

A refinement of the structure of cubanite, CuFe_2S_3 *

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Auszug

Die Kristallstruktur von Cubanit CuFe_2S_3 wurde auf Grund der Intensitäten von 1790 beobachteten Interferenzen bis zu $R = 0,045$ (und bis zu $R = 0,096$ für alle 3301 möglichen Interferenzen) verfeinert. Die Verfeinerung führte zu Atomabstands- und Bindungswinkel-Werten, die viel genauer als die bisher mitgeteilten sind. Die Deformation der Tetraeder um die Metallatome läßt sich durch Abstoßungskräfte zwischen den Eisenatomen in den Mittelpunkten zweier Tetraeder mit gemeinsamer Kante erklären. Diese Kante ist $2,804(1)$ Å lang. Die Metall-Schwefel-Abstände sind: $\text{Cu-S} = 2,276(1)$ bis $2,326(1)$ Å, $\text{Fe-S} = 2,258(1)$ bis $2,304(1)$ Å. Die Mehrdeutigkeit der Bestimmung der Raumgruppe, $Pc\bar{m}n$ oder $Pc2_1n$, wurde untersucht und die frühere Wahl der zentrosymmetrischen Raumgruppe $Pc\bar{m}n$ als richtig bestätigt.

Abstract

The crystal structure of cubanite, CuFe_2S_3 , has been refined to an R value of 0.096 (all 3301 data) and 0.045 (1790 "observed" data only), from multiple sets of four-circle diffractometer x-ray intensity data, collected from a spherical crystal. The anisotropic full-matrix least-squares refinement has yielded a set of bond lengths and angles which are much more precise than those of previous workers. The distortions from tetrahedral symmetry about the metal atoms are consistent with a repulsive force between Fe atoms, $2.804(1)$ Å apart, in adjacent edge-sharing Fe-S coordination tetrahedra. The Cu-S lengths range from $2.276(1)$ to $2.326(1)$ Å, and the Fe-S bonds from $2.258(1)$ to $2.304(1)$ Å. The ambiguity in the choice of space group between $Pc\bar{m}n$ and $Pc2_1n$ has been investigated, and the earlier choice of the centric space group $Pc\bar{m}n$ is favoured as being correct.

Introduction

The crystal structure of cubanite was first determined by **BUERGER** (1945, 1947). The present re-examination was undertaken as part of

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an overall crystallographic and mineralogical investigation into the central region of the Cu—Fe—S system. It was intended primarily that the study of cubanite, a mineral for which the stoichiometry was well-established, should provide accurate information about the atomic parameters and thus assist in the identification of metal sites in related minerals such as talnakhite, $\text{Cu}_9\text{Fe}_8\text{S}_{16}$, (HALL and GABE, 1972), mooihoekite, $\text{Cu}_9\text{Fe}_9\text{S}_{16}$, (HALL and ROWLAND, 1973), and haycockite, $\text{Cu}_8\text{Fe}_{10}\text{S}_{16}$, (CABRI and HALL, 1972).

Most minerals in the central region of the Cu—Fe—S system are antiferromagnetic. Cubanite is of particular interest because it exhibits weak ferromagnetism (PEACOCK and YATSEVITCH, 1936), which has recently been attributed to the canting of spins in the structure (FLEET, 1970; TOWNSEND *et al.*, 1973). At temperatures above 200°C, natural orthorhombic cubanite undergoes a transformation to a cubic polymorph with a sphalerite-like cell (CABRI *et al.*, 1973; FLEET, 1970; SZYMAŃSKI, 1974). This transformation has so far proved to be irreversible in the laboratory, yet it is the orthorhombic form that is found in nature. This raises the question as to the origin of cubanite, frequently found in ore deposits as laths in a chalcopyrite matrix, and the reasons for the apparent irreversibility of the transformation.

Cubanite has already been re-examined by a number of workers, including AZAROFF and BUERGER (1955) and FLEET (1970). However, these studies did not provide atomic parameters of an accuracy which is suitable for comparison with the recent study of chalcopyrite, CuFeS_2 (HALL and STEWART, 1973). Furthermore, the original assignment of cubanite to the centric space group $Pcmn$ (BUERGER, 1947), rather than to the non-centric $Pc2_1n$, was not based upon a quantitative analysis, but in the absence of evidence to the contrary, on a preference for "the more natural space group". This was an aspect of structure which deserved serious consideration, because all subsequent structural work on cubanite had been performed on the tacit assumption that the centric space group was correct.

The structure of cubanite was described by BUERGER as being made up of slabs of a wurtzite-like structure (ignoring here the difference between copper and iron atoms), which are parallel to (010), have a width of $b/2$, and are connected *via* inversion centres so that there is edge-sharing between adjacent iron coordination tetrahedra. In the wurtzite structure, the coordination tetrahedra all point one way, but in cubanite, the tetrahedra point one way in one slab $b/2$ wide, and in the opposite way in the adjacent slabs (Fig. 1).

Experimental

The two crystals used in this analysis were obtained from specimens donated by Dr. L. J. CABRI of this Division, and by Dr. J. D. SCOTT of Queen's University, Kingston, Ontario. Both specimens originated from a vug from the same locality.

The crystal data are as follows:

Source: Strathcona Mine, Sudbury, Ontario.

Microprobe analysis in atomic %: Cu: 16.8(1), Fe: 33.3(2), S: 50.0(2); Chemical composition $\text{Cu}_{1.01}\text{Fe}_{2.00}\text{S}_{3.00}$.

Cubanite, CuFe_2S_3 . Formula weight: 271.43.

Crystal System: orthorhombic.

Systematic absences: $0kl, k = 2n + 1; hk0, h + k = 2n + 1$.

Space group: $Pc2_1n$ ($Pnma$ with cba), or

$Pc2_1n$ ($Pna2_1$ with bca) from systematic absences;

$Pc2_1n$ favoured from structure analysis.

Cell dimensions: $a = 6.467(1)$, $b = 11.117(6)$, $c = 6.231(2)$ Å at 20°C using $\lambda(\text{MoK}\alpha_1) = 0.70926$ Å.

Linear absorption coefficient: $\mu(\text{MoK}\alpha) = 124.8$ cm⁻¹.

Density: $D_{\text{calc}} = 4.024$ g. cm³; $Z = 4$.

Intensity data: Crystal 1, 3516 reflections, measured once, 1965 observed.

Crystal 2, 3301 reflections, measured four times, 1790 observed.

Most cubanite crystals examined from the first batch were twinned on the (110) plane. The one untwinned fragment of suitable size that was found, was used in the initial analysis (crystal 1). It was an irregular hexagonal plate, approximately 0.2 mm across, and between 0.05 and 0.10 mm thick. A complete octant of x-ray intensity data was collected on a Picker four-circle diffractometer to a 2θ limit of 120° using graphite-monochromated $\text{MoK}\alpha$ radiation. Generalized Gaussian absorption corrections (GABE and O'BYRNE, 1970) were applied to the data, and of the 3516 reflections measured, 1965 were considered to be observed above the 10% significance level, *i.e.*, $I(\text{net}) > 1.65 \sigma(I)$. Details of the refinement, the scattering curves, and the programs used were identical to those used for the second crystal, and are described later.

During the course of intensity measurement with crystal 1, several unsatisfactory aspects became apparent. It was found that three "systematically absent" reflections were, in fact, visible on the x-ray

precession films taken of this crystal, but were not observed on the diffractometer, while for four other "systematically absent" reflections, the reverse was the case. Examination of one such reflection, 010, on the diffractometer showed that rotation of the crystal about the diffraction vector k by 0.1° caused the reflection to disappear and then to reappear at a different intensity on a further rotation of 1° . Still further rotation of 0.2° made the reflection disappear again. This behaviour was attributed to severe Renninger effects due undoubtedly to the very small mosaic spread of the crystal. Detailed examination of several small-angle, medium-intensity reflections showed that they had peak widths at half-height of about 0.10° in 2θ . It was, therefore, expected that extinction effects would also be serious, and this was borne out in the later refinement. In addition to this, the uneven and curved nature of the crystal "faces" made the generalized Gaussian corrections that were applied, unreliable. Pending the finding of a better crystal, the data were processed and refined. The final parameters obtained in the centric refinement are listed in Table 1 as Data Set III, for comparison with the more accurate analysis which followed.

In due course, a second, larger fragment of cubanite was identified as being a single crystal (labelled crystal 2) and was ground to a sphere 0.15 ± 0.01 mm diameter using the BOND (1951) method. During the detailed preliminary photographic examination of the crystal, and in the course of subsequent data collection, no evidence was found of the Renninger effects observed with crystal 1. The mosaic spread of diffraction peaks was considerably larger than with the first crystal, due probably to the mechanical shocks associated with the grinding of the sphere. The crystal was mounted in a general orientation on a Picker four-circle diffractometer, and intensity data were collected to a 2θ limit of 116° using graphite-monochromated $\text{MoK}\alpha$ radiation and a θ - 2θ scan mode. A scan speed of $2^\circ/\text{min}$ was used, with the 2θ peak base width of 2.8° increasing with 2θ to account for dispersion. Backgrounds were measured for 45 seconds on each side of the peak.

The cell parameters and standard deviations were obtained from a least-squares refinement of the 2θ , γ , and ω values (BUSING, 1970) of 42 reflections with clearly resolved α_1, α_2 doublets in the 2θ range 58 to 71° . The α_1 component was used in the cell refinement procedure. The parameters were refined as a triclinic cell, and it was found that the maximum deviation from orthogonality was 0.004° . The hkl and $hk\bar{l}$ octants of intensity data were each measured twice. Three standards were measured after every fifty reflections to maintain a check

Table 1. Comparison of refined cubanite parameters
 The anisotropic temperature factors are expressed in the form $T = \exp[-2\pi^2(U_{11}a^*2h^2 + 2U_{12}a^*b^*hk + \dots)]$
 The mean isotropic temperature factor is $\langle B \rangle = 8\pi^2 \langle U \rangle$

Atom	Site	Refine- ment set*	X/a	Y/b	Z/c	$U_{11} \cdot 10^2$	$U_{22} \cdot 10^2$	$U_{33} \cdot 10^2$	$U_{12} \cdot 10^2$	$U_{13} \cdot 10^2$	$U_{23} \cdot 10^2$	$\langle B \rangle$
Cu	4c	I	0.583	1/4	0.127	2.09 ^a						1.63 Å ²
		II	0.5792(9)	1/4	0.1205(7)	1.55(9) ^b						1.22(8)
		III	0.5835(1)	1/4	0.1229(1)	1.84(2)	2.04(2)	1.61(2)	0	0.02(2)	0	1.45
		IV	0.5833(1)	1/4	0.1230(1)	1.79(2)	1.80(2)	1.63(2)	0	0.01(2)	0	1.37
		V	0.5832(1)	1/4	0.1230(1)	1.79(2)	1.83(2)	1.64(2)	0	-0.04(2)	0	1.38
		VI	0.5834(1)	1/4	0.1230(1)	1.79(2)	1.81(3)	1.65(2)	0.16(4)	-0.03(2)	-0.21(6)	1.38
Fe	8d	I	0.0875	0.088	0.134	2.09 ^a						1.63
		II	0.0875(6)	0.0869(3)	0.1372(5)	1.02(6) ^b						0.81(5)
		III	0.0853(1)	0.0871(1)	0.1367(1)	1.10(1)	1.23(1)	1.23(1)	-0.01(1)	-0.06(1)	-0.04(1)	0.94
		IV	0.0853(1)	0.0870(1)	0.1367(1)	1.06(1)	1.07(1)	1.23(1)	0.00(1)	-0.06(1)	-0.04(1)	0.89
		V	0.0853(1)	0.0870(1)	0.1366(1)	1.07(1)	1.07(1)	1.24(1)	-0.02(1)	-0.05(1)	-0.03(1)	0.89
		VI	0.0855(2)	0.0851(3)	0.1368(3)	1.07(3)	1.10(4)	1.47(4)	0.09(3)	-0.19(2)	-0.05(3)	0.97
S(1)	4c	I	0.913	1/4	0.2625	2.09 ^a						1.63
		II	0.9307(18)	1/4	0.2595(10)	0.81(18) ^b						0.64(14)
		III	0.9134(2)	1/4	0.2575(2)	1.27(4)	1.35(3)	1.23(3)	0	0.07(3)	0	1.01
		IV	0.9129(3)	1/4	0.2577(2)	1.32(4)	1.14(3)	1.19(3)	0	0.07(3)	0	0.96
		V	0.9127(2)	1/4	0.2579(2)	1.31(4)	1.11(3)	1.19(3)	0	0.05(3)	0	0.95
		VI	0.9128(2)	0.2484(3)	0.2577(2)	1.31(3)	1.10(3)	1.22(3)	-0.19(6)	0.07(3)	0.12(8)	0.94
S(2)	8d	I	0.413	0.0835	0.274	2.09 ^a						1.63
		II	0.4038(10)	0.0863(9)	0.2672(7)	1.06(11) ^b						0.84(9)
		III	0.4120(1)	0.0847(1)	0.2671(1)	1.21(2)	1.43(2)	1.27(2)	0.09(3)	-0.16(2)	0.18(2)	1.03
		IV	0.4120(2)	0.0846(1)	0.2670(1)	1.16(2)	1.24(2)	1.29(2)	0.05(3)	-0.20(2)	0.20(2)	0.97
		V	0.4120(1)	0.0846(1)	0.2670(1)	1.15(2)	1.25(2)	1.28(2)	0.03(2)	-0.22(2)	0.19(2)	0.96
		VI	0.4116(2)	0.0831(3)	0.2669(5)	1.31(5)	1.27(6)	1.24(7)	0.27(6)	-0.24(4)	0.18(6)	1.01
S(2)	4a	VI	0.4125(2)	0.4138(3)	0.2671(5)	1.01(5)	1.24(7)	1.37(7)	0.18(5)	-0.17(4)	0.20(7)	0.96

* I: AZAROFF and BUERGER (1955).

II: FLEET (1970): 587 observed reflections, $R = 0.107$.

III: This work. Refinement using irregular hexagonal crystal, 1965 observed data, $R = 0.050$.

IV: This work. Refinement using spherical crystal, 1790 observed data, $R = 0.045$.

V: This work. Refinement using spherical crystal, all data included, 3301 reflections, $R = 0.096$. Final parameters of this study.

VI: This work. Details as in V, but refinement in noncentric space group, $Pc2_1n$. $R = 0.093$.

^a Overall U .

^b Isotropic U .

on crystal alignment and instrument stability. A uniform systematic decrease of about 5% in the intensity of all three standards was noted over the six weeks period of data collection. It was suspected that this was an instrumental problem as crystal alignment was found to be unchanged at the end of data collection. To account for this, a linear scaling procedure was applied to all the data before averaging the four equivalent data sets measured. Standard deviations were calculated for each reflection from counting statistics and the relative agreement of the four measurements. Spherical absorption corrections were applied to the data. Of the 3301 unique reflections collected, 1790 were considered observed at the 10% significance level.

Refinement

From the tetrahedral coordination exhibited by copper in minerals in the Cu—Fe—S system, and from its lack of any significant magnetic moment in chalcopyrite (DONNAY *et al.*, 1958), it is generally believed that copper is in the Cu^{1+} oxidation state. The Mössbauer spectrum of cubanite, even at 4 °K, indicates that the two iron atoms are in equal oxidation states (IMBERT and WINTENBERGER, 1967). This requires that an $\text{Fe}^{2\frac{1}{2}+}$ oxidation state should be used for iron in order to maintain charge neutrality in the structure¹. Initially, therefore, the atomic scattering curves used in the refinement were Cu^{1+} , and an arithmetic mean of the Fe^{2+} and Fe^{3+} curves of CROMER and MANN (1968), and the S^{2-} curve of TOMLIE and STAM (1958). The anomalous dispersion corrections were taken from CROMER and LIBERMANN (1970). All the structural computations were performed using the X-RAY system of programs (STEWART *et al.*, 1972). The refinements were carried out using the full-matrix least-squares program CRYLSQ (written for the X-RAY system by F. KUNDELL) with anisotropic thermal parameters and an isotropic extinction parameter (LARSON, 1970).

The structure was initially refined in the centrosymmetric space group using the data from crystal 1, to a final residual of 0.050. However, the difference synthesis compiled at the end of the refinement

¹ The exact nature of the charge distribution in cubanite, which is a semiconductor, is not well understood, so that the use of this ionization state represents only a convenient approximation upon which to base the atomic scattering curve. In the structure analysis of the related mineral chalcopyrite (HALL and STEWART, 1973) better agreement was obtained when scattering curves of *ionized* atoms, rather than *neutral* atoms were used. Consequently, the ionized curves described above were used in this analysis.

Table 2

Bond distances with standard deviations			
Cu—S(1)	2.291(1) Å	Fe—S(2)	2.264(1) Å
Cu—S(2)	2.326(1)	Fe—S(1) ²	2.258(1)
Cu—S(1) ⁵	2.276(1)	Fe—S(2) ⁹	2.304(1)
		Fe—S(2) ¹¹	2.293(1)
		Fe—Fe ³	2.804(1)
Bond angles with standard deviations			
S(1)—Cu—S(2)	107.53(3)°	Cu—S(1)—Fe ¹	109.70(4)°
S(1)—Cu—S(1) ⁵	110.85(5)	Cu—S(1)—Cu ⁴	112.18(5)
S(2)—Cu—S(1) ⁵	113.03(3)	Fe ¹ —S(1)—Cu ⁴	109.19(4)
S(2)—Cu—S(2) ⁷	104.45(5)	Fe ¹ —S(1)—Fe ⁶	106.72(5)
S(2)—Fe—S(1) ²	110.53(4)	Cu—S(2)—Fe	107.25(4)
S(2)—Fe—Fe ³	125.25(3)	Cu—S(2)—Fe ⁸	111.90(4)
S(2)—Fe—S(2) ⁹	110.59(3)	Cu—S(2)—Fe ¹⁰	121.75(4)
S(2)—Fe—S(2) ¹¹	110.63(3)	Fe—S(2)—Fe ⁸	111.45(3)
S(1) ² —Fe—Fe ³	124.23(4)	Fe—S(2)—Fe ¹⁰	124.04(4)
S(1) ² —Fe—S(2) ⁹	110.33(4)	Fe ⁸ —S(2)—Fe ¹⁰	75.17(3)
S(1) ² —Fe—S(2) ¹¹	109.80(4)		
Fe ³ —Fe—S(2) ⁹	52.24(3)		
Fe ³ —Fe—S(2) ¹¹	52.59(3)		
S(2) ⁹ —Fe—S(2) ¹¹	104.83(3)		
Nonbonded S—S distances across edges of coordination tetrahedra			
<i>(i)</i> . Cu tetrahedron		<i>(ii)</i> . Fe tetrahedron	
S(2)—S(2) ⁷	3.677(2) Å	S(2)—S(1) ²	3.716(1) Å
S(2)—S(1)	3.724(1)	S(2)—S(2) ¹¹	3.747(1)
S(2)—S(1) ⁹	3.838(1)	S(2)—S(2) ⁹	3.755(1)
S(1)—S(1) ⁹	3.760(2)	S(1) ² —S(2) ⁹	3.744(2)
		S(1) ² —S(2) ¹¹	3.723(2)
		S(2) ⁹ —S(2) ¹¹	3.642(1)

List of superscripts indicating symmetry operations used in text, table and Fig. 2

- | | |
|--|--|
| 1. $1 + x, y, z$ | 7. $x, \frac{1}{2} - y, z$ |
| 2. $-1 + x, y, z$ | 8. $\frac{1}{2} - x, y, \frac{1}{2} + z$ |
| 3. $-x, -y, -z$ | 9. $\frac{1}{2} - x, y, -\frac{1}{2} + z$ |
| 4. $1\frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2} + z$ | 10. $\frac{1}{2} + x, -y, \frac{1}{2} - z$ |
| 5. $1\frac{1}{2} - x, \frac{1}{2} - y, -\frac{1}{2} + z$ | 11. $-\frac{1}{2} + x, -y, \frac{1}{2} - z$ |
| 6. $1 + x, \frac{1}{2} - y, z$ | 12. $\frac{1}{2} - x, \frac{1}{2} - y, -\frac{1}{2} + z$ |

showed significant positive and negative residuals that were beyond the random error level at the respective atomic positions. It was assumed, therefore, that despite the low residual, the systematic errors present in the data, such as those due to absorption, extinction, and the previously described Renninger effects, were limiting further reliable refinement.

From that point, only the data obtained with the spherical crystal 2 were used in the refinement. At first this was carried out using an anisotropic full-matrix least-squares procedure, considering only the observed reflections and those whose calculated values were greater than the locally observable threshold minimum. The results of this refinement are given in Table 2 as Data Set IV. Subsequently, the refinement was repeated with all data at the actual mean observed values given in Table 3, and the results appear as Data Set V in Table 2. The final residuals obtained were 0.045 for observed only and 0.096 for all data, respectively.

The precision of the intensity data was considered adequate for an attempt to resolve the space group ambiguity between $Pcmn$ and $Pc2_1n$. Refinement of the structure assuming the space group $Pc2_1n$ entails removal of the constraints of the mirror plane in the space group $Pcmn$. Thus two iron atoms and two sulfur atoms, related by the mirror in $Pcmn$, become independent, and the sulfur atom on the mirror plane is permitted to move away. (The copper atom was placed in the plane $y = 1/4$ and thus specified the origin of the noncentric polar space group). In changing to the noncentric space group, the number of refinement parameters is increased from 32 to 55.

Starting from the refined parameters of $Pcmn$, the excessive number of 13 cycles of full-matrix least-squares refinement with $Pc2_1n$ were required before all the calculated shifts were less than one half of a standard deviation. The shifts oscillated from one cycle to the next despite the inclusion of a large "damping factor" which indicated that the refinement was ill-conditioned. In addition, the standard deviations at the end of the refinement were all larger than in the centric space group. The corresponding parameters for atoms previously related by the mirror plane in $Pcmn$ were highly correlated, and for some of these parameters the standard deviations were larger by a factor of five. Finally, the refined acentric model did not differ from the centric model in a rational way. Bond lengths, previously equivalent in $Pcmn$, now differed by as much as 0.03 Å (10σ), and there appears to be no explanation for such differences in the way that the variation in metal-

Table 3. Observed and calculated structure factors ($\times 10$)

k	F _o	F _c	k	F _o	F _c	k	F _o	F _c	k	F _o	F _c	k	F _o	F _c	k	F _o	F _c	k	F _o	F _c										
0	0	0	0	0	0	6	344	311	20	0*	10	12	144	148	3	240	235	5	621	622	20	38*	14							
2	236	255	0	1024	1038	8	615	577	22	35*	2	14	50*	48	5	0*	5	5	782	768	22	31*	34							
4	34	24	1	296	311	9	249	230	23	14*	18	15	236	235	6	121	113	6	1490	1462	23	11*	26							
6	2680	2563	2	108	109	10	662	631	24	34*	12	16	100	95	7	49*	31	7	855	837	24	6*	11							
8	288	275	3	474	470	11	58	64	25	51	48	17	27*	35	8	39*	19	8	186	186										
10	185	168	4	51*	53	12	201	184		1	5	18	89	85	9	203	192	9	434	421	2	2	7							
12	1597	1583	5	227	238	13	106	94		0	189	188	19	45*	29	10	18*	31	10	26*	14	0	61	67						
14	184	186	6	886	897	14	233	226		0	189	188	20	0*	18	11	39*	4	11	386	372	1	264	253						
16	184	182	7	299	302	15	57	51		1	73	56	21	118	122	12	74	81	12	896	890	2	100	99						
18	770	780	8	106	114	16	331	327		2	330	320	22	43*	56			13	521	506	3	155	147							
20	130	113	9	357	357	17	25*	30		3	1466	1519		1	9	1	14	14	14	113	122	4	84	73						
22	143	145	10	0*	14	18	117	112		4	310	308		0	40*	38	15	256	248	5	197	186								
24	326	349	11	141	136	19	82	91		5	21*	34		0	52	44	16	45*	54	6	77	71								
26	52	66	12	598	603	20	89	76		6	152	151		1	114	115	2	97	74	17	152	143								
0	0	2	13	233	229	21	46*	36		7	125	124		2	279	284	3	29*	42	18	431	446	8	82	80					
0	1412	1460	14	96	86	22	151	170		8	189	186		3	211	216	4	97	78	19	271	281	9	123	122					
1	1431	1484	15	209	221	23	16*	19		9	1071	1088		4	297	291	5	53	40	20	64	71	10	35*	25					
2	113	111	16	49*	52	24	60	65		10	204	182		5	66	67	6	40*	35	21	144	138	11	46	95					
3	511	488	17	67	58	25	60	69		11	77	65		6	30*	41	7	41*	55	22	64	53	12	64	58					
4	155	150	18	331	338	26	23*	17		12	82	78		7	148	142	8	60	55	23	23*	42	13	176	170					
5	1154	1141	19	151	146		1	2		13	131	135		8	208	204		2	4	24	185	198	14	46*	48					
6	1126	1053	20	66	57		0	265	265		14	91	80		9	171	171		25	130	147	15	100	99						
7	1200	1168	21	113	118		1	69	73		15	621	619		10	231	224		0	1540	1680									
8	32*	26	22	57	55		0	265	265		16	96	98		11	0*	25		2	121	125		17	38*	36					
9	335	308		0	10		2	729	731		17	63	56		12	31*	30		4	9*	8	0	414	434	18	34*	29			
10	117	109		0	398	403		3	726	684		18	47*	21		13	129	135		6	1342	1297		1	40*	13	19	116	110	
11	529	522		1	143	140		4	750	733		19	101*	114		14	115	112		8	137	134		2	71	65	20	0*	26	
12	686	676		2	96	79		5	36	34		20	33*	29		15	112	119		3	59	68		3	90	87	21	61	71	
13	640	623		3	0*	30		6	227	209		21	295	307		16	136	138		12	749	729		4	21*	9	22	11	15	
14	0*	18		4	96	94		7	70	67		22	61	56		17	18*	3		14	94	91		5	0*	21	23	37*	6	
15	197	189		5	112	111		8	419	393		23	20*	41		18	53	18		16	85	81		6	314	303				
16	76	67		6	353	359		9	474	452		24	41*	1		19	103	105		18	356	355		7	56	12		0	472	479
17	186	179		7	141	135		10	447	432			1	6		20	51	49		20	49*	35		8	69	68		1	135	138
18	345	342		8	70	50		12	132	121		0	253	261		1	1	10		24	152	159		10	46*	41	2	61	50	
19	326	331		9	25*	9		13	40*	44		1	116	122		0	0*	18		26	34*	32		11	38*	20	3	209	205	
20	0*	22		10	83	90		14	149	151		2	456	466		0	0*	18		2	136	140		12	156	140	4	22*	24	
21	128	125		11	70	65		15	256	255		3	155	160		1	41*	43		2	1			13	45*	7	5	97	104	
22	16*	38		12	263	259		16	217	225		4	480	488		2	77	62		0	408	439		14	38*	40	6	410	414	
23	52*	50		13	104	109		17	25*	11		5	94	95		3	195	196		1	1057	1069		15	0*	29	7	143	135	
24	152	147		14	0*	23		18	70	79		6	227	226		4	51*	68		2	55	60		16	73	58	8	65	53	
25	166	176		15	0*	14		19	0*	26		7	104	108		5	0*	31		3	428	383		17	34*	11	9	162	157	
26	24*	15		16	60	73		20	56	50		8	301	300		6	46*	11		4	40	38		18	61	10	10	0*	8	
0	0	4		17	40*	27		21	114	117		9	121	126		7	47*	45		5	822	785		10	40*	4	11	55	50	
0	865	934		18	159	158		22	106	122		10	355	362		8	46*	42		6	360	373		20	0*	24	12	275	278	
1	41	49		19	70	76		23	0*	9		11	65	55		9	164	157		7	842	807		21	47*	19	13	105	104	
2	124	121		0	12		24	60	50		12	160	158		10	65	60		8	87	74		22	12*	51	14	30*	41		
3	166	166		0	150	148		25	36*	14		13	80	76		11	0*	17		9	268	246		23	26*	6	15	102	98	
4	0*	10		1	31*	21		1	5			14	138	144		12	0*	15		10	95	89		24	34*	41	16	43*	25	
5	75	62		2	44*	12		1	5			15	54*	69		13	43*	40		11	363	355		25	36*	6	17	46*	15	
6	663	645		3	108	106		0	672	672		16	218	222		14	17*	21		12	97	76		2	6	5	18	151	156	
7	43	45		4	31*	36		1	181	185		17	38*	26		15	98	103		13	451	445		14	58	38	19	78	67	
8	134	129		5	58	29		2	993	1006		18	102	97		16	0*	46		14	58	38		0	1505	1554	20	25	27	
9	83	86		6	138	133		3	1707	1721		19	56	49		17	3*	6		15	161	149		1	315	310	21	55	53	
10	113	102		7	0*	8		4	1026	1030		21	27*	26		18	29*	9		16	109	96		2	29*	15	22	0*	26	
11	45*	54		8	0*	54		5	250	250		22	124	129		19	6*	30		17	128	131		3	170	176				
12	293	277		9	99	92		6	549	527		23	0*	10		1	1	11		18	50*	34		4	107	102		2	2	
13	27*	31		10	49*	52		7	53	47		24	64	52		0	267	262		20	30*	21		6	1288	1310	1	293	298	
14	90	78		11	44*	27		8	594	576		1	1	7		1	137	119		21	90	89		7	239	226		2	91	98
15	50*	47		12	93	97		9	1198	1193		1	1	7		2	264	265		22	72	82		8	55	49	3	41*	57	
16	130	129		13	0*	15		10	700	682		0	157	161		3	199	186		23	61	39		9	114	115	4	139	139	
17	55	29		14	38*	19		11	164	165		1	119	104		4	287	290		24	0*	29		10	140	137	5	232	240	
18	128	142		15	70	68		12	328	319		2	250	248		5	115	105		25	108	120		11	120	115	6	188	193	
19	0*	6		0	14		13	32*	35		3	61	61		6	246	236		26	9*	15		12	816	830	7	265	264		
20	26*	47		0	91	83																								

Table 3. (Continued)

k	F _o	F _c	k	F _o	F _c	k	F _o	F _c	k	F _o	F _c	k	F _o	F _c	k	F _o	F _c	k	F _o	F _c				
24	26*	37	17	15*	16	3	160	148	10	79	72	6	176	181	14	43*	20	14	97	87	13	35*	55	
	5	k	3	18	50*	54	4	243	244	11	308	292	7	534	545	15	33*	21	15	177	186	14	114	100
0	471	493	20	46*	35	5	78	84	12	456	445	8	98	94	16	67	60	16	150	150	15	50*	49	
1	82	77	21	0*	10	7	81	83	14	0*	9	10	127	123	9	270	271	6	k	11	17	0*	5	
2	643	647	22	92	87	8	172	158	15	155	160	11	275	277	0	32*	9	19	42*	21	18	101	93	
3	1237	1271	5	k	7	9	123	116	16	34*	50	12	117	112	1	53*	21	20	40*	32	19	46*	38	
4	714	684	10	213	214	17	125	121	13	394	394	2	46*	9	21	86	91	20	4*	40	20	4*	40	
5	122	121	0	128	127	11	52	59	18	241	233	14	58	52	3	34*	38	22	81	90	21	45*	20	
6	418	417	1	62	57	12	170	164	19	230	247	15	101	185	4	49*	9	23	0*	6	7	k	7	
7	0*	5	2	174	166	13	50*	57	20	0*	13	16	73	89	5	35*	19	0	298	300	1	54*	54	
8	416	404	3	73	70	14	94	86	21	102	107	17	121	124	6	39*	8	1	79	50	2	155	144	
9	912	921	4	180	187	15	78	72	22	48*	30	18	36*	49	7	0*	20	2	429	435	3	33*	41	
10	515	506	5	70	62	16	126	119	23	48*	34	19	236	243	8	0*	6	4	461	447	5	65	56	
11	93	104	6	126	119	17	40	27	24	112	105	20	39*	22	9	24*	31	2	835	821	4	163	163	
12	273	280	7	40	27	0	66	54	6	k	3	22	56	57	11	26*	13	4	61	447	5	65	56	
13	59	48	8	100	105	1	0*	5	0	131	134	6	k	7	12	25*	6	5	81	81	6	117	121	
14	182	187	9	60	59	2	0*	3	1	57	41	13	20*	15	6	275	264	7	57	33	7	57	33	
15	517	526	10	175	162	3	50*	48	2	0*	17	0	56	19	14	0*	4	7	19*	5	8	103	96	
16	315	314	11	44*	46	4	0*	7	3	72	78	2	15*	17	6	k	12	9	604	610	10	146	146	
17	71	71	12	107	103	5	0*	11	5	44*	33	3	0*	14	0	124	112	10	365	354	11	59	42	
18	156	169	13	10*	5	6	55	50	6	110	116	4	16*	19	1	43*	8	11	78	75	12	97	101	
19	63	56	14	71	50	7	38*	5	7	85	34	5	0*	16	2	29*	12	12	183	190	13	0*	10	
20	59	67	15	56*	34	8	7*	3	8	8*	9	6	62	16	3	92	87	13	40*	37	14	49*	47	
21	246	256	16	10	124	9	36*	39	9	38*	58	7	33*	16	4	15*	30	14	138	131	15	21*	19	
22	167	178	17	10*	28	10	0*	12	10	62	16	8	50*	11	5	29*	11	15	352	361	16	121	112	
23	34*	43	18	86	80	11	0*	13	11	15*	20	9	0*	10	6	100	101	16	225	234	17	47*	26	
24	73	91	19	0*	15	12	17*	11	12	83	77	10	40*	3	7	36*	8	17	66	54	18	69	73	
	5	k	4	21	40*	16	5	k	13	13	31*	27	11	25*	10	8	37*	6	18	116	120	19	35*	5
0	77	76	1	20*	29	5	k	8	0	123	107	14	26*	4	12	42*	10	9	72	75	19	47*	43	
1	20*	29	2	34*	4	0	148	145	1	45*	19	15	33*	35	13	0*	9	10	55	42	20	5*	47	
2	34*	4	3	25*	251	1	0*	23	2	44*	26	16	26*	11	14	0*	6	11	0*	16	21	181	182	
3	25*	251	4	35*	3	2	86	87	3	20*	19	17	5*	10	15	0*	4	6	k	13	22	138	137	
4	35*	3	5	71	51	3	340	341	4	0*	30	18	56	41	16	0*	12	23	30*	34	23	30*	34	
5	71	51	6	72	62	4	105	100	5	25*	8	19	0*	17	17	28*	4	0	43*	6	2	112	108	
6	72	62	7	49	14	5	24*	37	6	105	96	20	0*	1	18	0*	5	1	0*	6	7	k	4	
7	49	14	8	24*	8	6	132	128	7	16*	30	21	35*	19	19	43*	3	2	0*	2	0	22*	7	
8	24*	8	9	172	160	7	16*	3	8	15	19	22	50*	7	20	12*	2	3	38*	8	11	33*	31	
9	172	160	10	22*	5	8	39*	56	9	171	164	23	38*	4	21	0*	1	4	19*	3	2	272	42	
10	41*	41	11	41*	41	9	263	262	5	k	14	23	6*	4	21	0*	1	4	19*	3	2	272	42	
11	41*	41	10	101	89	0	0*	17	0	371	376	0	693	695	7	0*	4	5	32*	7	9	266	268	
12	43*	41	11	78	36	1	39*	33	12	63	43	1	63	43	3	58	43	8	252	251	5	35*	5	
13	24*	41	12	8*	7	2	55	50	2	29*	27	2	47*	46	7	k	0	7	68	57	11	0*	21	
14	0*	7	13	36*	20	6	k	0	3	78	73	3	320	322	1	39*	46	8	10*	32	12	106	120	
15	97	91	14	37*	27	4	47*	39	4	0*	8	3	921	930	3	921	930	9	83	82	13	34*	27	
16	0*	8	15	165	164	0	1689	1887	5	43*	34	5	164	163	5	0*	7	10	40*	28	14	43*	40	
17	18*	27	16	70	65	2	60	55	6	320	300	6	629	612	7	99	89	11	19*	6	15	162	174	
18	0*	8	17	46*	27	4	79	66	7	38*	33	7	220	211	9	688	686	12	0*	6	16	75	74	
19	0*	8	18	52	54	6	1603	1605	8	55	49	8	85	60	11	34*	30	13	74	67	17	0*	18	
20	11*	5	19	39*	25	8	120	113	9	29*	55	9	252	253	13	92	97	14	31*	18	18	64	71	
21	56	52	20	40*	9	10	147	144	10	100	94	10	100	94	15	38*	406	15	72	60	18	64	71	
22	28*	9	21	0*	15	12	1020	1029	11	17*	32	11	104	95	17	39*	31	16	28*	11	7	k	0	
23	34*	18	22	0*	15	14	106	102	12	187	188	12	436	429	19	92	81	17	0*	9	0	0*	14	
24	0*	15	1	109	111	16	149	153	13	0*	14	13	173	166	21	192	207	18	26*	9	1	82	71	
0	104	133	2	226	228	18	538	550	14	67	42	14	67	52	23	0*	25	19	77	60	2	175	149	
1	56	66	3	180	180	20	67	74	15	5*	11	15	160	164	7	k	1	21	45*	40	3	145	149	
2	185	181	4	236	235	22	118	120	16	110	110	16	34*	82	4	0*	7	21	45*	40	4	159	155	
3	1110	1150	5	70	70	24	247	259	17	49*	17	17	64	42	0	180	173	22	28*	2	5	68	41	
4	189	180	6	38*	56	6	k	1	18	117	120	18	246	250	1	32*	11	2	383	388	7	k	5	
5	0*	2	7	136	133	0	79	78	19	0*	6	19	108	110	2	383	388	3	159	144	0	47*	64	
6	119	108	8	156	166	1	61	29	20	28*	32	20	28*	32	4	412	408	1	61*	52	9	111	125	
7	115	116	9	190	186	2	1*	17	22	78	92	0	48*	5	5	0*	19	2	154	156	10	119	124	
8	868	857	10	35*	30	3	57	54	23	0*	9	1	0*	30	6	165	154	3	781	783	11	0*	14	
9	116	123	11	37*	40	4	33*	16	2	30*	24	7	50*	50	4	131	138	12	40*	10	12	40*	10	
10	1*	33	12	30*	54	5	33*	23	6	k	5	4	58	26	9	101	88	6	47*	50	14	50*	62	
11	1*	33	13	118	125	6	74	69	0	94	99	5	24*	25	10	322	309	7	65	92	15	75	88	
12	30*	54	14	94	93	7	44*	27	1	34*	17	6	0*	5	11	0*	22	8	95	94	16	84	80	
13	113	123	15	105	106	8	0*	13	2	33*	14	5	20*	23	12	123	116	9	614	599	17	27*	3	
14	50*	56	16	116	118	9	40*	39	3	39*	23	7	20*	23	13	76	70	10	99	105	18	0*	18	
15	505	513	17	35*	5	9	40*	39	4	30*	15	8	0*	17	13	76	70	10	99	105	18	0*	18	
16	68	78	18	0*	24	10	0*	11	4	36*	15	8	0*	17	13	76	70	10	99	105	18	0*	18	
17	46*	38	19	94	96	11	0*</																	

Table 3. (Continued)

k	F _o	F _c	k	F _o	F _c	k	F _o	F _c	k	F _o	F _c	k	F _o	F _c	k	F _o	F _c	k	F _o	F _c				
7	75	57	7	380	379	12	60	28	21	250	264	3	111	89	4	85	77	14	44*	34	12	151	153	
8	110	113	8	43*	53	13	106	110	9	k	1	4	32*	43	5	12*	43	15	93	106	13	66	63	
9	98	85	9	251	257	14	0*	24	10	44*	48	5	36*	13	6	0*	22	16	57	35	14	0*	9	
10	166	160	10	47*	43	15	75	81	11	0*	13	7	28*	15	8	58	61	17	35*	46	10	k	9	
11	55	42	11	188	184	16	20*	12	12	80	23	8	0*	10	9	174	164	19	123	120	0	117	111	
12	120	115	12	486	481	17	0*	22	13	30*	68	9	69	70	10	73	71	10	k	4	1	92	88	
13	0*	39	13	281	280	18	18*	15	14	9*	26	10	40*	10	11	53	25	12	0*	24	2	0*	39	
0	k	12	14	48*	49	19	83	81	15	0*	13	11	29*	9	12	0*	24	0	78	70	3	4*	6	
7	0*	34	15	165	173	20	0*	21	16	42*	43	12	16*	10	13	27*	12	0	45*	40	3	38*	5	
1	0*	27	17	78	81	0	210	220	7	45*	12	13	27*	12	9	k	11	2	2*	28	5	58	74	
2	8*	13	18	261	267	1	74	57	8	6*	16	14	0*	6	0	45*	40	3	38*	5	6	106	102	
3	57	63	19	168	178	2	48*	13	9	64	50	15	26*	46	1	22*	8	4	53*	46	7	99	82	
4	44*	9	20	45*	36	3	97	83	10	28*	22	16	11*	4	2	11*	21	5	0*	22	8	50*	19	
5	0*	15	21	99	102	4	23*	3	11	19*	10	17	0*	5	3	0*	9	6	73	66	9	0*	5	
6	40*	32	22	51	44	5	47*	42	12	31*	31	18	22*	4	4	0*	22	7	18*	21	10	74	63	
7	20*	34	23	148	147	6	201	195	13	23*	10	19	29*	10	5	21*	7	8	0*	12	11	10*	49	
8	26	14	24	156	155	7	70	60	14	32*	9	20	4*	4	6	0*	37	9	0*	5	12	78	78	
9	49*	52	25	165	173	8	0*	21	15	47*	27	21	0*	16	8	0*	17	11	63	14	10	k	10	
10	0*	3	26	178	181	9	60	67	16	0*	16	17	0*	7	1	89	89	9	6*	8	12	75	56	
7	k	13	27	186	187	10	34*	16	17	0*	7	18	0*	19	2	331	332	13	0*	11	0	115	97	
0	95	80	28	194	193	11	0*	23	18	0*	19	2	331	332	9	k	12	13	0*	11	1	35*	27	
1	27*	42	29	203	202	12	147	139	19	0*	8	3	107	107	3	107	107	14	0*	3	2	0*	19	
2	0*	16	30	212	211	13	73	50	20	0*	4	4	36*	362	4	36*	362	15	17*	6	3	27*	10	
3	161	160	31	221	220	14	62	55	21	29*	11	5	59	72	1	0	75	70	16	38*	4	4	27*	22
4	0*	20	32	230	229	15	61	45	22	0*	21	6	226	222	2	0*	4	17	0*	8	5	0*	20	
0	k	0	33	239	238	16	50	26	23	9	k	2	7	91	89	10	k	0	18	33*	40	6	90	89
8	508	506	34	248	247	17	0*	8	24	0	206	204	8	228	232	11	k	5	10	k	5	7	0*	29
2	27*	32	35	257	256	18	158	146	25	1	57	45	9	117	75	0	551	568	0	454	465	9	0*	11
4	0*	6	36	266	265	19	162	162	26	352	352	10	304	308	2	35*	39	1	87	83	10	k	11	
6	457	450	37	275	274	20	79	75	27	5	0*	24	11	57	46	4	65	70	2	50*	34	0	60	66
8	63	47	38	284	283	21	70	52	28	0*	4	12	175	169	6	492	500	3	0*	12	0	60	66	
10	33*	37	39	293	292	22	61	45	29	6	191	189	14	129	123	8	22*	8	5	0*	12	0	60	66
12	302	298	40	302	301	23	52	37	30	7	65	52	15	0*	39	12	332	340	5	76	69	2	34*	36
14	56	42	41	311	310	24	43	28	31	8	243	239	16	211	216	14	30*	9	6	427	413	3	112	110
16	33*	47	42	320	319	25	34	25	32	9	350	341	17	25*	23	16	80	75	7	77	78	4	50*	36
18	175	165	43	329	328	26	25	18	33	10	323	316	18	118	109	18	196	203	8	0*	5	5	93	88
20	0*	31	44	338	337	27	16	10	34	11	24*	4	11	24*	4	20	34*	14	9	0*	4	11	k	0
22	13*	40	45	347	346	28	10	103	105	13	59	43	0	34*	4	10	k	1	11	5*	44	1	0*	3
0	k	1	46	356	355	29	78	88	14	117	122	1	0*	17	0	86	91	12	304	296	3	238	240	
0	62	55	47	365	364	30	67	776	15	97	104	2	30*	14	1	207	213	13	55*	59	5	0*	16	
1	351	361	48	374	373	31	112	108	16	213	222	3	34*	15	2	4*	13	14	0*	12	7	21*	21	
2	30*	16	49	383	382	32	103	99	17	42*	6	4	0*	14	3	112	112	15	18*	5	9	203	189	
3	210	196	50	392	391	33	94	90	18	96	109	5	0*	13	4	50*	35	16	84	73	11	16*	22	
4	35*	47	51	401	400	34	85	81	19	0*	29	6	0*	9	5	168	170	17	25*	21	13	37*	32	
5	282	284	52	410	409	35	76	72	20	4*	45	7	0*	18	6	91	82	18	186	176	15	127	122	
6	38*	45	53	419	418	36	67	681	21	112	105	8	31*	10	7	202	202	10	k	6	17	0*	21	
7	324	327	54	428	427	37	58	54	22	103	106	9	58	11	8	29*	4	8	29*	4	11	k	1	
8	0*	4	55	437	436	38	49	45	23	94	91	10	20*	10	9	101	95	0	65	74	0	157	140	
9	157	159	56	446	445	39	40	38	24	85	82	11	0*	8	10	55*	53	1	175	185	1	45*	36	
10	77	71	57	455	454	40	31	27	25	76	73	12	0*	8	11	107	101	2	32*	44	1	45*	36	
11	161	163	58	464	463	41	22	18	26	67	64	13	31*	15	12	53*	67	3	171	168	2	181	177	
12	49*	36	59	473	472	42	13	9	27	58	55	14	0*	5	13	152	154	4	53*	48	3	16*	40	
13	225	234	60	482	481	43	4	0	28	49	46	15	32*	6	14	0*	9	5	153	140	4	198	194	
14	39*	7	61	491	490	44	0*	21	29	40	37	16	0*	5	15	70	70	6	85	63	5	38*	19	
15	111	112	62	500	499	45	0*	10	30	31	28	17	17*	3	16	88	86	7	180	179	6	130	129	
16	79	76	63	509	508	46	0*	24	31	22	19	18	8	9	17	68	45	8	0*	32	7	34*	54	
17	46*	71	64	518	517	47	0*	24	32	10	59	38	9	k	8	18	49*	47	9	142	138	8	118	124
18	57	34	65	527	526	48	0*	25	33	9	81	89	0	214	220	19	95	100	10	25*	43	9	53*	40
19	132	146	66	536	535	49	0*	21	34	8	72	80	1	48*	4	20	0*	10	11	105	92	10	163	168
20	0*	9	67	545	544	50	0*	9	35	7	63	71	2	132	125	10	k	2	12	28*	40	11	14*	7
22	68	62	68	554	553	51	0*	9	36	6	54	62	3	436	438	13	132	140	13	132	140	12	103	101
0	k	2	69	563	562	52	0*	11	37	5	45	53	4	149	143	0	256	265	14	0*	19	13	56*	60
0	178	186	70	572	571	53	0	110	105	14	0*	14	5	0*	19	1	169	162	15	92	95	14	76	66
1	215	228	71	581	580	54	0	118	125	15	0*	14	6	198	198	2	23*	21	16	20*	33	15	51*	36
2	37*	14	72	590	589	55	2	68	62	16	0*	22	7	0*	30	3	102	113	17	26*	44	16	124	121
3	86	87	73	599	598	56	3	187	185	17	15*	3	8	91	85	4	31*	29	10	k	7	17	0*	3
4	22*	22	74	608	607	57	4	28*	42	18	59	27	9	354	351	5	120	129	0	k	7	18	65	67
5	184	179	75	617	616	58	5	76	61	19	0*	10	10	139	130	6	241	232	0	34*	19	11	k	2
6	165	162	76	626	625	59	6	108	94	20	34*	7	12	147	145	7	168	157	1	93	107	0	75	63
7	196	206																						

Table 3. (Continued)

k	F _o	F _c	k	F _o	F _c	k	F _o	F _c	k	F _o	F _c	k	F _o	F _c	k	F _o	F _c	k	F _o	F _c	k	F _o	F _c
7	46*	36	9	23*	4	2	27*	37	13	0*	22	6	0*	7	9	116	108	9	39*	24	9	107	111
8	143	144	10	75	80	4	79	74	14	0*	5	7	0*	7	10	86	86	13	k	7	14	k	4
9	344	350	11	39*	10	6	518	512	15	50	29	8	39*	8	11	29*	5	0	90	79	0	62	61
10	206	202	12	0*	26	8	35*	5	12	k	4	9	24*	2	12	54*	66	1	0*	14	1	24*	11
11	40*	20	13	37*	21	10	105	91	10	151	146	11	21*	5	13	k	3	2	62	60	2	16*	2
12	149	150	14	0*	29	12	370	370	0	20*	4	12	k	8	0	107	113	3	32*	7	3	37*	28
13	47*	45	15	21*	4	14	38*	18	2	31*	26	4	0*	26	4	75	70	4	75	70	4	31*	8
14	75	76	11	k	7	16	101	89	4	33*	30	1	97	81	2	117	115	6	64	74	6	56	55
15	216	225	12	k	1	0	58*	42	5	0*	5	2	0*	9	3	224	219	7	35*	8	7	0*	12
16	145	147	0	96	93	1	74	74	6	141	134	3	126	130	4	133	130	13	k	8	8	23*	5
17	0*	21	1	20*	10	1	35*	19	7	8*	19	12	100	104	10	121	117	0	108	112	3	0*	6
11	k	4	2	74	74	2	0*	10	7	50*	4	4	0*	26	5	26*	7	0	87	82	14	k	5
0	47*	43	4	88	87	3	0*	36	8	30*	7	5	38*	28	6	112	104	7	0*	20	1	12*	15
1	0*	2	5	0*	15	4	0*	10	9	24*	34	6	247	238	7	0*	20	1	12*	15	0	257	248
2	48*	11	6	87	88	5	12*	15	10	80	66	7	90	84	8	89	79	14	k	0	1	27*	34
3	86	98	7	0*	3	6	56*	36	11	5*	4	8	42*	5	9	178	176	2	48*	39	2	48*	39
4	0*	14	8	49*	50	7	8*	19	12	100	104	12	k	9	10	121	117	0	108	112	3	0*	6
5	30*	9	9	13*	17	8	38*	9	13	28	8	12	k	9	11	38*	14	2	0*	1	4	57	54
6	28*	39	10	90	84	9	30*	29	14	32*	7	0	0*	9	12	80	81	4	14*	11	5	16*	27
7	25*	15	11	0*	15	10	40*	9	15	23*	26	1	34*	22	13	26*	26	6	93	101	6	229	224
8	21*	7	12	71	74	11	61	10	12	k	5	2	0*	18	13	k	4	8	0*	7	14	k	6
9	73	80	13	0*	9	12	52*	23	4	73	67	0	0*	4	1	27*	33	14	k	1	0	18*	9
10	0*	15	11	k	8	14	0*	7	1	50*	8	13	k	0	2	46*	11	1	103	101	3	0*	16
11	37*	13	0	67	45	15	49*	20	2	0*	13	3	59	10	1	26*	49	3	49*	54	2	36*	26
12	46*	29	0	25*	3	16	48*	8	3	59	10	3	310	305	4	35*	11	2	105	106	15	k	0
13	33*	23	1	25*	3	12	k	2	4	0*	14	5	0*	7	5	38*	28	3	93	91	3	93	91
14	0*	2	2	38*	27	12	k	2	4	0*	14	7	34*	61	6	18*	4	4	26*	37	1	48*	46
15	40*	54	3	116	118	0	250	233	6	60	61	7	18*	7	9	242	246	7	28*	42	5	84	80
16	26*	13	4	39*	33	0	203	206	7	18*	7	11	0*	9	8	39*	9	6	42*	41	5	0*	23
17	38*	12	5	25*	6	1	203	206	7	18*	7	15	31*	60	9	36	47	7	100	101	15	k	1
11	k	5	6	53*	41	2	45*	23	8	0*	10	11	0*	9	8	39*	9	6	42*	41	5	0*	23
0	35*	17	7	0*	11	3	148	150	8	0*	7	15	31*	60	9	36	47	7	100	101	15	k	1
1	47*	62	9	105	95	5	168	164	11	12*	5	13	k	1	11	29*	9	9	80	78	0	45*	25
2	77	56	10	49*	32	6	208	206	12	40*	45	0	71	75	12	0*	5	10	38*	43	1	35*	7
3	458	442	11	11*	10	7	209	204	13	0*	4	1	0*	25	13	k	5	11	50*	50	2	0*	12
4	76	60	12	30*	31	8	0*	11	14	0*	6	2	108	100	0	29*	8	14	k	2	3	33*	19
5	0*	32	9	138	130	9	138	130	12	k	6	3	60*	72	0	29*	8	14	k	2	4	23*	13
6	18*	12	11	k	9	10	47*	31	4	111	111	1	47*	40	0	19*	29	5	38*	7	6	20*	23
7	85	81	0	54*	39	11	83	100	0	45*	41	5	5*	12	2	57*	44	1	60	60	6	20*	23
8	37*	41	1	58	64	12	158	146	1	198	199	6	86	70	3	249	241	2	11*	4	15	k	2
9	368	355	2	95	90	15	161	165	2	71	47	7	27*	37	4	140*	48	3	47*	40	3	47*	40
10	52*	53	3	102	104	14	27*	1	3	165	150	8	74	70	5	0*	20	4	33*	6	0	107	103
11	43*	7	4	106	95	15	96	98	4	48*	54	9	71	62	6	29*	9	5	46*	47	1	0*	17
12	0*	2	5	0*	43	16	11*	24	5	153	159	10	92	99	7	47*	53	6	39*	26	2	95	99
13	88	82	6	48*	35	12	k	3	6	40*	34	11	0*	2	8	25*	32	7	47*	60	3	119	105
14	43*	22	7	68	75	7	207	197	12	26	25	9	208	196	8	0*	2	4	111	112	4	111	112
15	240	235	8	68	67	0	83	84	8	33*	34	13	42*	41	10	35*	42	9	40*	35	5	32*	11
16	45*	40	9	70	88	1	32*	28	9	137	131	14	40*	37	11	24*	3	10	0*	7	15	k	3
11	k	6	11	k	10	2	0*	13	10	54*	50	13	k	2	13	k	6	14	k	3	0	50*	35
0	0*	33	0	0*	15	4	6*	16	12	30*	20	0	79	88	0	119	115	0	238	237	1	0*	11
1	0*	23	1	0*	27	5	14*	23	12	k	7	1	0*	17	1	30*	27	1	134	121	2	0*	17
2	80	82	2	3*	30	6	74	75	12	k	7	2	85	84	2	95	98	2	0*	14	3	47*	50
3	21*	4	3	59	65	7	33*	27	0	0*	8	3	147	136	3	55*	33	3	129	132	3	129	132
4	88	91	4	36*	33	8	21*	9	1	0*	8	4	103	94	4	109	109	4	0*	27	5	40	95
5	18*	17	5	19*	20	9	36*	42	2	0*	12	5	54*	11	5	40*	22	5	40	95	5	40	95
6	45*	32	12	k	0	10	32*	15	3	35*	4	6	83	82	6	100	105	6	215	213	6	215	213
7	0*	24	11	0*	15	4	15*	14	7	44*	19	7	55	28	7	55	28	7	130	122	7	130	122
8	52*	37	12	59	54	5	19*	7	8	45*	59	8	72	70	8	72	70	8	27*	2	8	27*	2

The structure factors marked with an asterisk can be considered unobserved at the 10% significance level, those which were derived from a negative net intensity were given a value of zero

sulfur bond lengths in the centric space group can be explained (see later).

In changing from refinement in the centric space group to the acentric, the overall residual decreased slightly from 0.096 to 0.093. In terms of the Hamilton R (significance) test (HAMILTON, 1965), this difference is significant, as the ratio of weighted residuals for the two space groups, 1.032, is larger than the expected value, 1.007, at the $\frac{1}{2}0/0$ significance level, for the change in the number of parameters and the number of observations used. However, criteria for the acceptance of the Hamilton test when applied to space group differences have been discussed earlier (NYBURG, OZIN and SZYMAŃSKI, 1971). It is felt that the ill-conditioned refinement, the larger standard deviations, and the

gross distortions of chemically equivalent bonds in the acentric case contradict the result of the Hamilton test. In the absence of any further evidence to support it, the result of the test should be discounted and the centric space group should be chosen as being correct for the structure. Nevertheless, for the sake of completeness, the parameters from the acentric refinement are set out in Table 1 as Data Set VI. The parameters from the centric refinement, which are considered as being the most accurate in the present work, are set out in Data Set V, Table 1.

Comparison of refinement results

The atomic parameters from the four refinements of the present study and those obtained by earlier workers are all listed in Table 1. Refinement Set I is taken from AZAROFF and BUEGER (1955), Refinement Set II from FLEET (1970). Refinement III consists of the data from crystal 1, refined in the centric space group. Set IV consists of the data from crystal 2 using only reflections considered as observed at the 10⁰/₀ significance level. Sets V and VI are the data from crystal 2 refined in space groups *Pcmn* and *Pc2₁n* respectively, but with all data being considered as observed. With the exception of Refinement Set VI, which should be considered separately, there is good agreement between the positional parameters determined in this present work (Sets III, IV, V). There are, however, significant differences between the atomic positions in Sets I and V. The differences are 0.025, 0.024, 0.029, 0.046 Å for Cu, Fe, S(1) and S(2), respectively. Surprisingly, some differences between the more recent values in Set II and Set V are even larger—0.026, 0.015, 0.117, 0.056 Å.

It is difficult to compare the thermal parameters of Sets I and II with those of the present work because of the use of an overall temperature factor in Set I, and individual, but isotropic temperature factors in Set II. It can be said, however, that the values obtained in Set II are within 2 σ (FLEET's σ) of our mean isotropic temperature factors. Despite the suspected systematic errors in Refinement Set III, the positional parameters, and most of the thermal parameters, agree well with our final values (Set V), with the exception of the U_{22} values in the two sets, which are grossly different. This is no doubt caused by the fact that the *b*-axis direction was approximately normal to the irregular hexagonal plate, and the absorption corrections are likely to be very poorly evaluated in this direction. As is often the case, it appears that the thermal parameters may have "taken up the slack" in this refinement.

The difference syntheses calculated at the end of the refinements for Sets IV and V showed positive and negative excursions above the level of significance. However, these did not fall into a systematic pattern expected from aspherical scattering of the atoms. Some positive peaks of density $1.5e/\text{\AA}^3$ were found in or near the interatomic regions, but not all these regions had positive peaks, nor were the peaks found restricted to such regions. Consequently, no inference could be drawn from these peaks. It was felt that although the use of spherical form factors in the refinement was a contributing factor to the residual errors, an attempt to use aspherical form factors would not be justified. At the atomic sites themselves, no features were observed; this seems to substantiate the choice of the scattering curves, though this is not a sensitive test.

Refinement Set VI has been included for the sake of completeness, though it is felt that acceptance of the noncentric space group is not warranted. It can be seen that for Set VI, the values of the refined positional parameters, or the mean of the refined parameters (in the case where mirror-related atoms are now independent), or the mean of y , $\frac{1}{2}-y$ for Fe and S(2) are within one standard deviation of the values of Set V. The agreement in the thermal parameters is not as good. This is probably caused by the fact that U_{12} and U_{23} are now refinable parameters for Cu and S(1), and that their refinement away from zero causes the corresponding cross-product terms for the other two atoms to change significantly.

Discussion of the structure

Figure 1 illustrates the structure of cubanite projected down the a and c axes, and shows the nearly hexagonal close-packed layers of sulfur atoms found in the structure. The layers themselves, however, are not ideally planar. Within each wurtzitic slab $b/2$ wide, the sulfur on the mirror plane is displaced in the c direction by 0.057 \AA relative to the two sulfur atoms not on the mirror plane, and there is a displacement of about 0.2 \AA along the c direction between sulfur layers in adjacent wurtzitic slabs.

Figure 2*a* shows the geometry around the two atoms Cu and S(1) on the mirror plane and Fig. 2*b* shows the corresponding geometry for the Fe and S(2) atoms which are not on the mirror plane. More details of bond lengths and angles with standard deviations are found in Table 2.

The full list of observed and calculated structure factors is given in Table 3, where the values of F_o are given as derived directly from the mean net count of intensity. The asterisks denote the reflections that are considered as unobserved in Data Set IV.

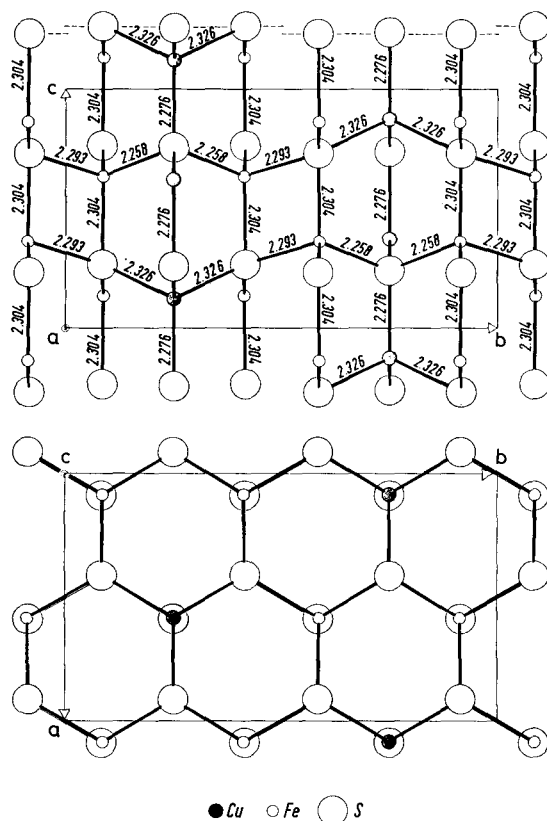


Fig. 1. The structure of cubanite projected down the a and c axes. The upper diagram also illustrates the relative displacement in the c direction of the close-packed sulfur layers between adjacent wurtzitic slabs $b/2$ wide

The structure of cubanite, as described by BUERGER (1945) and more recent workers, is basically correct. However, the present refinement has yielded a more consistent set of bond lengths and angles, than have been given in some recent work. Particularly significant is the shortening of the Cu—S(1) bond to 2.291(1)₃, from the value reported by FLEET as 2.433(11) Å, and that the mean Cu—S distance,

$2.305 \pm 0.02 \text{ \AA}$, is significantly less than the mean given previously $2.34 \pm 0.09 \text{ \AA}$ (FLEET, 1970). The values given here agree better with those given by AZAROFF and BUEGER (1955): $\text{Cu—S}(1) = 2.29_2$, mean $\text{Cu—S} = 2.31 \pm 0.04 \text{ \AA}$. The mean Cu—S distance, 2.30_5 \AA , compares very well with that recently found in chalcopyrite, $2.302(1) \text{ \AA}$ (HALL and STEWART, 1973) and the Fe—S distance in chalcopyrite, $2.257(1) \text{ \AA}$, is in good agreement with the two shorter Fe—S distances in cubanite.

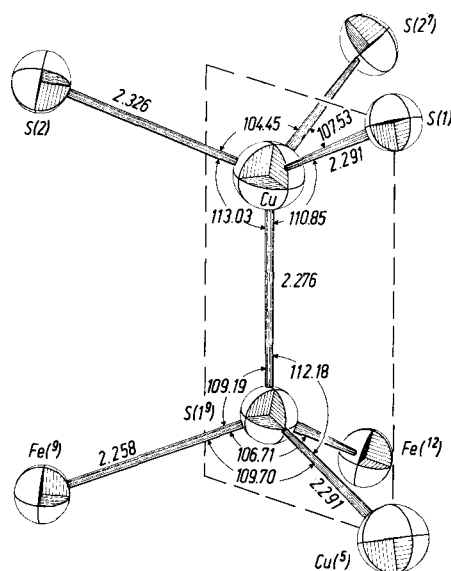


Fig. 2a. Bond lengths and angles around Cu and S(1), the atoms on the mirror plane, which is shown as the broken line

The two Fe—S bonds to the two sulfur atoms, $2.304(1)$, $2.293(1) \text{ \AA}$, which define the shared tetrahedral edge in the structure are longer than the other two Fe—S distances, $2.264(1)$ and $2.258(1) \text{ \AA}$. This has been noted earlier (FLEET, 1970) but the individual bond lengths now follow a systematic pattern which, together with the distortions from tetrahedral symmetry around the metals, can be described in terms of a Fe—Fe repulsion force. This is in contrast to the Fe—Fe attraction force suggested by FLEET (1970). Such a repulsion should result in a lengthening of the adjacent $\text{Fe—S}(2)$ bonds, a shortening of the $\text{S}(2)—\text{S}(2)$ distances, and a decrease in the $\text{S}(2)—\text{Fe—S}(2)$ angle. The two Fe—S bonds are longer, as noted above, the $\text{S}(2)—\text{S}(2)$ tetrahedral-

edge distance is decreased to 3.642(1) Å, compared with the mean of the other five edges 3.737 ± 0.02 Å².

The S(2)—Fe—S(2) angle is decreased to 104.83(3)°, compared with the expected tetrahedral value. A Fe—Fe repulsion would also result in a lengthening of the two metal-sulfur bonds attached³ to S(2)⁹, *i.e.*, S(2)⁹—Cu⁹, S(2)⁹—Fe⁹, and a shortening of iron-sulfur bonds attached to Fe, *i.e.*, Fe—S(1)², Fe—S(2). However, the Fe—S(2) is

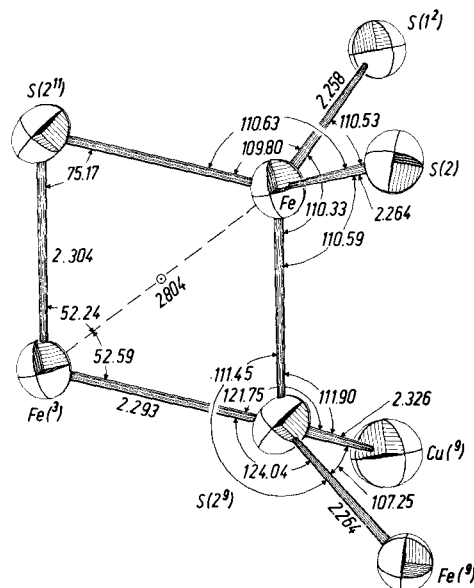


Fig. 2b. Bond lengths and angles around Fe and S(2) which are in general positions in the structure. The close approach of 2.804 Å between two Fe atoms across a centre of symmetry is shown. Bond lengths are in Å units, bond angles in degrees

symmetry-related to the Fe⁹—S(2)⁹ bond, so one could reasonably expect the expansion and contraction forces to cancel out. This would

² The value of 4.04 Å, given in the text by FLEET (1970, p. 284) for the S(2)—S(2) distance across the centre of symmetry, appears to be in error. The corresponding value in his Table 5 (3.696 Å), is correct as calculated from his atomic parameters. The use of the value 4.04 Å in his discussion detracts from his reasoning that this S(2)—S(2) distance has been lengthened, “compared to the average S—S distance of S atoms coordinated about Fe, 3.70 Å”. This study shows, in fact, that this is by far the shortest of the tetrahedral edges around iron.

³ A superscript indicates an atom related to the equivalent atom of *xyz* by the symmetry operation listed at the end of Table 2.

