarrowite and spionkopite, no attempt was made to measure their density. Instead, the composition *versus* density relationships for known copper sulfides shown in Table 5 and Figure 5 were used to determine the most probable density of yarrowite and spionkopite. Compositions of $Cu_{1.12}S$ and $Cu_{1.32}S$ were used, as determined by Goble & Smith (1973) and confirmed by Goble (1980). A spionkopite composition of $Cu_{1.40}S$, consistent with the data of Figure 4, was also used. For spionkopite, the data of Table 5 and Figure 5 are consistent with a unit-cell content of 14 $Cu_{1.32\text{-}1.40}S$; for yarrowite, cell contents of either 24 $Cu_{1.12}S$ or 25 $Cu_{1.12}S$ are acceptable (although 24 $Cu_{1.12}S$ seems more likely), depending upon the choice of the density–composition relationship in Figure 5.

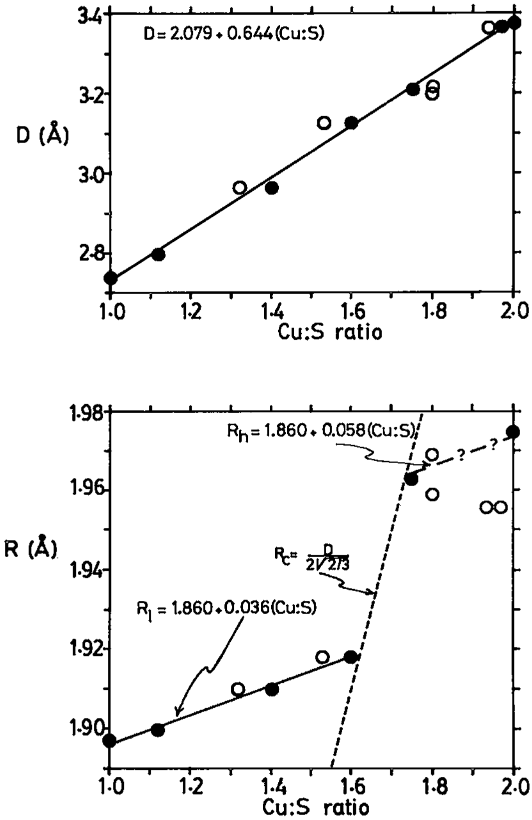

FIG. 4. The relationship (A) between average distance D between sulfur layers and composition and (B) between radius R of sulfur atoms within sulfur layers and composition for the copper sulfides (after Goble 1981). Open circles for spionkopite and geerite indicate analyzed compositions ($Cu_{1.32}S$, $Cu_{1.53}S$); open circles for digenite ($Cu_{1.8}S$) indicate two possible distances; open circles for djurleite indicate two possible compositions ($Cu_{1.93}S$, $Cu_{1.97}$). Correlations were determined by omitting all data represented by open circles except those for digenite, which were averaged. The dashed line in B represents the equation derived in A if ideal close-packing of sulfur atoms is present.

The difficulty in the choice of a unit-cell content and density for yarrowite was resolved by examining the relationship between ratios of the differently bonded types of layers (close-packed or covalently bonded) and composition. In those copper sulfides with less than 1.75 copper atoms per sulfur atom, there is an increasing degree of development of covalent sulfur–sulfur bonding with loss of copper, as shown by the data of Table 5. These data were converted to a ratio of the number of interlayers of covalently bonded sulfur to the number of close-packed or tetrahedrally co-ordinated interlayers, C/T, and plotted as a function of composition in Figure 6. For spionkopite a C/T value of 0.167, corresponding to 2 covalent and 12 tetrahedral interlayers in the cell, is consistent with the data; for yarrowite, of the three possible C/T values, only 0.412, corresponding to 7 covalent and 17 tetrahedral interlayers, is consis-

TABLE 5. POSSIBLE NUMBERS OF COVALENTLY BONDED SULFUR LAYERS AND CLOSE-PACKED SULFUR LAYERS IN ONE HEXAGONAL UNIT CELL OF SELECTED COPPER SULFIDES

mineral	a_{obs}(Å)	D' (Å)	nC + mT	a_{calc}(Å)	Z	density (g/cm^3)
covelline	16.341	3.098	2C + 4T	16.533	6	4.68
yarrowite	67.26	3.101	1C + 21T	67.19	22	4.48
			4C + 19T	67.20	23	4.69
			7C + 17T	67.21	24	4.89
			10C + 15T	67.23	25	5.09
spionkopite	41.429	3.119	2C + 12T	41.57	14	5.13/5.35
			5C + 10T	41.55	15	5.49/5.74
			8C + 8T	41.52	16	5.86/6.12
geerite	9.37	3.132	0C + 3T	9.40	3	5.42/5.61
anilite	19.24	3.189	0C + 6T	19.14	6	5.55
digenite						5.63/5.71
djurleite						5.76/5.82a
chalcocite						5.79

a_{obs}: observed a cell dimension; geerite and anilite cells were converted to their hexagonal equivalents. R: observed radius of sulfur atoms within sulfur layers. D': calculated distance between layers of close-packed sulfur (= $2R\sqrt{2/3}$; R from Table 4). C: layers of covalently bonded sulfur; spacing is 2.071 Å (Evans & Konnert 1976). T: layers of close-packed sulfur; spacing is D' Å. nC + mT: number of C and T layers in one a length; other values of n lead to nonintegral values of m. a_{calc}: calculated a cell dimension. Z: number of sulfur atoms in hexagonal unit-cell; the $a' = a/6$ = 3.827 Å subcell of spionkopite is used. Density is calculated from unit-cell parameters. Densities of spionkopite are for $Cu_{1.32}S/Cu_{1.40}S$. Densities of geerite are for $Cu_{1.53}S/Cu_{1.60}S$. Data sources are as in Table 4 except for djurleite (a), taken from Takeda *et al.* (1967b).

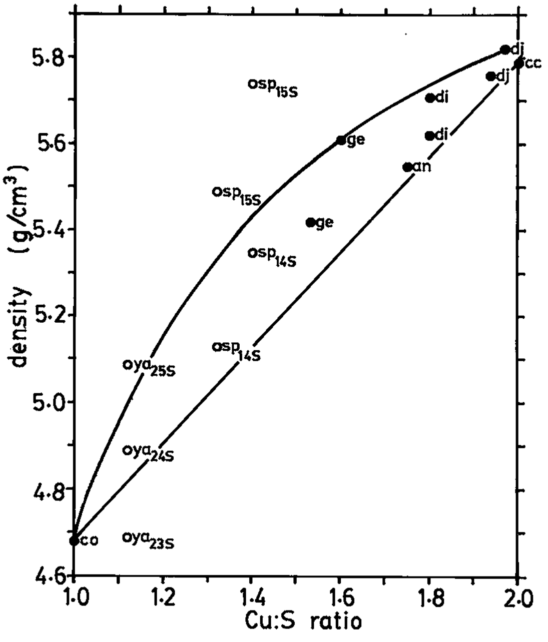

FIG. 5. Calculated density of the copper sulfides as a function of composition. Filled circles represent values calculated from known structures; open circles represent possible densities for yarrowite and spionkopite. Different points shown for a single mineral represent different possible compositions for this mineral. The two curves represent the range fo densities to be expected.

tent with the data. Once again, compositions of $Cu_{1.40}S$ and $Cu_{1.60}S$ for spionkopite and geerite better fit the data than do the analyzed compositions of $Cu_{1.32}S$ and $Cu_{1.53}S$.

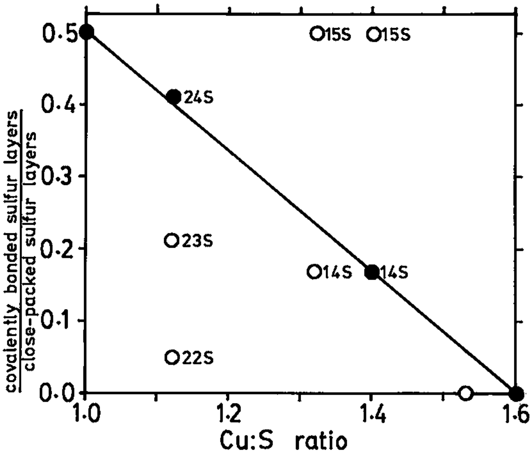

FIG. 6. Ratio between the number of layers of covalently bonded sulfur to the number of close-packed or tetrahedral sulfur layers (ionically bonded) as a function of composition. Different points shown for yarrowite, spionkopite and geerite represent different possible structures and compositions.

TABLE 6. AVERAGE DISTANCE BETWEEN SULFUR LAYERS, D, AND RADIUS OF SULFUR ATOMS WITHIN SULFUR LAYERS, R, IN COPPER-IRON SULFIDES

mineral	Cu:S	Fe:S	D (Å)	hkℓ	R (Å)	hkℓ	data source
sulfur	0.0	0.0	2.048	calc	1.856	calc	1,2
cubanite	0.333	0.667	3.12	002	1.867	123,330	3
chalcopyrite	0.5	0.5	3.03	112	1.865	220	3
haycockite	0.5	0.625	3.07	226	1.889	440	4
talnakhite	0.55	0.55	3.06	222	1.874	440	5
mooihoekite	0.5625	0.5625	3.07	221	1.871	440	4
idaite	0.833	0.167	2.82	006	1.890	112	6
idaite ?	0.845	0.155	2.792	004	1.887	110	7
bornite	1.25	0.25	3.18	224	1.937	440,408	3

The value of D for sulfur is the average covalent S-S distance determined from the structure of orthorhombic sulfur. The value of R for sulfur is half the minimum intermolecular distance of Abrahams (1955) scaled to allow for the revised cell-parameters of Cooper et al.(1961).

Data sources: (1) Abrahams (1955); (2) Cooper et al. (1961); (3) Berry & Thompson (1962); (4) Cabri & Hall (1972); (5) Hiller & Probsthain (1956); (6) Frenzel (1959); (7) Yund (1963).

The crystal-structure – composition relationships shown in Figure 4 can be extended to include sulfur and copper–iron sulfides, as shown in Table 6 and Figure 7. In Figure 7a the interlayer distance D for copper–iron sulfides, is plotted as a function of the ratio of metal (Cu + Fe) to sulfur. The lines plotted are for different ratios of copper to total metal and satisfy the equation: $D = 2.063 + 0.654$ (Cu:S) + 1.183 (Fe:S), $R^2 = 0.993$. In Figure 7b the ionic radius R of sulfur for the same copper–iron sulfides is shown as a function of metal-to-sulfur ratio. Each copper-to-metal ratio is represented by three straight-line segments. The central high-slope segment of each line represents the equation $R = D/(2\sqrt{2/3})$ plotted for the values of D in Figure 7a, and was used to determine whether a given sulfide belongs to the "low-metal" (left) or "high-

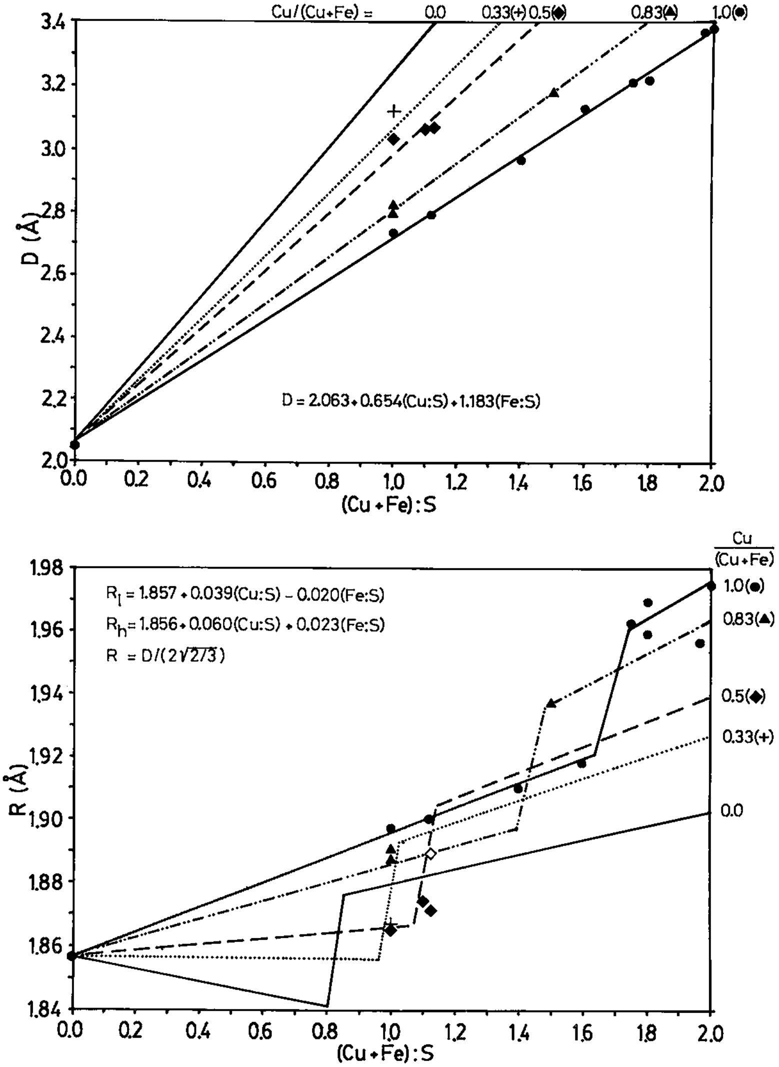

FIG. 7. The relationship (A) between average distance D between sulfur layers and composition and (B) between radius R of sulfur atoms within sulfur layers and composition for the copper and copper–iron sulfides. Values of the Cu/(Cu+Fe) ratio represented are 1.0 (—●—), 0.83 (—▲. .), 0.5 (—◆—), 0.33 (.. + ..) and 0 (—). The open diamond in B represents a Cu/(Cu+Fe) value of 0.44, but a separate set of curves for this value is not included; this point is obscured by a closed diamond in A. In B, each group of minerals with a single value of the Cu/(Cu + Fe) ratio is represented by three straight-line segments; the middle, high-slope segment represents the ideal relationship, $R_c = D/2\sqrt{2/3}$, with D taken from A; the high-Cu (right-hand) segment represents the calculated relationship $R_h = 1.856 + 0.060$ (Cu:S) + 0.023 (Fe:S); the low-Cu (left-hand) segment represents the calculated relationship $R_l = 1.857 + 0.039$ (Cu:S) − 0.020 (Fe:S).

metal" (right) group of sulfides. Approximate equations used for the low-metal and high-metal copper–iron sulfides are: $R_l = 1.857 + 0.039$ (Cu:S) − 0.020 (Fe:S), $R^2 = 0.992$, and $R_h = 1.856 + 0.060$ (Cu:S) + 0.0234 (Fe:S), $R^2 = 0.999$, respectively. The positions of the lines shown are more tenuous than in Figure 7a because of the possibility of a sulfide having a behavior similar to that of high-Cu sulfides (anilite to chalcocite) or low-Cu sulfides (covelline to geerite).

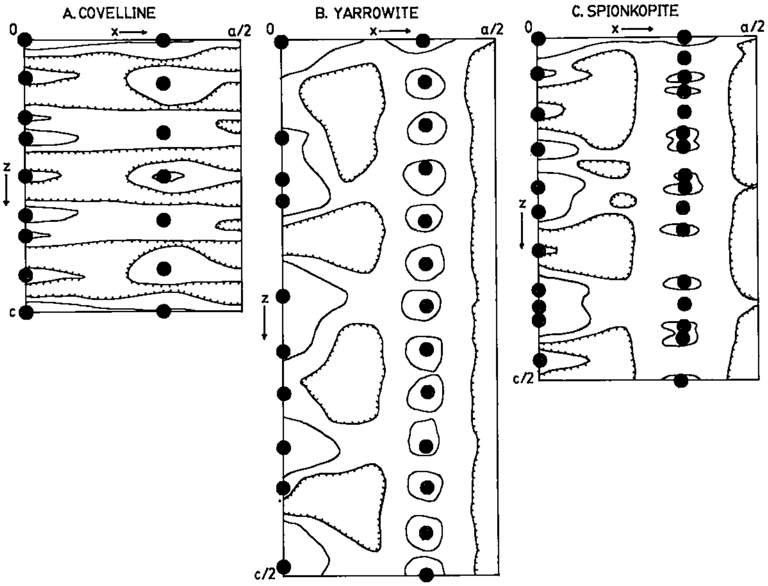

FIG. 8. *h0l* Patterson projections for covelline, yarrowite and spionkopite. Peak positions are indicated by filled circles.

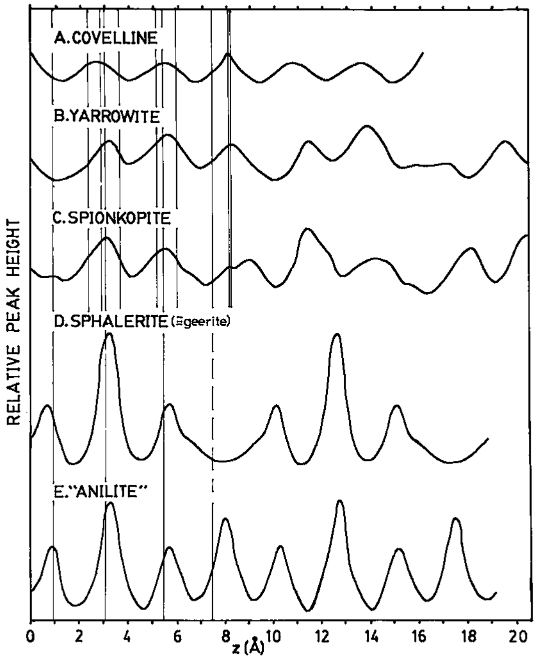

FIG. 9. Patterson sections along $x = 0, y = 0$ for coveline, yarrowite, spionkopite, sphalerite and "anilite". Lines indicate the interatomic distances of Table 7.

In Figure 7, an increase in iron content results in an increase in *D* but a decrease in *R*. This is due to the presence of iron in the structures inhibiting the formation of covalent S–S layers (*i.e.*, covelline and chalcopyrite both have a metal-to-sulfur ratio of one, but only covelline has layers of covalent sulfur). Because *D* is an average spacing and does not include any of the small covalent interlayer distances in the copper–iron sulfides (≃ 2 Å for a covalent interlayer as opposed to ≃ 3 Å for a tetrahedral interlayer), an increase in iron content increases the average spacing of interlayers. Also, the lack of covalent layers results in fewer metal atoms, on average, per tetrahedral interlayer in the copper–iron sulfides than in the corresponding copper sulfides, and a decrease in *R*. As an example, covelline and chalcopyrite both have a metal-to-sulfur ratio of one. *D* for chalcopyrite is the average of six tetrahedral interlayers of approximately 3 Å each, or 3 Å; *D* for covelline is the average of four tetrahedral interlayers of approximately 3 Å each and two covalent interlayers of approximately 2 Å each, or 2.7 Å. Similarly, in chalcopyrite there is one metal atom for each sulfur or one per tetrahedral interlayer, whereas in covelline, there are six metal atoms spread through four tetrahedral interlayers or one and one-half per tetrahedral interlayer. This increases the S–S distance and, therefore, the radius of sulfur *R* from 1.80 Å in chalcopyrite to 1.90 Å covelline.

It is interesting to note that the minerals shown in Figure 7b tend to cluster on or near points at which the high-slope R_{calc} lines or extensions of the R_{calc} lines cut the observed R_l and R_h lines for the various metal-to-sulfur ratios, even if the various lines have different values of the ratio Cu:(Cu + Fe) [*i.e.*, idaite lies at the point where the R_{calc} line for a Cu/(Cu + Fe) value of 0.33 cuts the R_{l} line for a Cu/(Cu + Fe) value of 0.83]. These presumably represent particularly stable structural arrangements in the copper–iron sulfides. It is also interesting to note that the chalcopyrite, mooihoekite, haycockite, talnakhite group of minerals represents a series extending along a single R_{calc} line at Cu/(Cu + Fe) = 0.5 (haycockite is actually on a slightly different line). A second series extends from anilite and digenite to geerite. L. Whiteside (pers. comm. 1983) has observed five intermediate structures in a leaching study of members of this series.

In Figures 4 and 7, the spacings *R* and *D* represent the radius of sulfur atoms and the average spacing between sulfur layers in the copper and copper–iron sulfides, respectively. For the copper sulfides in the composition ranges $\mathrm{Cu_{1.0-1.6}S}$ and $\mathrm{Cu_{1.75-2.0}S}$, *R* would appear to vary continuously. However, although not represented in this way in the figures, *D* must vary in a stepwise fashion since it depends partly upon the number of times a constant quantity, the spacing of layers of covalently bonded sulfur ($\simeq$ 2.07 Å) is averaged with a variable quantity, $2R\sqrt{2/3}$. A similar relationship would apply to the various composition ranges shown for copper–iron sulfides in Figure 7. Therefore, for each mineral in Figures 4 and 7, *D* will be nearly constant, particularly because of the limited solid-solution shown by most copper and copper–iron sulfides.

Iron sulfide data are not shown in Table 6 and Figure 7. Both pyrite and pyrrhotite have octahedral Fe co-ordination and do not fit the data presented. Theoretical FeS in the sphalerite structure is consistent with the data of Figure 7a but not 7b.

Patterson syntheses and space-group determination

Patterson projections on (010) for yarrowite and spionkopite are shown in Figures 8b and c (space group $P\bar{3}m1$); filled circles represent Patterson peaks. A similar projection for covelline prepared from the data of Berry (1954) is shown in Figure 8a. One-dimensional Patterson syntheses prepared for lines through $x = 0$, $a/3$ and $2a/3$ for the yarrowite, spionkopite, covelline [data from Berry (1954)] and "idealized" anilite unit-cells are shown in Figures 9 ($x = 0$), 10 ($x = a/3$) and 11 ($x = 2a/3$). Because of a lack of reliable data, Patterson syntheses could not be prepared for geerite. However, the strong resemblance of the geerite and sphalerite X-ray patterns suggests that the Patterson syntheses would resemble those of sphalerite, which are also presented in Figures 9 and 10. Representative interatomic distances from the covelline, sphalerite and "anilite" structures of Figure 1 are listed in Table 7 and indicated in Figures 9 and 10. The sphalerite and "anilite" distances have been scaled to the covelline cell and are therefore displaced slightly from the positions of the Patterson peaks.

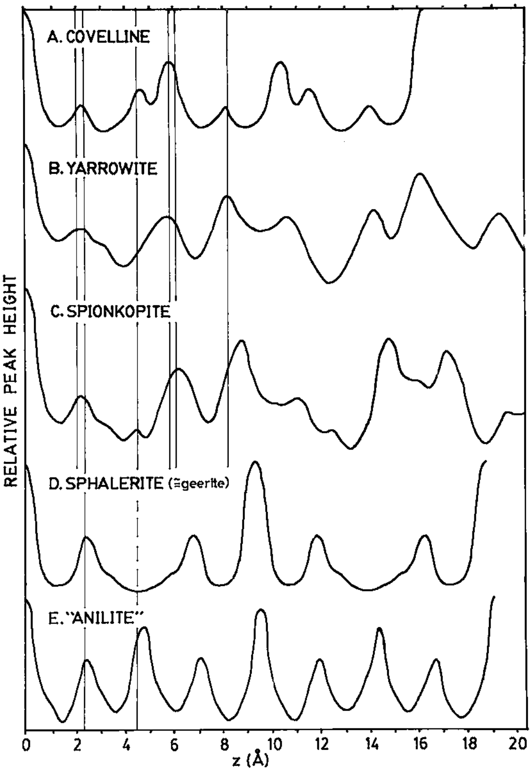

FIG. 10. Patterson sections along $x = a/3$, $y = 2a/3$ for covelline, yarrowite, spionkopite, sphalerite and "anilite". Lines indicate the interatomic distances of Table 7.

Several features are immediately apparent on the yarrowite, spionkopite, covelline, sphalerite and "anilite" one-dimensional syntheses:

a) The Patterson syntheses of yarrowite and spionkopite are, in general, intermediate in form with respect to the covelline and "anilite" syntheses. This is to be expected because these minerals are intermediate in the alteration sequence anilite → spionkopite → yarrowite → covelline and presumably represent structures intermediate to those of anilite and covelline. However, the Patterson syntheses for yarrowite and spionkopite more closely resemble those of covelline than those of "anilite". Patterson syntheses of yarrowite closely resemble those of covelline, whereas spionkopite syntheses more closely resemble those of sphalerite.

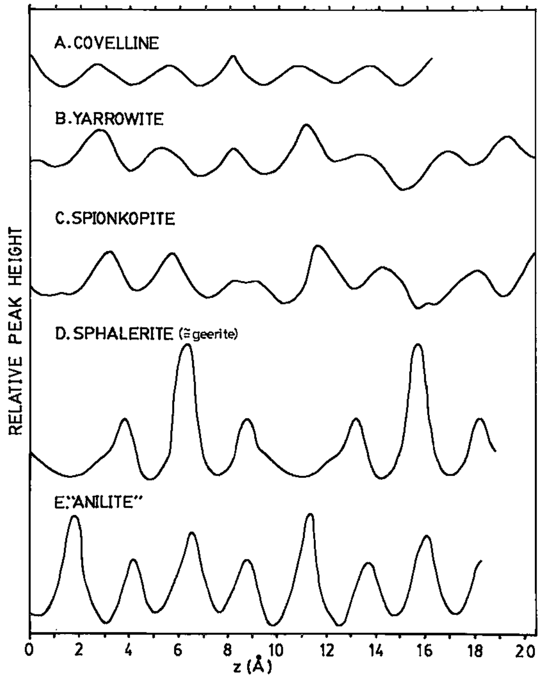

FIG. 11. Patterson sections along $x = 2a/3$, $y = a/3$ for covelline, yarrowite, spionkopite, sphalerite and "anilite".

TABLE 7. DISTANCES BETWEEN ATOMS IN THE COVELLINE, SPHALERITE AND "ANILITE" STRUCTURES

	distance between atoms along Z-axis (Å)			
mineral	atoms	$\Delta x, \Delta y, = 0,0$	atoms	$\Delta x, \Delta y = a/3, 2a/3$
covelline	S_c-S_c	2.07 (≡ 1C)	S-^{iii}Cu	0.00
	^{iv}Cu-S_c	2.29	S_c-^{iv}Cu	0.76
	^{iv}Cu-^{iv}Cu	4.58	^{iv}Cu-^{iii}Cu	2.29
	^{iii}Cu-^{iv}Cu	5.88	S_c-^{iv}Cu	2.83
	S_c-S_c	6.10	S_c-S	3.05 (≡ 1T)
	S_c-S_c	8.17	^{iv}Cu-^{iv}Cu	3.60
	^{iii}Cu-S	8.17	S_c-S	5.12
			S_c-^{iv}Cu	5.34
			S-^{iv}Cu	5.88
			S_c-^{iv}Cu	7.41
			^{iv}Cu-^{iv}Cu	8.13
			S-S	8.17
sphalerite	S-^{iv}Cu	2.29	S-^{iv}Cu	0.76
			S-S	3.05
			^{iv}Cu-^{iv}Cu	3.05
			^{iv}Cu-S	5.34
"anilite"	S-^{iv}Cu	2.29	^{iv}Cu-S	0.76
	^{iv}Cu-^{iv}Cu	4.58	S-S	3.05
			^{iv}Cu-^{iv}Cu	3.05
			S-^{iv}Cu	5.34
			^{iv}Cu-^{iv}Cu	7.62

^{iii}Cu is copper in triangular coordination.
^{iv}Cu is copper in tetrahedral coordination.
S_c is covalently bonded sulfur.
S is ionically bonded sulfur.
The order of atoms in atom pairs is arbitrary (i.e., ^{iv}Cu-S may refer to both distances ^{iv}Cu-S and S-^{iv}Cu).
The distances listed for sphalerite and "anilite" are based upon the S-S and ^{iv}Cu-S distances of covelline (i.e., are not to the same scale as the unit cells for these minerals). This results in negative displacements of these distances from the Patterson peaks in Figures 5 and 6.

b) Sets of pseudomirror planes are present at approximately 16.8 and 8.4 Å for yarrowite and 17.6 and 8.8 Å for spionkopite. These reflect the presence of the 16.8 and 17.6 Å subcells noted by Goble (1980) and suggest possible additional subcells at 8.4 and 8.8 Å. The 16.8 and 17.6 Å subcells show a close correspondence in peak positions with the 16.36 Å unit-cell of covelline and explain the application of the covelline unit-cell to the *blaubleibender* covellines by earlier workers. A similar set of pseudomirror planes exists on the Patterson syntheses of "anilite", representing the basic 5.5 Å cubic close-packed subcell.

c) The strong peak at a z of 8.2 to 8.8 Å ($z = c/2$ for covelline) is shifted somewhat from $x = a/3$ in the covelline synthesis to $x = 0$ in the yarrowite and spionkopite syntheses. The shift is more pronounced in the spionkopite than in the yarrowite syntheses and is further developed in the "anilite" syntheses.

d) The Patterson syntheses of yarrowite and spionkopite show small peaks at $x = a/3$, $z = 0$, corresponding to triangularly bonded copper atoms. The small size of these peaks and the lack of such peaks on $P6/mmm$ Patterson maps indicate that space groups having equivalent positions with x differing by $a/3$ and z equal ($P\bar{3}1m$, $P312$, $P31m$) are not possible for these minerals. Therefore, the space group for yarrowite and spionkopite must be one of $P\bar{3}m1$, $P3m1$ or $P321$.

e) The peak at $x = 0$, $z = 4.6$ Å on the Patterson syntheses corresponds to the distance between two copper atoms occupying apex-sharing copper–sulfur tetrahedra (*i.e.*, ^{iv}Cu–^{iv}Cu in covelline). It is moderately strong in covelline, very strong in "anilite", but weak in both yarrowite and spionkopite. This suggests that in yarrowite and spionkopite the occupied copper–sulfur tetrahedra, rather than facing alternately up and down along c as in covelline and "anilite" (see Fig. 1), face either up or down along c in a given region of the cell.

f) There is a general broadening of peaks in the Patterson syntheses of both yarrowite and spionkopite, suggesting that there may be considerable displacement of copper atoms from the ideal tetrahedral and triangular co-ordination polyhedra found in covelline and in the idealized "anilite" structure of Figure 1. This will probably be reflected in statistical occupancy of the four triangularly co-ordinated sites surrounding a given tetrahedrally co-ordinated site in the structure.

Relationship between structure and bonding

Structures have been proposed for covelline, anilite, digenite, djurleite and chalcocite. In the covelline structure (Fig. 1), Evans & Konnert (1976) determined copper to be in tetrahedral (4 sites) and triangular (2 sites) co-ordination, with Cu–S distances of 2.31 and 2.19 Å, respectively. In the anilite structure (approximated in Fig. 1), Koto & Morimoto (1970) found copper in distorted tetrahedral (8 sites) and triangular (20 sites) co-ordination, with Cu–S distances varying from 2.28 to 2.52 Å (weighted average 2.37 Å) and 2.24 to 2.35 Å (weighted average 2.30 Å), respectively. Of the 112 possible bonds in the tetrahedral co-ordination polyhedra, 84 cluster closely around a Cu–S distance of 2.30 Å, with the remainder having distances of 2.52 Å (8 bonds), 2.94 Å (8 bonds), and 3.22 Å (12 bonds). In the structure proposed for metastable digenite (Fig. 1) by Morimoto & Kullerud (1963), copper atoms are in distorted tetrahedral co-ordination, with copper atoms statistically displaced toward the triangular faces of the tetrahedra. Cu–S distances are not given by the authors but, by analogy with the related structure of metastable bornite (Morimoto 1964), the average distance from the copper atom to the three closest atoms of sulfur can be estimated as 2.29 Å, whereas the average distance from the fourth atom of sulfur would be 2.74 Å. In the djurleite and chalcocite structures, Evans (1981) determined that the copper atoms were mainly in distorted triangular co-ordination, with Cu–S distances varying from 2.18 to 2.90 Å (average 2.31 Å). Two copper atoms in chalcocite and one in djurleite have or approach linear two-fold co-ordination, with Cu–S distances of approximately 2.2 Å.

Calculated and observed Cu–S bond lengths for the copper sulfide minerals are presented in Table 8. Observed bond-lengths cluster at approximately 2.2 and 2.3 Å. Comparison with the calculated bond-lengths in Table 8 shows that yarrowite, spionkopite and geerite will all readily accommodate copper atoms in both triangular and tetrahedral co-ordination without significantly distorting these sites. Assuming that the difference in size of the copper atoms in these sites reflects a difference in charge (*i.e.*, Cu^+ being the larger and Cu^{2+} the smaller ion), it may be possible to predict the relative distribution of copper atoms between the two types of sites. Whereas studies such as those of Tossell (1978) and Vaughan & Tossell (1980) show that such a bonding model is grossly oversimplified, it may be used as a first approximation in predicting co-ordination.

If sulfur is regarded as having a charge of -2, the covalently bonded S_2 pair in covelline a charge of -2, the tetrahedrally bonded Cu in covelline a charge of + 1, and the triangularly bonded Cu in covelline a charge of + 2, one can make the following empirical observations using an ionic model (whether or not the reduced Cu–S distance in triangularly bonded Cu is due to Cu^+ bonded to S^- rather than to Cu^{2+} bonded to S^{2-}, as suggested by Folmer & Jellinek (1980), is immaterial; the result is the same). The superscripts on the copper ions refer to the co-ordination number:

TABLE 8. CALCULATED AND OBSERVED BOND-LENGTHS IN COPPER SULFIDES

mineral	^{iii}Cu-S (calculated, Å)	^{iv}Cu-S (calculated, Å)	average Cu-S (observed, Å)	data source
covelline	2.191	2.323	2.19, 2.31	1
yarrowite	2.193	2.326		
spionkopite	2.205	2.339		
geerite	2.215	2.349		
anilite	2.267*	2.404*	2.30, 2.37	2
digenite	2.262 - 2.274*	2.399 - 2.412*	2.29	3,4
djurleite	2.258 - 2.340**	2.462	2.2, 2.31	5
chalcocite	2.280 - 2.352**	2.477	2.2, 2.31	5

Bond lengths are calculated for ideal close-packed structures.
*For anilite the "idealized" cubic close-packed cell is used; variations in the digenite data reflect different data sources.
**Variations in the djurleite and chalcocite data reflect differences in location and shape of the coordination polyhedra (parallel or oblique to the close-packed layers.

Data sources: (1) Evans & Konnert (1976); (2) Koto & Morimoto (1970); (3) Morimoto & Kullerud (1963); (4) Morimoto (1964); (5) Evans (1981).

a) The formula of covelline can be written as $(^{iv}Cu^+)_4(^{iii}Cu^{2+})_2(S_2)^{2-}{}_2(S^{2-})_2$; $^{iv}Cu\text{–}S \simeq 2.32$ Å and $^{iii}Cu\text{–}S \simeq 2.19$ Å. Overall charge-balance is maintained; charge balance between the close-packed sulfur layers is also maintained, as shown in Figure 12a.

b) The formula of chalcocite can be written as $(^{iii}Cu^+)_{192}(S^{2-})_{96}$; $^{iii}Cu\text{–}S \simeq 2.31$ Å. Overall charge-balance and charge balance between the layers is maintained as shown in Figure 12b (modified after Evans 1981).

c) The formula of djurleite can be written as $(^{iii}Cu^+)_{60}(^{ii}Cu^{2+})_2(S^{2-})_{32}$ for $Cu_{1.94}S$ or as $(^{iii}Cu^+)_{62}(^{ii}Cu^{2+})_2(S^{2-})_{32}$ for $Cu_{1.97}S$. Evans (1979) reported only 62 copper atoms in the structure, of which one, Cu(62), is in linear two-fold co-ordination ($^{ii}Cu\text{–}S \simeq 2.2$ Å); a second, Cu(13), would appear to approach linear co-ordination. The remainder of the copper ions is approximately in triangular three-fold co-ordination ($^{iii}Cu\text{–}S \simeq 2.3$ Å). As shown in Figure 12c (modified after Evans 1981), whether or not overall charge-balance and a balance of charge between the layers are maintained would depend on the location of a second cupric ion or on the location of the "missing" cuprous ion in $Cu_{63}S_{32}$.

d) Distortions in tetrahedrally co-ordinated sites in anilite and displacements from tetrahedrally co-ordinated sites in metastable digenite reflect the fact that neither tetrahedral nor triangular co-ordination polyhedra in these minerals fit our model. Instead, both Cu^+ and Cu^{2+} tend to be in intermediate positions.

e) Figure 4 shows that there is a basic difference between copper sulfides with $Cu:S \geq 1.75$ and those with $Cu:S \leq 1.60$. This is reflected in the co-ordination number of cuprous and cupric ions. Structurally, yarrowite, spionkopite, and geerite will approximate the behavior of covelline and contain cuprous ions in tetrahedrally co-ordinated sites and cupric ions in triangularly co-ordinated sites. Also,

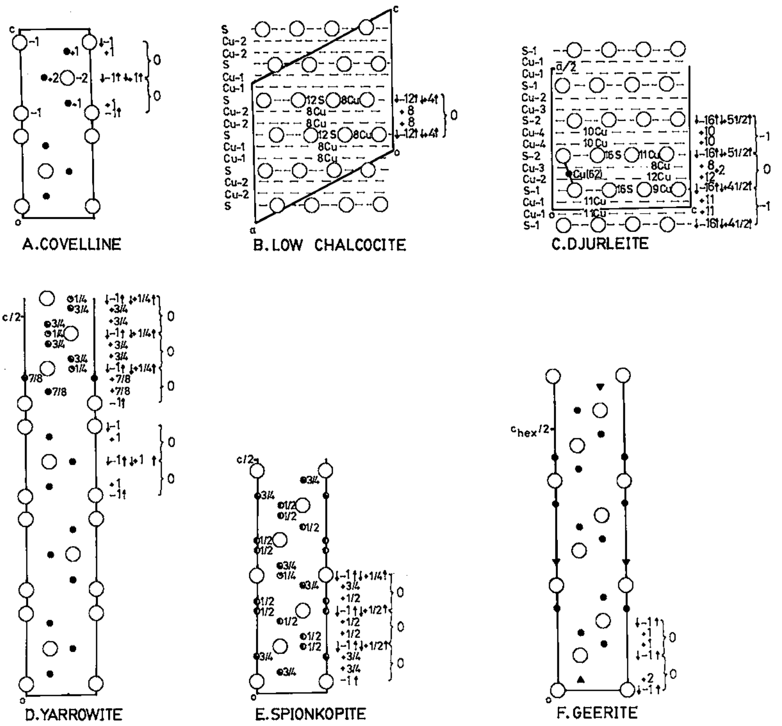

FIG. 12. Ionic bonding in covelline, low chalcocite (Evans 1981), djurleite (Evans 1981), yarrowite, spionkopite and geerite. Numbers within the covelline structure in A represent ionic charges; in other structures they represent site occupancies other than one. Numbers to the right of each structure represent charges; arrows indicate the amount of charge above (↑) and below (↓) the ion.

TABLE 9. STRUCTURAL DATA FOR COVELLINE, YARROWITE, SPIONKOPITE AND GEERITE

	covelline	yarrowite	spionkopite	geerite
analyzed composition:	$Cu_{1.00}S$	$Cu_{1.12}S$	$Cu_{1.32}S$	$Cu_{1.53}S$
structural composition (from Figs. 6,9):	$Cu_{1.00}S$	$Cu_{1.11}S$	$Cu_{1.36-1.40}S$	$Cu_{1.60-1.61}S$
crystal system:	hexagonal	hexagonal	hexagonal	rhombohedral
space group:	$P6_3/mmc$	$P\bar{3}m1$, P321 or P3m1	$P\bar{3}m1$, P321 or P3m1	$R\bar{3}m$?
cell dimensions:	a = 3.7938 Å c = 16.341 Å	a = 3.800 Å c = 67.26 Å	a = 22.962 Å c = 41.429 Å	a = 15.77 Å α = 13°56'
formula:	CuS	$Cu_{27}S_{24}$	$Cu_{19.5}S_{14}$	Cu_8S_5
unit cell content:	Z = 6	Z = 1	Z = 36	Z = 1
calculated density:	4.68 g/cm³	4.91 g/cm³	5.33 g/cm³	5.61 g/cm³
number of sulfur layers in unit cell:	6	24	14	5
number of covalently-bonded sulfur layers in unit cell:	2	7	2	0
average number of copper atoms per close-packed sulfur layer:	1.50	1.58	1.59-1.63	1.53-1.60

Data are from Potter & Evans (1976), Goble & Smith (1973), Goble (1980), and Goble & Robinson (1980). The density of spionkopite is wrongly reported as 5.13 g/cm³ by Goble (1980); this is the value for the analyzed composition, $Cu_{1.32}S$.

atoms in the structures of yarrowite and spionkopite are, like those in covelline, constrained to atomic positions with $x = 0$, $a/3$, $2a/3$ by peak positions on Patterson syntheses.

f) The formula of yarrowite can be written as $(^{iv}Cu^+)_{20}(^{iii}Cu^{2+})_7(S_2)^{2-}{}_7(S^{2-})_{10}$; ^{iv}Cu-S ≃ 2.33 Å and ^{iii}Cu-S ≃ 2.19 Å. To maintain charge balance between the sulfur layers, a distribution of copper atoms such as in Figure 12d is required. Within this general model, sulfur atoms can be shifted to many possible positions as long as the symmetry requirements of the space group are maintained and seven layers of covalently bonded sulfur are retained. Cu atoms in triangularly co-ordinated sites can be shifted perpendicular to *c*, and Cu atoms in tetrahedrally co-ordinated sites can be shifted within the two sites in any layer.

g) The formula of spionkopite can be written as $36_{\circ}$ $(^{iv}Cu^+)_{15}(^{iii}Cu^{2+})_{4.5}(S_2)^{2-}{}_2(S^{2-})_{10}$; ^{iv}Cu-S ≃ 2.34 Å and ^{iii}Cu-S ≃ 2.20 Å. To maintain charge balance between the sulfur layers, a distribution of copper atoms for the a' subcell such as in Figure 12e is required. Shifts in the position of sulfur and copper atoms are possible as long as the requirements of symmetry are maintained and two layers of covalently bonded sulfur are retained in the structure. h) The formula of geerite can be written as $({}^{iv}\mathrm{Cu}^{+})_6({}^{iii}\mathrm{Cu}^{2+})_2(\mathrm{S}^{2-})_5$; ^{iv}Cu–S $\simeq$ 2.35 Å and ^{iii}Cu–S $\simeq$ 2.22 Å. To maintain charge balance between the sulfur layers, a distribution of copper atoms such as is shown in Figure 12f is suggested. This structure is based upon that presented for metastable digenite by Morimoto & Kullerud (1963), with the restrictions that copper atoms be located only in undistorted triangular and tetrahedral co-ordination polyhedra and that rather than one out of every five Cu–S–Cu sandwiches having one empty Cu position, two of five must be empty.

It is to be expected that in each of these structures (yarrowite, spionkopite, geerite), there will be some distortion of the ideal Cu–S triangular and tetrahedral co-ordination polyhedra, as has been noted in previously determined copper sulfide structures.

The basic structural data for covelline, yarrowite, spionkopite and geerite are summarized in Table 9. For each structure, the average number of copper atoms per tetrahedral layer is calculated based on the ideal composition as determined from Figures 4 and 6 and structural data. For yarrowite, spionkopite and geerite, this number approximates 1.60, whereas for covelline it is 1.50. This suggests that in the tetrahedral layers between the layers of covalently bonded sulfur, the structures of yarrowite, spionkopite and geerite probably have a similar co-ordination of copper atoms, and that this is somewhat different than in covelline.

PARTIAL DETERMINATION OF THE CRYSTAL STRUCTURE OF SPIONKOPITE

The numerous methods of arranging 2 covalent and 12 tetrahedral layers parallel to the *c* axis of the spionkopite cell may be reduced to four types as shown in Figure 13a,b,c,d (assumed space group $P\bar{3}m1$). All other possible arrangements may be derived by shifting the sulfur atoms parallel to the *c* axis (*i.e.*, by changing the origin). All possible positions for copper in tetrahedral co-ordination are indicated; triangularly co-ordinated sites have been omitted. Numerous attempts were made at solving the 8.8 and 17.6 Å subcells and the 41.4 Å cell of spionkopite, starting with the basic structural arrangements shown in Figure 13 and assuming that large areas of the subcells would resemble either the covelline or "idealized anilite" structures (the $a' = a/6 = 3.827$ Å subcell was used in all attempts at determining the structure). In every case, splitting of atomic positions became a problem. Figure 13e shows the bottom half of the 41.4 Å cell with atomic positions indicated for that structure giving the lowest *R*-value. *R* for this structure is 0.280 for observed data but increases to 0.404 if unobserved data are included. This was found to be the general case for spionkopite; *R* could readily be reduced to below 0.20 for observed data, but inclusion of unobserved reflections caused a sharp increase in *R*. For this reason, an attempt was made to find the relationship governing the unobserved reflections. It should be noted that for most of the attempts to determine the structure, scattering factors for copper were used; sulfur would be expected to show up as Cu with approximately ½ occupancy. Attempts to change selected positions of copper to sulfur did not result in an improvement in the *R* factor. A possible interpretation of the structure in Figure 13e is shown in Figure 13f. The interpreted structure is inconsistent with a centric space-group. It is also missing several copper atoms.

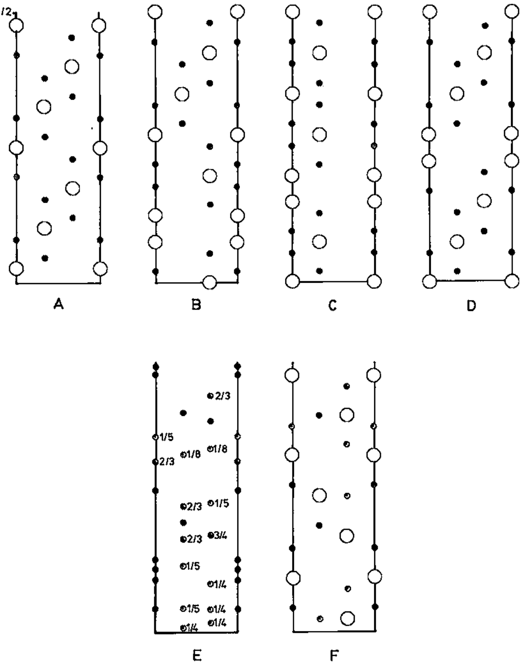

FIG. 13. A, B, C, D: Possible arrangement of layers of ionically bonded and covalently bonded sulfur in spionkopite. E. Attempted crystal-structure determination of spionkopite; fractions indicate site occupancy; scattering factors for copper were used for all positions. F. Possible interpretation of the partial crystal-structure of E.

An examination of the structure factors (Table 2) shows that for the spionkopite cell ($a' = a/6$), the *l* Miller index for reflections of the type *h* minus *k*

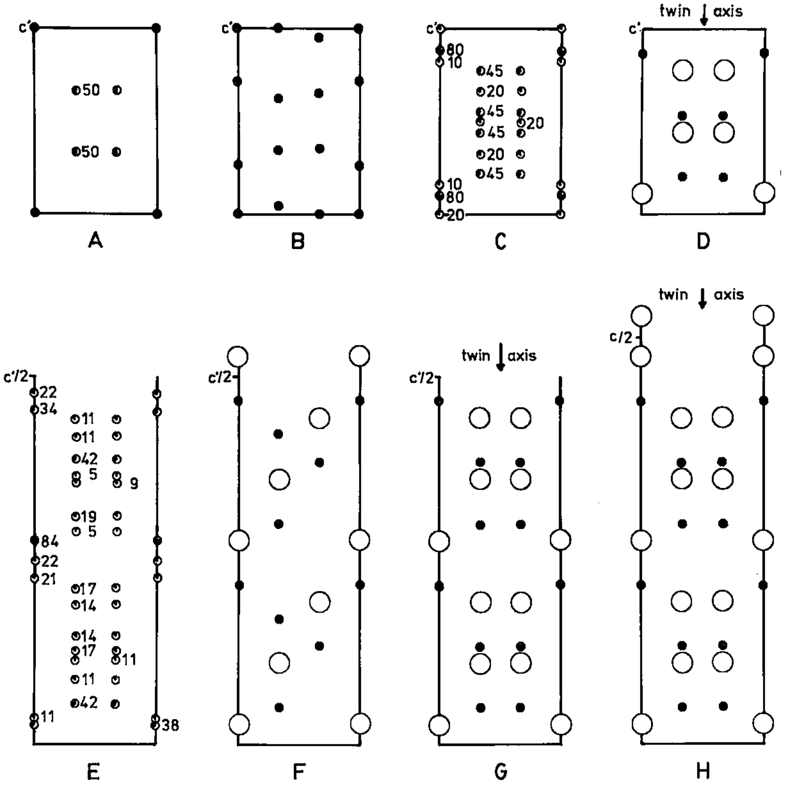

FIG. 14. A. Atomic positions in the 8.9 Å subcell of spionkopite necessary to account for the systematic absences; fractional occupancies are indicated as percentages. B. Position of Patterson peaks for the 8.9 Å subcell. C. Structure derived for the 8.9 Å subcell: positions on $x = a/3$ and $x = 2a/3$ have the same occupancy. D. A twinned-sphalerite subcell for comparison with C. E. Structure derived for the 35.5 Å subcell; positions on $x = a/3$ and $x = 2a/3$ have the same occupancy. F. A possible interpretation of the structure in E. G. A twinned-sphalerite subcell for comparison with E. H. A twinned-sphalerite 41.4 Å cell for spionkopite.

equals $3n$ is 4, 7, 11, 14, 18, 21, 25, 29, 32, 36. If the cell is re-indexed on the basis of a 35.5 Å pseudocell, this index approximates 3, 6, 9, 12, 15, 18, 21, 24, 27, 30. The data set re-indexed on this basis has two sets of extinctions: if h minus k is equal to $3n$, then l is not equal to $3n$, and if h minus k is not equal to $3n$, then l is equal to $3n$ (but l is not equal to 0). These extinctions require that atoms be placed in the cell in the positions $0, 0, z$; $\frac{1}{3}, \frac{2}{3}, z + \frac{1}{3}$; $\frac{2}{3}, \frac{1}{3}, z + \frac{2}{3}$; $\frac{1}{3}, \frac{2}{3}, z + \frac{2}{3}$; $\frac{2}{3}, \frac{1}{3}, z + \frac{1}{3}$ ($P\bar{3}m1$ space group). The atom at $0, 0, z$ must have double the weight of the remaining atoms. These atomic positions (with $z = 0$) are indicated on Figure 14a, together with peak positions for a Patterson synthesis on an 8.9 Å subcell based upon the above re-indexed data (Figure 14b). The peak positions on this Patterson map are identical with those of a sphalerite-type structure using the body diagonal as a c axis. In Figure 14, less than full occupancy of the sites is indicated as a percentage.

Various attempts were made at solving the 8.9 Å re-indexed subcell of spionkopite using least-squares refinement and the minimum residual method of Ito (1973). The final structure derived for the 8.9 Å re-indexed subcell is shown in Figure 14c. R for all reflections is 0.292 (again scattering factors were used for copper only). The correspondence with the atomic positions derived from consideration of extinction data is obvious, as is the similarity to a "twinned-sphalerite" structure (Fig. 14d). This 8.9 Å re-indexed subcell was expanded into the 35.5 Å re-indexed cell as shown in Figure 14e. A possible interpretation is shown in Figure 14f. A "twinned-sphalerite" 35.5 Å cell is again shown for comparison (Fig. 14g). The interpreted cell shown in Figure 14f is again inconsistent with a centric unit-cell and, once again, several atoms of copper are missing. The prediction that there would be fewer apex-sharing tetrahedra than in the covelline structure is shown by the distribution of copper atoms. All attempts at solving the 41.4 Å cell of spionkopite using these data failed. No atomic arrangement could be derived that would account for the observed systematic extinctions, although expansion would appear to take place by the insertion of a 6 Å segment between the two halves of the 35.5 Å re-indexed subcell, such as is shown in Figure 14h for a "twinned-sphalerite" 41.4 Å structure.

DISCUSSION

In attempting to solve the structure of spionkopite, we are trying to derive a minimum of seventeen independent atomic positions using just 147 observed reflections. If, as is suggested by the partial structures shown in Figures 13f and 14f, the structure is acentric rather than centric ($P3m1$ rather than $P\bar{3}m1$), this number would increase to thirty-four. The full cell is in fact thirty-six times this large. In addition, features such as the diffuse nature of the X-ray patterns, broadening of peaks on Patterson syntheses and splitting of atomic positions during structure determinations all suggest that Cu is statistically distributed between the two possible tetrahedrally co-ordinated sites of copper between sulfur layers and among the four possible triangularly co-ordinated sites of copper situated around each tetrahedrally co-ordinated site. Any attempt at removing constraints on the x and y atomic positions during determinations invariably lead to splitting of peak positions in these directions as well as along z. Given these observations, it is extremely doubtful that the structure of spionkopite can be fully solved with the currently available data.

Most of the problems that exist in attempting to solve the spionkopite structure can be applied equally well to the yarrowite structure. The only factor that might make it more amenable to structure determination would be the previous observation that large areas of the cell should strongly resemble the covelline structure (*e.g.*, Fig. 12d). However, attempts at solving the spionkopite structure using the structure of covelline as a model were unsuccessful.

The structure of geerite may be solvable. Peaks observed on X-ray patterns are relatively sharp. The major hindrance in determining the structure may lie in the scarcity and small size of natural material. Experiments such as those conducted by Globe (1981) may provide a method for synthesizing larger fragments of geerite for single-crystal studies.

ACKNOWLEDGEMENTS

The author thanks Dr. G.W. Robinson for providing the specimen of geerite used in the single-crystal studies. Discussions with Dr. J.D. Scott were particularly helpful during the attempts to solve the crystal structure of spionkopite. Finally, I thank Mr. L. Whiteside for helpful discussions during the writing of this paper and Helen Betenbaugh for typing the manuscript.

REFERENCES

ABRAHAMS, S.C. (1955): The crystal and molecular structure of orthorhombic sulfur. *Acta Cryst.* **8**, 661-671.

BERRY, L.G. (1954): The crystal structure of covellite, CuS, and klockmannite, CuSe. *Amer. Mineral.* **39**, 504-509.

______ & THOMPSON, R.M. (1962): X-ray powder data for ore minerals: the Peacock Atlas. *Geol. Soc. Amer. Mem.* **85**.

CABRI, L.J. & HALL, S.R. (1972): Mooihoekite and haycockite, two new copper–iron sulfides, and their relationship to chalcopyrite and talnakhite. *Amer. Mineral.* **57**, 689-708.

COOPER, A.S., BOND, W.L. & ABRAHAMS, S.C. (1961): The lattice and molecular constants in orthorhombic sulfur. *Acta Cryst.* **14**, 1008.

DONNAY, G., DONNAY, J.D.H. & KULLERUD, G. (1958): Crystal and twin structure of digenite, Cu_9S_5. *Amer. Mineral.* **43**, 228-242.

EVANS, H.T., JR. (1971): Crystal structure of low chalcocite. *Nature* **232**, 69-70.

______ (1979): Djurleite ($Cu_{1.94}S$) and low chalcocite (Cu_2S): new crystal structure studies. *Science* **203**, 356-358.

______ (1981): Copper coordination in low chalcocite and djurleite and other copper-rich sulfides. *Amer. Mineral.* **66**, 807-818.

______ & KONNERT, J.A. (1976): Crystal structure refinement of covellite. *Amer. Mineral.* **61**, 996-1000.

FOLMER, J.C.W. & JELLINEK, F. (1980): The valence of copper in sulphides and selenides: an X-ray photoelectron spectroscopy study. *J. Less Common Metals* **76**, 153-162.

FRENZEL, G. (1959): Idait und "blaubleibender Covellin". *Neues Jahrb. Mineral. Abh.* **93**, 87-132.

GOBLE, R.J. (1980): Copper sulfides from Alberta: yarrowite Cu_9S_8 and spionkopite $Cu_{39}S_{28}$. *Can. Mineral.* **18**, 511-518.

______ (1981): The leaching of copper from anilite and the production of a metastable copper sulfide structure. *Can. Mineral.* **19**, 583-591.

______ & Robinson, G. (1980): Geerite, $Cu_{1.60}S$, a new copper sulfide from deKalb Township, New York. *Can. Mineral.* **18**, 519-523.

______ & Smith, D.G.W. (1973): Electron microprobe investigation of copper sulphides in the Precambrian Lewis series of S.W. Alberta, Canada. *Can. Mineral.* **12**, 95-103.

Hiller, J.-E. & Probsthain, K. (1956): Thermische und röntgenographische Untersuchungen an Kupferkies. *Z. Krist.* **108**, 108-129.

Ito, T. (1973): On the application of a minimum residual method to the structure determination of superstructures. *Z. Krist.* **137**, 399-411.

Kalbskopf, R., Pertlik, F. & Zeeman, J. (1975): Verfeinerung der Kristallstruktur des Covellins, CuS, mit Einkristalldaten. *Tschermaks Mineral. Petrog. Mitt.* **22**, 242-249.

Koto, K. & Morimoto, N. (1970): The crystal structure of anilite. *Acta Cryst.* **B26**, 915-924.

Moh, G.H. (1971): Blue-remaining covellite and its relations to phases in the sulfur rich portion of the copper-sulfur system at low temperatures. *Mineral. Soc. Japan Spec. Pap.* **1**, 226-232.

Morimoto, H. & Uyeda, R. (1963): A second comparison of various commercially available X-ray films. *Acta Cryst.* **16**, 1107-1119.

Morimoto, N. (1964): Structures of two polymorphic forms of Cu_5FeS_4. *Acta Cryst.* **17**, 351-360.

______ & Kullerud, G. (1963): Polymorphism in digenite. *Amer. Mineral.* **48**, 110-123.

Oftedal, I. (1932): Die Kristallstruktur des Covellins (CuS). *Z. Krist.* **83**, 9-25.

Potter, R.W. II & Evans, H.T., Jr. (1976): Definitive X-ray powder data for covellite, anilite, djurleite, and chalcocite. *J. Res. U.S. Geol. Surv.* **4**, 205-212.

Putnis, A., Grace, J. & Cameron, W.E. (1977): Blaubleibender covellite and its relationship to normal covellite. *Contr. Mineral. Petrology* **60**, 209-217.

Rickard, D.T. (1972): Covellite formation in low temperature aqueous solutions. *Mineral. Deposita* **7**, 180-188.

Sadanaga, R., Ohmasa, M. & Morimoto, N. (1965): On the statistical distribution of copper ions in the structure of β-chalcocite. *Mineral. J.* **4**, 275-290.

Takeda, H., Donnay, J.D.H. & Appleman, D.E. (1967a): Djurleite twinning. *Z. Krist.* **125**, 414-422.

______, ______, Roseboom, E.H. & Appleman, D.E. (1967b): The crystallography of djurleite, $Cu_{1.97}S$. *Z. Krist.* **125**, 404-413.

Tossell, J.A. (1978): Theoretical studies of the electronic structure of copper in tetrahedral and triangular coordination with sulfur. *Phys. Chem. Minerals* **2**, 225-236.

Vaughan, D.J. & Tossell, J.A. (1980): The chemical bond and the properties of sulfide minerals. 1. Zn, Fe and Cu in tetrahedral and triangular coordinations with sulfur. *Can. Mineral.* **18**, 157-163.

Wilson, A.J.C. (1942): Determination of absolute from relative X-ray intensity data. *Nature* **150**, 151-152.

Wuensch, B.J. (1974): Sulfide crystal chemistry. *In* Sulfide Mineralogy (P.H. Ribbe, ed.). *Mineral. Soc. Amer., Rev. Mineral.* **1**, W21-44.

Yund, R.A. (1963): Crystal data for synthetic $Cu_{5.5x}Fe_xS_{6.5x}$ (idaite). *Amer. Mineral.* **48**, 672-676.

Received February 7, 1984, revised manuscript accepted July 31, 1984.