A refinement of the structure of cubanite, $CuFe_2S_3$*

By J. T. Szymański

Mineral Sciences Division, Mines Branch, Department of Energy,
Mines and Resources, Ottawa, Ontario**

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 mit-geteilten 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: $Cu-S = 2,276(1)$ bis $2,326(1)$ Å, $Fe-S = 2,258(1)$ bis $2,304(1)$ Å. Die Mehrdeutigkeit der Bestimmung der Raumgruppe, $Pcmn$ oder $Pc2_1n$, wurde untersucht und die frühere Wahl der zentrosymmetrischen Raumgruppe $Pcmn$ 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 $Pcmn$ and $Pc2_1n$ has been investigated, and the earlier choice of the centric space group $Pcmn$ 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

---

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, $Cu_9Fe_8S_{16}$, (HALL and GABE, 1972), mooihoekite, $Cu_9Fe_9S_{16}$, (HALL and ROWLAND, 1973), and haycockite, $Cu_8Fe_{10}S_{16}$, (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 $Cu_{1.01}Fe_{2.00}S_{3.00}$.

Cubanite, $CuFe_2S_3$. Formula weight: 271.43.

Crystal System: orthorhombic.

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

Space group: $Pcmn$ ($Pnma$ with cba), or
$$Pc2_1n \ (Pna2_1 \text{ with } bca) \text{ from systematic absences;}$$
$Pcmn$ favoured from structure analysis.

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

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

Density: $D_{calc} = 4.024$ g. cm^3; $Z = 4$.

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 $MoK\alpha$ 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(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 Mo$K\alpha$ radiation and a θ-2θ scan mode. A scan speed of 2°/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 $T = \exp\left[-2\pi^2\,(U_{11}a^{*2}h^2 + 2U_{12}a^*b^*hk + \cdots)\right]$

The mean isotropic temperature factor is $<B> = 8\pi^2 <U>$

Atom	Site	Refinement set*	X/a	Y/b	Z/c	$U_{11} \cdot 10^2$	$U_{22} \cdot 10^2$	$U_{33} \cdot 10^2$	$U_{12} \cdot 10^2$	$U_{13} \cdot 10^2$	$U_{23} \cdot 10^2$	$<B>$
Cu	4c	I	0.583	1/4	0.127	2.09[a]						1.63 Å²
		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
	4a	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
	4a	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
	4a	VI	0.0850(2)	0.4113(2)	0.1365(2)	1.10(3)	1.08(4)	1.04(3)	0.09(3)	0.06(2)	−0.01(3)	0.85
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
	4a	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
	4a	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
	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 $Fe^{2^{1}/_{2}+}$ oxidation state should be used for iron in order to maintain charge neutrality in the structure[1]. 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 TOMIIE 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). Cu tetrahedron			(ii). 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. $1 + x, y, z$
2. $-1 + x, y, z$
3. $-x, -y, -z$
4. $1\frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2} + z$
5. $1\frac{1}{2} - x, \frac{1}{2} - y, -\frac{1}{2} + z$
6. $1 + x, \frac{1}{2} - y, z$
7. $x, \frac{1}{2} - y, z$
8. $\frac{1}{2} - x, y, \frac{1}{2} + z$
9. $\frac{1}{2} - x, y, -\frac{1}{2} + z$
10. $\frac{1}{2} + x, -y, \frac{1}{2} - z$
11. $-\frac{1}{2} + x, -y, \frac{1}{2} - z$
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* (×10)

0 k 0

k	F_o	F_c
2	236	255
4	34	24
6	2680	2563
8	288	275
10	185	168
12	1597	1583
14	184	186
16	184	182
18	770	780
20	130	113
22	143	145
24	326	349
26	52	66

0 k 2

k	F_o	F_c
0	1412	1460
1	1431	1484
2	113	111
3	511	488
4	155	150
5	1154	1141
6	1126	1053
7	1200	1168
8	32*	26
9	335	308
10	117	109
11	520	502
12	686	676
13	640	625
14	0*	18
15	197	189
16	76	67
17	186	179
18	345	342
19	326	331
20	0*	22
21	128	125
22	16*	38
23	52*	50
24	152	147
25	166	176
26	24*	15

0 k 4

k	F_o	F_c
0	865	934
1	41	49
2	124	121
3	166	166
4	0*	10
5	75	62
6	663	645
7	43	45
8	134	129
9	83	86
10	113	102
11	45*	54
12	293	277
13	27*	31
14	90	78
15	50*	47
16	130	129
17	55	29
18	128	142
19	0*	6
20	26*	47
21	0*	33
22	106	112
23	0*	14
24	63	81
25	33*	9

0 k 6

k	F_o	F_c
0	301	309
1	965	987
2	220	223
3	456	470
4	234	237
5	759	773
6	270	281
7	845	855
8	144	146
9	360	363
10	184	183
11	421	424
12	184	187
13	560	568
14	69	76
15	240	237
16	106	122
17	186	180
18	66	84
19	318	329
20	30*	32
21	134	137
22	75	74
23	67	57
24	38*	28

0 k 8

k	F_o	F_c
0	1024	1038
1	296	311
2	108	109
3	474	470
4	51*	55
5	227	238
6	886	897
7	299	302
8	106	114
9	357	357
10	0*	14
11	141	136
12	598	603
13	233	229
14	96	86
15	209	221
16	49*	52
17	67	58
18	331	338
19	151	146
20	66	57
21	113	118
22	57	55

0 k 10

k	F_o	F_c
0	398	403
1	143	140
2	96	79
3	0*	30
4	96	94
5	112	111
6	353	359
7	141	135
8	70	50
9	25*	9
10	83	90
11	70	65
12	263	259
13	104	109
14	0*	23
15	19*	14
16	60	73
17	40*	27
18	159	158
19	70	76

0 k 12

k	F_o	F_c
0	150	148
1	31*	21
2	44*	12
3	108	106
4	31*	36
5	58	29
6	138	133
7	0*	8
8	0*	12
9	99	92
10	49*	52
11	44*	27
12	93	97
13	0*	15
14	38*	19
15	70	68

0 k 14

k	F_o	F_c
0	91	83
1	161	153
2	104	92
3	74	68
4	114	108
5	132	129
6	63	77
7	153	144
8	60	61
9	74	58

1 k 0

k	F_o	F_c
1	0*	47
3	1855	1778
5	143	133
7	86	69
9	1175	1130
11	125	111
13	98	97
15	584	580
17	71	71
19	84	86
21	254	269
23	36*	43
25	56	61

1 k 1

k	F_o	F_c
0	449	424
1	54	35
2	1075	1054
3	483	471
4	1103	1052
5	100	97
6	344	311
7	72	69
8	615	577
9	249	230
10	662	631
11	58	64
12	201	184
13	106	94
14	233	226
15	57	51
16	331	327
17	25*	30
18	117	112
19	82	91
20	89	76
21	46*	36
22	151	170
23	16*	19
24	60	65
25	60	69
26	23*	17

1 k 2

k	F_o	F_c
0	265	265
1	69	73
2	729	731
3	726	684
4	750	733
5	36	34
6	227	209
7	70	67
8	419	393
9	474	452
10	447	432
11	0*	2
12	132	121
13	40*	44
14	149	151
15	256	255
16	217	225
17	25*	11
18	70	79
19	0*	26
20	56	50
21	114	117
22	106	122
23	0*	9
24	60	50
25	36*	14
26	35*	10

1 k 3

k	F_o	F_c
0	672	672
1	181	185
2	993	1006
3	1707	1721
4	1026	1030
5	230	230
6	549	527
7	53	47
8	594	576
9	1198	1193
10	700	682
11	164	165
12	328	319
13	32*	35
14	245	241
15	631	643
16	381	384
17	89	98
18	188	182
19	70	54
20	74	82
21	290	300
22	208	207
23	60	55
24	85	97
25	6*	44

1 k 4

k	F_o	F_c
0	79	81
1	35*	24
2	57	34
3	404	412
4	25*	29
5	67	63
6	53	55
7	58	38
8	30*	35
9	226	204
10	40*	25
11	46*	47
12	40*	26
13	83	65
14	18*	22
15	87	91
16	0*	11
17	40*	27
18	40*	18
19	63	65
20	0*	10
21	42*	53
22	35*	2
23	14*	18
24	34*	12
25	51	48

1 k 5

k	F_o	F_c
0	189	188
1	73	56
2	330	320
3	1466	1519
4	310	308
5	21*	34
6	152	151
7	125	124
8	189	186
9	1071	1088
10	204	182
11	77	65
12	82	78
13	131	135
14	91	80
15	621	619
16	96	98
17	63	56
18	47*	21
19	103	114
20	35*	29
21	295	307
22	61	56
23	29*	41
24	41*	1

1 k 6

k	F_o	F_c
0	253	261
1	116	122
2	456	466
3	155	160
4	480	488
5	94	95
6	227	226
7	104	108
8	301	300
9	121	126
10	355	362
11	65	55
12	160	158
13	80	76
14	138	144
15	54*	69
16	218	222
17	38*	26
18	102	97
19	56	49
20	51*	54
21	27*	26
22	122	122
23	0*	10
24	64	52

1 k 7

k	F_o	F_c
0	157	161
1	119	104
2	250	248
3	61	61
4	269	269
5	108	104
6	142	143
7	50*	58
8	153	148
9	73	65
10	218	210
11	76	69
12	116	114
13	0*	13
14	67	65
15	62	42
16	141	149
17	58	38
18	78	88
19	39*	10
20	0*	19
21	26*	19
22	96	97
23	0*	19

1 k 8

k	F_o	F_c
0	253	252
1	59	41
2	141	145
3	503	509
4	159	163
5	62	57
6	219	218
7	50*	8
8	93	96
9	377	383
10	138	138
11	61	50
12	144	148
13	48*	19
14	50*	48
15	236	233
16	100	95
17	27*	35
18	89	85
19	45*	29
20	0*	18
21	118	122
22	43*	56

1 k 9

k	F_o	F_c
0	52	44
1	114	115
2	279	284
3	211	216
4	297	291
5	66	67
6	30*	41
7	148	142
8	208	204
9	171	171
10	231	224
11	0*	25
12	31*	30
13	129	135
14	115	112
15	112	119
16	136	138
17	18*	3
18	53	18
19	103	105
20	51	49
21	67	71

1 k 10

k	F_o	F_c
0	0*	18
1	41*	43
2	77	62
3	195	196
4	51*	68
5	9*	31
6	46*	11
7	47*	45
8	46*	42
9	164	157
10	63	60
11	0*	17
12	0*	2
13	43*	40
14	17*	21
15	98	103
16	0*	46
17	9*	6
18	29*	9
19	6*	30

1 k 11

k	F_o	F_c
0	267	262
1	137	119
2	264	265
3	199	186
4	287	290
5	115	105
6	246	236
7	107	103
8	188	186
9	150	143
10	257	250
11	66	73
12	176	176
13	73	70
14	98	100
15	98	87
16	174	178
17	24*	41

1 k 12

k	F_o	F_c
0	52*	52
1	33*	15
2	20*	15
3	80	74
4	42*	9
5	27*	4
6	34*	48
7	27*	26
8	46*	16
9	65	60
10	0*	4
11	0*	6
12	27*	39
13	20*	30
14	0*	13
15	14*	40

1 k 13

k	F_o	F_c
0	129	127
1	0*	18
2	32*	27
3	240	235
4	20*	32
5	0*	5
6	121	113
7	49*	31
8	39*	19
9	203	192
10	18*	31
11	39*	4
12	74	81

1 k 14

k	F_o	F_c
0	40*	38
1	57	53
2	97	74
3	29*	42
4	97	78
5	53*	40
6	40*	35
7	41*	55
8	60	55

2 k 0

k	F_o	F_c
0	1540	1680
2	121	125
4	9*	8
6	1342	1297
8	137	134
10	59	68
12	749	729
14	94	91
16	85	81
18	356	355
20	49*	55
22	71	66
24	152	159
26	34*	32

2 k 1

k	F_o	F_c
0	408	439
1	1057	1069
2	55	60
3	428	383
4	40	38
5	822	785
6	360	373
7	842	807
8	87	74
9	268	246
10	95	89
11	363	355
12	97	76
13	451	443
14	58	38
15	161	149
16	109	96
17	128	131
18	50*	34
19	230	234
20	30*	21
21	90	89
22	72	82
23	61	39
24	0*	29
25	108	120
26	9*	15

2 k 2

k	F_o	F_c
0	617	607
1	699	725
2	79	47
3	225	211
4	65	65
5	537	528
6	495	465
7	563	542
8	0*	10
9	151	136
10	49	49
11	246	233
12	302	297
13	310	293
14	37*	8
15	85	87
16	20*	31
17	81	84
18	147	150
19	152	158
20	33*	10
21	70	58
22	44*	18
23	36*	24
24	57	65
25	74	84
26	30*	7

2 k 3

k	F_o	F_c
0	1694	1764
1	1006	1036
2	197	201
3	621	622
4	103	95
5	782	768
6	1490	1462
7	855	837
8	186	186
9	434	421
10	26*	14
11	386	372
12	896	890
13	521	506
14	113	122
15	256	248
16	45*	54
17	152	143
18	431	446
19	271	281
20	64	71
21	144	138
22	64	53
23	23*	42
24	185	198
25	130	147

2 k 4

k	F_o	F_c
0	414	434
1	40*	13
2	71	65
3	90	87
4	21*	9
5	0*	21
6	314	303
7	56	12
8	69	66
9	63	51
10	46*	41
11	38*	20
12	156	140
13	45*	7
14	38*	40
15	0*	29
16	73	58
17	34*	11
18	60	73
19	40*	4
20	0*	24
21	47*	19
22	12*	51
23	26*	6
24	32*	41
25	36*	6

2 k 5

k	F_o	F_c
0	1505	1554
1	315	310
2	29*	15
3	170	176
4	107	102
5	249	237
6	1288	1310
7	239	226
8	55	49
9	114	115
10	140	137
11	120	115
12	816	830
13	122	124
14	75	58
15	0*	45
16	130	128
17	54*	46
18	443	441
19	53*	72
20	38*	46
21	0*	6
22	83	97
23	0*	14
24	203	208

2 k 6

k	F_o	F_c
0	129	129
1	440	448
2	94	98
3	188	191
4	103	105
5	344	350
6	106	117
7	390	389
8	64	65
9	154	150
10	93	82
11	193	192
12	78	77
13	258	260
14	0*	34
15	114	100
16	30*	56
17	73	82
18	26*	34
19	150	151
20	38*	14
21	71	59
22	31*	34
23	11*	26
24	6*	11

2 k 7

k	F_o	F_c
0	61	67
1	264	253
2	100	99
3	155	147
4	84	73
5	197	186
6	77	71
7	242	229
8	82	80
9	123	122
10	35*	25
11	96	95
12	64	58
13	176	170
14	46*	48
15	100	99
16	45*	7
17	38*	36
18	34*	29
19	116	119
20	0*	26
21	61	71
22	11*	15
23	37*	6

2 k 8

k	F_o	F_c
0	472	479
1	135	138
2	61	50
3	209	205
4	22*	24
5	97	104
6	419	414
7	143	135
8	65	53
9	34*	11
10	0*	8
11	55	59
12	275	278
13	105	104
14	30*	41
15	102	98
16	43*	25
17	46*	25
18	151	156
19	56	67
20	24*	27
21	55	53
22	0*	26

2 k 9

k	F_o	F_c
0	224	218
1	293	298
2	91	98
3	41*	57
4	139	139
5	252	249
6	188	193
7	265	264
8	34*	49
9	69	47
10	143	147
11	147	156
12	146	143
13	173	181
14	33*	14
15	44*	30
16	122	124
17	64	77
18	84	93
19	98	102
20	16*	5

2 k 10

k	F_o	F_c
0	183	190
1	81	72
2	51*	41
3	0*	9
4	48*	49
5	61	57
6	170	170
7	51*	69
8	53*	26
9	93	82
10	16*	47
11	33*	34
12	125	122
13	49*	55
14	0*	12
15	0*	8
16	58	38
17	27*	14
18	77	74

Table 3. (Continued)

Column group 1

k	F_o	F_c
19	52	37
2 k 11		
0	200	189
1	276	285
2	115	115
3	266	262
4	131	114
5	232	229
6	181	165
7	287	275
8	78	89
9	222	214
10	85	87
11	140	142
12	123	113
13	216	215
14	46*	55
15	140	147
16	57	53
17	68	67
2 k 12		
0	68	66
1	0*	6
2	52*	3
3	71	55
4	0*	10
5	25*	10
6	66	59
7	0*	4
8	0*	10
9	45*	47
10	8*	19
11	0*	10
12	57	43
13	0*	10
14	22*	11
15	0*	35
2 k 13		
0	240	237
1	47*	32
2	35*	11
3	127	123
4	51*	24
5	48*	25
6	223	215
7	56	33
8	19*	0
9	96	98
10	34*	34
11	22*	16
12	161	160
2 k 14		
0	43*	38
1	70	70
2	32*	40
3	42*	27
4	58	48
5	58	58
6	23*	35
7	66	66
8	0*	27
3 k 0		
1	64	70
3	2633	2572
5	224	215
7	127	117
9	1874	1867
11	197	193
13	187	176
15	1022	1019
17	119	128
19	156	160
21	467	485
23	74	79
25	105	113
3 k 1		
0	90	48
1	0*	17
2	36	22
3	75	49
4	35*	23
5	25*	14
6	47	36
7	46	12
8	82	13
9	43*	39
10	40*	16
11	0*	8
12	12*	21
13	39*	6
14	0*	6
15	40*	23
16	45*	10
17	35*	4

Column group 2

k	F_o	F_c
18	0*	11
19	0*	4
20	34*	2
21	0*	9
22	23*	6
23	24*	2
24	34*	6
25	20*	3
26	0*	1
3 k 2		
0	425	442
1	117	116
2	1130	1159
3	1086	1054
4	1172	1172
5	58	55
6	368	348
7	122	114
8	682	660
9	792	780
10	763	744
11	27*	3
12	239	220
13	77	79
14	273	269
15	452	446
16	418	410
17	0*	20
18	155	149
19	46*	48
20	94	91
21	200	207
22	216	228
23	32*	17
24	93	93
25	0*	26
3 k 3		
0	60	62
1	27*	15
2	21*	28
3	93	92
4	43	30
5	0*	10
6	54	50
7	0*	13
8	15*	18
9	81	67
10	12*	22
11	42*	4
12	24*	31
13	43*	9
14	0*	9
15	55	38
16	0*	14
17	29*	1
18	21*	16
19	32*	5
20	0*	4
21	33*	18
22	35*	8
23	29*	0
24	44*	8
25	25*	3
3 k 4		
0	143	140
1	42	41
2	46	56
3	653	656
4	54	48
5	106	106
6	104	101
7	81	66
8	50	57
9	379	356
10	17*	37
11	91	84
12	73	55
13	131	118
14	0*	36
15	179	177
16	0*	13
17	50*	52
18	49*	38
19	123	119
20	30*	18
21	97	105
22	47*	7
23	13*	35
24	0*	25
25	79	89
3 k 5		
0	0*	15
1	15*	11
2	7*	10
3	68	67
4	17*	11

Column group 3

k	F_o	F_c
5	26*	9
6	0*	14
7	27*	9
8	0*	8
9	55	50
10	19*	8
11	0*	5
12	33*	9
13	41*	6
14	21*	5
15	51*	30
16	0*	4
17	27*	2
18	35*	4
19	0*	4
20	0*	2
21	28*	15
22	0*	1
23	37*	1
24	0*	1
3 k 6		
0	436	443
1	205	209
2	777	799
3	266	278
4	822	840
5	167	164
6	391	389
7	178	189
8	528	525
9	206	215
10	641	639
11	100	97
12	283	278
13	129	137
14	258	257
15	99	115
16	392	402
17	44*	46
18	170	172
19	65	89
20	91	97
21	32*	44
22	210	224
23	18*	17
3 k 7		
0	26*	10
1	0*	11
2	14*	12
3	0*	13
4	32*	12
5	7*	10
6	37*	9
7	31*	12
8	61	9
9	0*	14
10	37*	9
11	47*	5
12	20*	5
13	38*	10
14	0*	5
15	0*	5
16	37*	4
17	29*	2
18	0*	1
19	46*	6
20	23*	2
21	0*	2
22	17*	1
3 k 8		
0	437	440
1	86	67
2	249	256
3	879	900
4	279	288
5	93	98
6	382	383
7	0*	8
8	169	169
9	686	687
10	240	247
11	93	88
12	257	264
13	39*	41
14	91	84
15	426	424
16	179	172
17	54*	63
18	136	153
19	45*	56
20	40*	31
21	216	223
3 k 9		
0	0*	29
1	51*	17
2	56*	19

Column group 4

k	F_o	F_c
3	27*	2
4	16*	20
5	0*	14
6	0*	25
7	0*	17
8	39*	14
9	0*	2
10	0*	16
11	25*	9
12	39*	17
13	0*	12
14	0*	8
15	0*	2
16	0*	10
17	28*	4
18	26*	10
19	6*	8
20	0*	3
3 k 10		
0	0*	23
1	80	84
2	113	119
3	354	361
4	134	131
5	55	62
6	0*	12
7	101	90
8	97	82
9	282	289
10	134	116
11	34*	34
12	0*	9
13	68	79
14	63	41
15	183	192
16	89	87
17	0*	12
18	12*	19
19	63	59
3 k 11		
0	0*	25
1	46*	6
2	1*	13
3	46*	6
4	0*	13
5	27*	5
6	38*	22
7	0*	6
8	32*	10
9	17*	5
10	30*	11
11	29*	3
12	12*	16
13	32*	4
14	0*	6
15	0*	8
16	40*	8
17	0*	2
3 k 12		
0	95	103
1	58	23
2	39*	22
3	146	134
4	43*	11
5	0*	6
6	108	96
7	0*	43
8	54	25
9	120	109
10	0*	10
11	0*	15
12	78	77
13	62	51
14	46*	21
3 k 13		
0	0*	5
1	0*	2
2	24*	4
3	33*	3
4	43*	4
5	0*	1
6	0*	5
7	39*	2
8	26*	4
9	31*	3
10	0*	4
11	0*	1
3 k 14		
0	85	66
1	96	95
2	134	133
3	74	78
4	154	141
5	85	72
6	69	61

Column group 5

k	F_o	F_c
7	111	100
4 k 0		
0	1387	1488
2	40	33
4	60	57
6	1271	1219
8	103	75
10	122	101
12	744	732
14	65	64
16	115	98
18	357	372
20	51*	44
22	80	75
24	154	171
4 k 1		
0	376	431
1	785	784
2	43	46
3	288	265
4	40*	27
5	620	587
6	280	263
7	645	622
8	53	58
9	201	189
10	85	74
11	288	285
12	93	82
13	374	368
14	59	34
15	123	123
16	72	86
17	115	111
18	34*	46
19	199	203
20	0*	23
21	74	76
22	46*	74
23	13*	33
24	0*	33
25	85	106
4 k 2		
0	579	588
1	587	557
2	54	44
3	215	211
4	63	60
5	446	411
6	530	505
7	465	437
8	32*	12
9	150	144
10	20*	49
11	203	196
12	339	328
13	258	259
14	41*	6
15	101	97
16	18*	32
17	77	76
18	174	168
19	135	149
20	0*	9
21	56	65
22	0*	18
23	0*	22
24	65	74
25	70	82
4 k 3		
0	1332	1391
1	783	786
2	159	154
3	463	459
4	927	928
5	617	592
6	1155	1164
7	667	661
8	158	150
9	347	329
10	0*	12
11	307	301
12	716	722
13	429	422
14	100	103
15	211	204
16	39*	47
17	118	119
18	370	370
19	242	243
20	56	62
21	115	117
22	49*	47
23	47*	34
24	156	167
25	118	129

Column group 6

k	F_o	F_c
4 k 4		
0	277	272
1	27*	46
2	11*	13
3	39*	29
4	57	33
5	34*	44
6	210	193
7	25*	40
8	42*	28
9	34*	15
10	78	65
11	38*	31
12	109	97
13	48*	24
14	0*	22
15	32*	12
16	88	71
17	0*	16
18	47*	60
19	0*	7
20	0*	16
21	0*	11
22	44*	58
23	38*	7
24	0*	36
4 k 5		
0	1217	1258
1	270	245
2	0*	13
3	123	127
4	97	85
5	198	194
6	1069	1068
7	195	190
8	30*	39
9	88	81
10	115	121
11	102	102
12	691	691
13	98	115
14	45*	49
15	0*	29
16	104	116
17	25*	43
18	377	375
19	57	68
20	62	41
21	26*	2
22	71	88
23	19*	13
24	176	179
4 k 6		
0	152	168
1	411	425
2	83	98
3	250	260
4	91	104
5	337	335
6	142	148
7	379	379
8	70	67
9	205	204
10	87	84
11	193	191
12	90	95
13	263	263
14	28*	37
15	134	133
16	50*	58
17	78	84
18	47*	43
19	153	157
20	34*	16
21	85	76
22	7*	36
23	17*	27
4 k 7		
0	70	57
1	215	224
2	105	90
3	145	144
4	57	69
5	173	168
6	24*	57
7	219	210
8	70	73
9	126	123
10	22*	30
11	105	90
12	46*	43
13	167	161
14	41*	45
15	96	98
16	0*	4
17	0*	36

Column group 7

k	F_o	F_c
18	0*	22
19	99	112
20	58	25
21	71	68
22	31*	10
4 k 8		
0	475	469
1	146	150
2	49*	36
3	218	232
4	0*	13
5	114	117
6	411	409
7	141	146
8	63	42
9	177	179
10	38*	14
11	66	69
12	279	281
13	113	111
14	42*	34
15	115	112
16	14*	28
17	47*	31
18	157	161
19	73	71
20	36*	23
21	63	60
4 k 9		
0	199	194
1	231	239
2	79	75
3	40*	27
4	117	110
5	207	201
6	184	174
7	209	213
8	45*	35
9	0*	23
10	121	121
11	125	127
12	121	131
13	144	148
14	32*	7
15	49*	15
16	101	105
17	72	63
18	88	85
19	90	84
4 k 10		
0	180	182
1	80	54
2	30*	31
3	0*	12
4	56	37
5	42*	41
6	167	163
7	51*	55
8	17*	21
9	0*	3
10	54*	36
11	0*	24
12	126	119
13	59	46
14	32*	10
15	30*	8
16	60	30
17	0*	9
18	82	73
4 k 11		
0	164	160
1	243	241
2	106	94
3	97	88
4	100	93
5	194	193
6	144	141
7	241	236
8	85	74
9	190	178
10	78	71
11	126	119
12	99	97
13	190	186
14	40*	46
15	123	123
16	45*	44
4 k 12		
0	93	75
1	14*	14
2	16*	17
3	62	43
4	31*	30
5	31*	17

Column group 8

k	F_o	F_c
6	55*	68
7	53	6
8	20*	5
9	41*	38
10	0*	35
11	37*	15
12	59	50
13	31*	5
14	0*	4
4 k 13		
0	211	213
1	26*	25
2	18*	14
3	106	106
4	43*	27
5	56	19
6	192	193
7	23*	27
8	5*	3
9	85	85
10	19*	35
11	29*	12
4 k 14		
0	64	44
1	74	74
2	62	48
3	60	42
4	74	56
5	70	62
5 k 0		
1	53	45
3	991	978
5	90	92
7	38*	26
9	692	673
11	81	82
13	75	60
15	390	370
17	42*	56
19	46*	61
21	181	180
23	0*	35
25	50*	44
5 k 1		
0	288	294
1	26*	15
2	639	624
3	231	210
4	657	643
5	17*	30
6	268	247
7	61	67
8	387	379
9	81	72
10	463	446
11	32*	27
12	162	169
13	106	88
14	168	170
15	44*	35
16	267	263
17	13*	17
18	114	108
19	82	84
20	44*	61
21	51*	31
22	137	146
23	46*	13
24	70	62
25	57	63
5 k 2		
0	142	138
1	17*	36
2	416	407
3	372	344
4	429	419
5	35*	16
6	134	117
7	39*	39
8	266	244
9	272	256
10	289	288
11	7*	2
12	76	86
13	46*	29
14	114	108
15	155	147
16	176	171
17	24*	7
18	49*	61
19	0*	19
20	59	37
21	77	70
22	94	97
23	45*	7

Table 3. *(Continued)*

(orphan)

k	Fo	Fc
24	26*	37

5 k 3

k	Fo	Fc
0	471	493
1	82	77
2	643	647
3	1237	1271
4	714	684
5	122	121
6	418	417
7	0*	5
8	416	404
9	912	921
10	515	506
11	93	104
12	273	280
13	59	48
14	182	187
15	517	526
16	315	314
17	71	71
18	156	169
19	63	56
20	59	67
21	246	256
22	167	178
23	34*	43
24	73	91

5 k 4

k	Fo	Fc
0	77	76
1	20*	29
2	34*	4
3	257	251
4	33*	3
5	71	51
6	72	62
7	49	14
8	24*	8
9	172	160
10	22*	5
11	41*	41
12	43*	41
13	24*	41
14	0*	7
15	97	91
16	0*	8
17	18*	27
18	0*	26
19	0*	45
20	11*	5
21	56	52
22	28*	9
23	34*	18
24	0*	15

5 k 5

k	Fo	Fc
0	124	133
1	56	66
2	185	181
3	1110	1150
4	189	180
5	0*	2
6	119	108
7	126	116
8	115	116
9	868	857
10	126	123
11	1*	33
12	50*	54
13	113	125
14	50*	56
15	505	513
16	68	78
17	46*	38
18	0*	13
19	95	105
20	32*	21
21	258	264
22	52	47
23	34*	31

5 k 6

k	Fo	Fc
0	132	120
1	59	71
2	277	283
3	72	78
4	303	301
5	69	55
6	97	108
7	57	67
8	200	189
9	65	58
10	234	236
11	13*	33
12	87	82
13	53*	51
14	110	94
15	43*	29
16	162	153
17	15*	16
18	50*	54
19	29*	35
20	46*	15
21	0*	10
22	92	87

5 k 7

k	Fo	Fc
0	128	127
1	62	57
2	174	166
3	73	70
4	180	187
5	70	62
6	126	119
7*	40	27
8	109	105
9	60	59
10	175	162
11	44*	46
12	107	103
13	10*	5
14	71	50
15	56*	34
16	105	124
17	10*	28
18	86	80
19	0*	15
20	31*	14
21	40*	16

5 k 8

k	Fo	Fc
0	148	145
1	0*	23
2	86	87
3	340	341
4	105	100
5	24*	37
6	132	128
7	16*	3
8	39*	56
9	263	262
10	101	89
11	78	36
12	84	90
13	36*	20
14	37*	27
15	165	164
16	70	65
17	48*	27
18	52	54
19	39*	25
20	40*	9

5 k 9

k	Fo	Fc
0	78	63
1	109	111
2	226	228
3	180	180
4	236	235
5	70	70
6	38*	56
7	136	133
8	156	166
9	151	149
10	190	186
11	35*	30
12	37*	40
13	118	125
14	94	93
15	105	106
16	116	118
17	35*	5
18	0*	24
19	94	96

5 k 10

k	Fo	Fc
0	0*	3
1	30*	45
2	79	60
3	143	148
4	54*	65
5	33*	33
6	17*	5
7	12*	48
8	27*	42
9	120	119
10	48*	56
11	0*	18
12	0*	10
13	43*	41
14	55*	22
15	81	80
16	55	41
17	0*	6

5 k 11

k	Fo	Fc
0	250	240
1	95	95
2	225	222
3	160	148
4	243	244
5	78	84
6	220	217
7	81	83
8	172	158
9	123	116
10	213	214
11	52	59
12	170	164
13	50*	57
14	94	86
15	78	72

5 k 12

k	Fo	Fc
0	66	54
1	0*	5
2	0*	3
3	50*	48
4	0*	7
5	0*	11
6	55	50
7	38*	5
8	7*	3
9	38*	39
10	0*	12
11	0*	13
12	33*	39
13	17*	11

5 k 13

k	Fo	Fc
0	123	107
1	45*	19
2	44*	26
3	203	199
4	0*	30
5	25*	8
6	105	96
7	16*	30
8*	15	19
9	171	164

5 k 14

k	Fo	Fc
0	0*	17
1	39*	33
2	55	50

6 k 0

k	Fo	Fc
0	1689	1887
2	60	55
4	79	66
6	1603	1605
8	120	113
10	147	144
12	1020	1029
14	106	102
16	149	153
20	67	74
22	118	120
24	247	259

6 k 1

k	Fo	Fc
0	79	78
1	61	29
2	1*	17
3	57	54
4	33*	16
5	33*	23
6	74	69
7	44*	27
8	0*	13
9	49*	39
10	0*	11
11	0*	13
12	53*	45
13	34*	19
14	16*	9
15	23*	24
16	0*	8
17	26*	6
18	0*	21
19	0*	33
20	0*	5
21	43*	13
22	14*	6
23	0*	2
24	0*	7

6 k 2

k	Fo	Fc
0	750	780
1	706	722
2	66	56
3	285	278
4	83	80
5	556	554
6	678	676
7	641	614
8	38*	15
9	234	218
10	79	72
11	308	292
12	456	445
13	401	406
14	0*	9
15	155	160
16	34*	50
17	125	121
18	241	233
19	230	247
20	0*	13
21	102	107
22	48*	30
23	48*	34
24	112	105

6 k 3

k	Fo	Fc
0	131	134
1	57	41
2	0*	17
3	72	78
4	25*	19
5	44*	33
6	110	116
7	85	38
9	38*	58
10	62	16
11	15*	20
12	83	77
13	31*	27
14	26*	4
15	33*	35
16	26*	11
17	0*	10
18	56	41
19	0*	17
20	0*	1
21	32*	19
22	50*	7
23	38*	4

6 k 4

k	Fo	Fc
0	371	376
1	63	43
2	29*	27
3	78	73
4	47*	39
5	43*	44
6	320	300
7	38*	33
8	55	49
9	29*	55
10	100	94
11	17*	32
12	187	188
13	0*	14
14	67	42
15	51*	41
16	110	110
17	49*	17
18	117	120
19	0*	6
20	28*	32
21	30*	29
22	78	92
23	0*	9

6 k 5

k	Fo	Fc
0	94	99
1	34*	17
2	33*	14
3	39*	23
4	36*	15
5	0*	15
6	93	87
7	55	15
8	0*	10
9	47*	17
10	24*	12
11	0*	9
12	64	59
13	0*	9
14	0*	5
15	0*	8
16	34*	9
17	8*	4
18	43*	34
19	29*	3
20	28*	3
21	0*	2
22	0*	6

6 k 6

k	Fo	Fc
0	199	210
1	574	593
2	123	134
3	335	335
4	149	145
5	475	473
6	176	181
7	534	545
8	98	94
9	270	271
10	127	123
11	275	277
12	117	112
13	394	394
14	58	52
15	191	185
16	73	89
17	121	124
18	36*	49
19	236	243
20	39*	22
21	112	109
22	56	57

6 k 7

k	Fo	Fc
0	56	19
1	0*	18
2	15*	17
3	0*	14
4	16*	19
5	0*	16
6	62	16
7	33*	58
8	50*	11
9	0*	10
10	40*	17
11	25*	10
12	42*	10
13	0*	9
14	0*	6
15	0*	4
16	0*	12
17	28*	4
18	0*	5
19	43*	3
20	12*	2
21	0*	1

6 k 8

k	Fo	Fc
0	693	695
1	216	212
2	47*	46
3	320	322
4	0*	8
5	164	163
6	620	612
7	220	211
8	85	60
9	252	253
10	0*	33
11	104	95
12	436	429
13	173	166
14	67	52
15	169	164
16	34*	52
17	64	42
18	246	250
19	108	110

6 k 9

k	Fo	Fc
0	48*	5
1	0*	30
2	30*	24
3	58	43
4	58	26
5	24*	25
6	0*	5
7	20*	28
8	0*	17
9	0*	10
10	6*	23
11	0*	16
12	32*	5
13	18*	20
14	0*	10
15	0*	4
16	49*	16
17	3*	8
18	0*	4

6 k 10

k	Fo	Fc
0	283	292
1	104	103
2	66	65
3	0*	4
4	79	77
5	94	82
6	279	263
7	112	103
8	32*	42
9	0*	13
10	59	75
11	0*	3
12	189	194
13	85	86

6 k 11

k	Fo	Fc
0	32*	9
1	53*	21
2	46*	9
3	34*	38
4	49*	9
5	35*	19
6	39*	8
7	0*	20
8	0*	6
9	24*	31
10	0*	7
11	26*	13
12	25*	6
13	20*	15
14	0*	4

6 k 12

k	Fo	Fc
0	124	112
1	45*	8
2	29*	12
3	92	87
4	15*	30
5	29*	14
6	109	101
7	36*	8
8	37*	6
9	72	75
10	55	42
11	0*	16

6 k 13

k	Fo	Fc
0	0*	6
1	0*	6
2	0*	2
3	38*	8
4	19*	3
5	0*	7
6	25*	6
7	0*	4

7 k 0

k	Fo	Fc
1	39*	46
3	921	930
5	0*	7
7	99	89
9	688	686
11	34*	30
13	92	97
15	388	406
17	39*	31
19	92	81
21	192	207
23	0*	25

7 k 1

k	Fo	Fc
0	180	173
1	32*	11
2	383	388
3	159	144
4	412	408
5	0*	19
6	165	154
7	50*	50
8	252	251
9	101	88
10	322	309
11	0*	22
12	123	116
13	76	70
14	130	121
15	58	59
16	196	197
17	24*	17
18	60	78
19	62	69
20	54	44
21	0*	42
22	108	113
23	28*	14

7 k 2

k	Fo	Fc
0	149	153
1	41*	38
2	282	278
3	411	419
4	304	294
5	94	82
6	135	135
7	39*	6
8	177	179
9	320	316
10	229	226
11	0*	3
12	108	104
13	39*	33
14	97	87
15	177	186
16	150	150
17	0*	5
18	79	75
19	42*	21
20	40*	32
21	86	91
22	81	90
23	0*	6

7 k 3

k	Fo	Fc
0	298	300
1	79	50
2	833	821
3	461	447
4	81	81
5	19*	5
6	604	610
7	365	354
8	78	75
9	183	190
10	40*	37
11	138	131
12	352	361
13	225	234
14	66	54
15	116	120
16	47*	43
17	45*	47
18	181	182
19	138	137
20	30*	34

7 k 4

k	Fo	Fc
0	22*	7
1	33*	31
2	27*	42
3	123	112
4	52	40
5	32*	7
6	37*	6
7	68	57
8	19*	32
9	40*	28
10	0*	6
11	74	67
12	31*	18
13	72	60
14	28*	11
15	0*	9
16	26*	9
17	77	60
18	0*	8
19	45*	40
20	28*	2

7 k 5

k	Fo	Fc
0	47*	64
1	61	52
2	134	136
3	781	783
4	131	138
5	35*	5
6	65	92
7	95	94
8	614	599
9	99	105
10	49*	23
11	39*	21
12	105	102
13	66	49
14	372	370
15	40*	30
16	18*	1
17	89	86
18	13*	19
19	195	196

7 k 6

k	Fo	Fc
0	219	230
1	46*	75
2	264	275
3	123	125
4	287	296
5	54*	61
6	196	205
7	65	71
8	182	190
9	89	92
10	234	243
11	35*	39
12	141	150
13	35*	55
14	114	100
15	50*	49
16	167	165
17	0*	20
18	101	93
19	46*	38
20	4*	40
21	45*	20

7 k 7

k	Fo	Fc
0	128	129
1	54*	54
2	155	144
3	163	163
4	117	121
5	65	56
6	275	264
7	57	33
8	103	96
9	31*	32
10	146	146
11	59	42
12	97	101
13	0*	10
14	49*	47
15	21*	19
16	121	112
17	47*	26
18	69	73
19	35*	5
20	34*	14

7 k 8

k	Fo	Fc
0	180	190
1	52*	6
2	112	108
3	351	340
4	122	120
5	0*	19
6	162	169
7	38*	13
8	70	74
9	266	268
10	101	104
11	0*	21
12	106	120
13	34*	27
14	43*	40
15	162	174
16	75	74
17	0*	18
18	64	71

7 k 9

k	Fo	Fc
0	0*	14
1	82	71
2	175	149
3	145	149
4	159	155
5	68	41
6	24*	13
7	93	90
8	124	110
9	111	125
10	119	124
11	0*	14
12	40*	10
13	89	89
14	50*	62
15	75	88
16	84	80
17	27*	3

7 k 10

k	Fo	Fc
0	0*	4
1	47*	28
2	43*	35
3	138	137
4	46*	41
5	38*	21
6	26*	4
7	0*	30
8	51*	23
9	124	113
10	58	40
11	0*	13
12	25*	8
13	47*	27
14	0*	10
15	82	77

7 k 11

k	Fo	Fc
0	180	167
1	85	65
2	170	161
3	118	108
4	194	179
5	54*	58
6	156	152

Table 3. *(Continued)*

k	F_o	F_c
7	75	57
8	110	113
9	98	85
10	166	160
11	55	42
12	120	115
13	0*	39
7 k 12		
0	0*	34
1	0*	27
2	8*	13
3	57	63
4	44*	8
5	0*	15
6	40*	32
7	20*	34
8	26*	14
9	49*	52
10	0*	3
7 k 13		
0	95	80
1	27*	22
2	0*	16
3	161	160
4	0*	20
8 k 0		
0	508	526
2	27*	32
4	0*	6
6	457	450
8	63	47
10	33*	37
12	302	298
14	56	42
16	33*	47
18	175	165
20	0*	31
22	13*	40
8 k 1		
0	62	55
1	351	361
2	30*	16
3	210	196
4	35*	47
5	282	284
6	38*	45
7	324	327
8	0*	4
9	157	159
10	77	71
11	161	163
12	40*	56
13	223	234
14	39*	7
15	111	112
16	79	76
17	46*	71
18	57	34
19	132	146
20	0*	9
21	67	69
22	68	62
8 k 2		
0	178	186
1	215	228
2	37*	14
3	86	87
4	22*	22
5	184	179
6	165	162
7	196	206
8	30*	3
9	75	75
10	0*	22
11	106	101
12	112	108
13	145	148
14	51*	3
15	69	57
16	50*	17
17	52*	43
18	81	59
19	87	93
20	37*	4
21	57	37
22	40*	11
8 k 3		
0	793	826
1	397	406
2	18*	34
3	310	322
4	0*	9
5	321	318
6	699	716

k	F_o	F_c
7	380	379
8	43*	53
9	251	257
10	47*	43
11	188	184
12	486	481
13	281	280
14	48*	49
15	165	173
16	56	53
17	78	81
18	261	267
19	168	178
20	45*	36
21	99	102
22	51	44
8 k 4		
0	148	157
1	41*	9
2	0*	20
3	52*	57
4	40*	4
5	23*	5
6	125	135
7	17*	12
8	35*	26
9	44*	45
10	35*	25
11	33*	1
12	93	94
13	47*	13
14	47*	23
15	48*	30
16	47*	34
17	0*	1
18	67	58
19	0*	12
20	27*	17
21	39*	18
8 k 5		
0	763	776
1	103	104
2	47*	45
3	72	63
4	80	87
5	86	85
6	691	681
7	110	93
8	29*	5
9*	29	38
10	102	107
11	33*	53
12	487	474
13	56*	70
14	35*	16
15	0*	10
16	95	99
17	0*	24
18	279	275
19	45*	47
20	0*	21
8 k 6		
0	38*	32
1	162	173
2	37*	37
3	52*	63
4	28*	42
5	143	138
6	21*	26
7	175	164
8	13*	26
9	50*	55
10	48*	38
11	89	82
12	0*	14
13	123	123
14	0*	14
15	60	41
16	0*	30
17	32*	36
18	0*	4
19	74	78
20	0*	5
8 k 7		
0	35*	51
1	134	123
2	37*	32
3	98	109
4	58	19
5	103	94
6	48*	44
7	139	128
8	0*	32
9	111	100
10	31*	4
11	45*	55

k	F_o	F_c
12	60	28
13	106	110
14	0*	24
15	75	81
16	20*	12
17	0*	22
18	18*	15
19	83	81
8 k 8		
0	210	220
1	74	57
2	48*	13
3	97	83
4	23*	3
5	47*	42
6	201	195
7	70	60
8	0*	21
9	60	67
10	34*	16
11	0*	23
12	147	139
13	73	50
14	39*	20
15	61	45
16	0*	21
17	0*	8
8 k 9		
0	158	146
1	162	162
2	79	75
3	70	52
4	96	100
5	129	136
6	133	134
7	145	148
8	46*	41
9	54*	42
10	103	105
11	78	88
12	97	104
13	112	108
14	48*	15
15	21*	27
16	77	90
8 k 10		
0	100	106
1	30*	49
2	55*	33
3	28*	12
4	42*	40
5	60	40
6	109	96
7	37*	48
8	0*	21
9	29*	13
10	59	38
11	40*	25
12	63	71
13	24*	38
14	0*	9
8 k 11		
0	119	105
1	188	175
2	68	62
3	187	185
4	76	61
5	148	141
6	108	94
7	179	173
8	64	49
9	147	153
10	48*	48
11	102	88
8 k 12		
0	31*	31
1	26*	9
2	32*	10
3	36*	45
4	25*	4
5	0*	5
6	15*	28
7	31*	13
9 k 0		
1	49*	47
3	1033	1047
5	111	106
7	811	804
9	61	46
11	133	128
13	502	499
15	63	49
19	101	111

k	F_o	F_c
21	250	264
9 k 1		
0	44*	48
1	0*	13
2	80	23
3	30*	68
4	9*	26
5	0*	13
6	42*	43
7	45*	12
8	6*	16
9	64	50
10	28*	22
11	19*	10
12	31*	31
13	23*	10
14	32*	9
15	47*	27
16	0*	16
17	0*	7
18	0*	19
19	0*	8
20	0*	4
21	29*	11
9 k 2		
0	206	204
1	57	45
2	352	352
3	453	445
4	386	380
5	0*	24
6	191	189
7	65	52
8	243	239
9	350	341
10	323	316
11	24*	4
12	155	154
13	59	43
14	117	122
15	209	206
16	213	222
17	42*	6
18	96	109
19	0*	29
20	42*	45
21	112	105
9 k 3		
0	68	72
1	0*	18
2	50*	35
3	101	116
4	6*	38
5	0*	13
6	54*	64
7	14*	18
8	40*	25
9	81	89
10	0*	32
11	0*	7
12	53*	45
13	28*	15
14	0*	14
15	58	56
16	0*	22
17	15*	3
18	59	27
19	0*	10
20	34*	7
9 k 4		
0	47*	51
1	49*	32
2	45*	22
3	201	206
4	58	18
5	0*	6
6	0*	47
7	82	70
8	24*	19
9	171	168
10	17*	7
11	0*	18
12	54*	40
13	87	90
14	0*	12
15	112	120
16	29*	6
17	49*	21
18	0*	29
19	78	83
20	0*	7
9 k 5		
0	0*	21
1	44*	15
2	36*	14

k	F_o	F_c
3	111	89
4	32*	14
5	36*	13
6	37*	17
7	28*	15
8	0*	10
9	69	70
10	40*	10
11	29*	9
12	16*	10
13	27*	12
14	0*	6
15	26*	46
16	0*	4
17	0*	5
18	22*	4
19	29*	9
9 k 6		
0	239	244
1	89	89
2	331	332
3	107	107
4	360	362
5	59	72
6	226	222
7	91	89
8	228	232
9	117	75
10	304	308
11	57	46
12	175	169
13	57*	73
14	129	123
15	0*	39
16	211	216
17	25*	23
18	118	109
9 k 7		
0	34*	11
1	0*	17
2	38*	14
3	34*	15
4	0*	14
5	0*	13
6	0*	9
7	0*	18
8	31*	10
9	58	11
10	20*	10
11	0*	8
12	0*	4
13	31*	15
14	0*	5
15	32*	6
16	0*	5
17	17*	3
9 k 8		
0	214	220
1	48*	4
2	132	125
3	436	438
4	149	143
5	0*	19
6	198	198
7	0*	30
8	91	85
9	354	351
10	139	130
11	0*	28
12	147	145
13	28*	46
14	29*	44
15	229	231
16	108	97
9 k 9		
0	50*	43
1	30*	25
2	53*	27
3	0*	8
4	10*	29
5	45*	21
6	50*	38
7	13*	25
8	0*	20
9	45*	7
10	14*	24
11	27*	14
12	24*	28
13	79	20
14	20*	42
9 k 10		
0	0*	20
1	63	57
2	74	68
3	205	198

k	F_o	F_c
4	85	77
5	12*	43
6	0*	22
7	53	61
8	58	46
9	174	164
10	73	71
11	53	25
12	0*	24
9 k 11		
0	45*	40
1	22*	8
2	11*	21
3	0*	9
4	0*	22
5	21*	7
6	0*	37
7	36*	8
8	0*	17
9	6*	8
9 k 12		
0	75	70
1	0*	18
2	0*	4
10 k 0		
0	551	568
2	35*	39
4	65	70
6	492	500
8	22*	8
10	80	83
12	332	349
14	30*	9
16	80	75
18	196	203
20	34*	14
10 k 1		
0	86	91
1	207	213
2	4*	13
3	112	112
4	50*	35
5	168	170
6	91	82
7	202	202
8	29*	4
9	101	95
10	55*	53
11	107	101
12	53*	67
13	152	154
14	0*	9
15	70	70
16	58	56
17	68	45
18	49*	47
19	95	100
20	0*	10
10 k 2		
0	256	265
1	169	162
2	23*	21
3	102	113
4	31*	29
5	120	129
6	241	232
7	168	157
8	0*	10
9	104	99
10	59*	27
11	72	78
12	166	158
13	120	124
14	2*	1
15	79	75
16	18*	20
17	47*	36
18	92	89
19	79.	84
10 k 3		
0	446	456
1	248	241
2	43*	21
3	189	181
4	14*	6
5	194	190
6	410	401
7	237	234
8	48*	35
9	153	150
10	36*	28
11	108	112
12	275	278
13	179	182

k	F_o	F_c
14	44*	34
15	93	106
16	57	35
17	35*	49
18	156	160
19	123	120
10 k 4		
0	78	70
1	36*	26
2	2*	28
3	38*	5
4	53*	46
5	0*	22
6	73	66
7	18*	21
8	0*	12
9	0*	5
10	48*	56
11	63	14
12	75	56
13	0*	11
14	0*	3
15	17*	6
16	38*	54
17	0*	8
18	33*	40
10 k 5		
0	454	465
1	87	83
2	50*	34
3	0*	12
4	83	64
5	76	69
6	427	413
7	77	78
8	0*	5
9	0*	4
10	83	79
11	5*	44
12	304	296
13	55*	59
14	0*	12
15	18*	5
16	84	73
17	25*	21
18	186	176
10 k 6		
0	65	74
1	175	185
2	32*	44
3	171	168
4	53*	48
5	153	149
6	85	63
7	180	179
8	0*	32
9	142	138
10	25*	43
11	105	92
12	28*	40
13	132	140
14	0*	19
15	92	95
16	20*	33
10 k 7		
0	34*	19
1	93	107
2	39*	32
3	99	106
4	31*	25
5	83	83
6	0*	17
7	94	111
8	29*	30
9	84	93
10	48*	11
11	52*	49
12	12*	12
13	100	94
14	0*	21
15	66	70
10 k 8		
0	239	231
1	71	79
2	0*	4
3	123	128
4	12*	16
5	72	63
6	213	208
7	88	79
8	35*	5
9	106	104
10	27*	25
11	19*	39

k	F_o	F_c
12	151	153
13	66	63
14	0*	9
10 k 9		
0	117	111
1	92	88
2	0*	39
3	4*	6
4	68	57
5	58	74
6	106	102
7	99	82
8	50*	19
9	0*	5
10	74	63
11	10*	49
12	78	78
10 k 10		
0	115	97
1	35*	27
2	0*	19
3	27*	10
4	27*	22
5	0*	20
6	90	89
7	0*	29
8	18*	14
9	0*	11
10 k 11		
0	60	66
1	116	111
2	34*	36
3	112	110
4	50*	36
5	93	88
11 k 0		
1	0*	3
3	238	240
5	0*	16
7	21*	21
9	201	189
11	16*	22
13	37*	32
15	127	122
17	0*	21
11 k 1		
0	137	140
1	45*	36
2	181	177
3	16*	40
4	198	194
5	38*	19
6	130	129
7	34*	54
8	118	124
9	53*	40
10	163	168
11	14*	7
12	103	101
13	56*	60
14	76	66
15	51*	36
16	124	121
17	0*	3
18	65	67
11 k 2		
0	75	63
1	38*	10
2	104	109
3	90	77
4	115	120
5	37*	5
6	64	·59
7	0*	13
8	68	75
9	87	60
10	100	104
11	0*	1
12	42*	47
13	0*	12
14	35*	39
15	55	38
16	80	74
17	35*	2
18	47*	33
11 k 3		
0	208	217
1	0*	15
2	205	208
3	441	445
4	233	230
5	0*	8
6	188	198

Table 3. *(Continued)*

Column 1

k	F_o	F_c
7	46*	36
8	143	144
9	344	350
10	206	202
11	40*	20
12	149	150
13	47*	45
14	75	76
15	216	225
16	145	147
17	0*	21
11 k 4		
0	47*	43
1	0*	2
2	48*	11
3	86	98
4	0*	14
5	30*	9
6	28*	39
7	25*	15
8	21*	7
9	73	80
10	0*	15
11	37*	13
12	46*	29
13	33*	23
14	0*	2
15	49*	54
16	26*	13
17	38*	12
11 k 5		
0	35*	17
1	47*	62
2	77	56
3	458	442
4	76	60
5	0*	32
6	18*	12
7	85	81
8	37*	41
9	368	355
10	52*	53
11	43*	7
12	0*	2
13	88	82
14	43*	22
15	240	235
16	45*	40
11 k 6		
0	0*	33
1	0*	23
2	80	82
3	21*	4
4	88	91
5	18*	17
6	45*	32
7	0*	24
8	52*	57

Column 2

k	F_o	F_c
9	23*	4
10	75	80
11	39*	10
12	0*	26
13	37*	21
14	0*	29
15	21*	4
11 k 7		
0	96	93
1	20*	10
2	74	74
3	41*	22
4	88	87
5	0*	15
6	87	88
7	0*	3
8	49*	50
9	13*	17
10	90	84
11	0*	15
12	71	74
13	0*	9
11 k 8		
0	67	45
1	25*	3
2	38*	27
3	116	118
4	39*	33
5	25*	6
6	53*	41
7	0*	11
8	37*	16
9	105	95
10	49*	32
11	11*	10
12	30*	31
11 k 9		
0	54*	39
1	58	64
2	95	90
3	102	104
4	106	95
5	0*	43
6	48*	35
7	68	75
8	68	67
9	70	88
11 k 10		
0	0*	15
1	0*	27
2	3*	30
3	59	65
4	36*	33
5	19*	20
12 k 0		
0	677	573

Column 3

k	F_o	F_c
2	27*	37
4	79	74
6	518	512
8	35*	3
10	105	94
12	370	370
14	38*	18
16	101	89
12 k 1		
0	58*	42
1	35*	19
2	0*	10
3	0*	36
4	0*	10
5	12*	15
6	56*	36
7	8*	19
8	38*	9
9	30*	29
10	40*	9
11	61	10
12	52*	23
13	0*	16
14	0*	7
15	49*	20
16	48*	8
12 k 2		
0	250	233
1	203	206
2	45*	23
3	148	150
4	0*	31
5	168	164
6	208	206
7	209	204
8	9*	11
9	138	130
10	47*	31
11	83	100
12	158	146
13	161	165
14	27*	1
15	96	98
16	11*	24
12 k 3		
0	83	84
1	32*	28
2	0*	13
3	57*	52
4	6*	16
5	14*	23
6	74	75
7	33*	27
8	21*	9
9	36*	42
10	32*	15
11	0*	15
12	59	54

Column 4

k	F_o	F_c
13	0*	22
14	0*	5
15	50	29
12 k 4		
0	151	146
1	20*	4
2	31*	26
3	37*	39
4	33*	50
5	0*	5
6	141	134
7	50*	4
8	30*	7
9	24*	34
10	80	66
11	5*	4
12	100	104
13	28*	8
14	32*	7
15	23*	26
12 k 5		
0	73	67
1	50*	8
2	0*	13
3	59	10
4	0*	14
5	0*	7
6	60	61
7	18*	7
8	0*	10
9	0*	7
10	0*	13
11	12*	5
12	40*	45
13	0*	4
14	0*	6
12 k 6		
0	45*	41
1	198	199
2	71	47
3	165	156
4	48*	54
5	153	159
6	40*	34
7	207	197
8	33*	34
9	137	131
10	54*	50
11	104	98
12	30*	20
12 k 7		
0	0*	8
1	0*	8
2	0*	12
3	35*	4
4	15*	14
5	19*	7

Column 5

k	F_o	F_c
6	0*	7
7	0*	7
8	39*	8
9	24*	2
10	0*	13
11	21*	5
12 k 8		
0	268	264
1	97	81
2	0*	9
3	126	130
4	0*	26
5	56*	63
6	247	238
7	90	84
8	42*	5
12 k 9		
0	0*	9
1	34*	22
2	0*	18
3	48*	33
4	39*	20
13 k 0		
1	26*	49
3	310	305
5	38*	28
7	34*	61
9	242	246
11	0*	9
13	31*	60
13 k 1		
0	71	75
1	0*	25
2	108	100
3	60*	72
4	111	111
5	5*	12
6	86	70
7	27*	37
8	74	70
9	71	62
10	92	99
11	0*	2
12	76	55
13	42*	41
14	40*	37
13 k 2		
0	79	88
1	0*	17
2	85	84
3	147	136
4	103	94
5	54*	11
6	83	82
7	44*	19
8	45*	59

Column 6

k	F_o	F_c
9	116	108
10	86	86
11	29*	5
12	54*	66
13	48*	16
13 k 3		
0	107	113
1	12*	7
2	117	115
3	224	219
4	133	130
5	26*	7
6	112	104
7	0*	20
8	89	79
9	178	176
10	121	117
11	38*	14
12	80	81
13	26*	26
13 k 4		
0	0*	4
1	27*	33
2	46*	11
3	49*	54
4	33*	11
5	44*	21
6	18*	4
7	28*	42
8	39*	9
9	56	47
10	37*	7
11	29*	9
12	0*	5
13 k 5		
0	29*	8
1	47*	40
2	57*	44
3	249	241
4	40*	48
5	0*	20
6	29*	9
7	47*	33
8	25*	32
9	208	196
10	35*	42
11	24*	3
13 k 6		
0	119	115
1	30*	27
2	95	98
3	55*	33
4	109	109
5	40*	22
6	100	105
7	55	28
8	72	70

Column 7

k	F_o	F_c
9	39*	24
13 k 7		
0	90	79
1	0*	14
2	62	60
3	32*	7
4	75	70
5	40*	16
6	64	74
7	35*	8
13 k 8		
0	87	82
1	12*	15
14 k 0		
0	108	112
2	0*	1
4	14*	11
6	93	101
8	0*	7
10	0*	19
14 k 1		
0	53*	43
1	103	101
2	36*	26
3	93	91
4	26*	37
5	84	80
6	42*	41
7	100	101
8	0*	14
9	80	78
10	38*	43
11	50*	50
14 k 2		
0	19*	29
1	60	60
2	11*	4
3	47*	40
4	33*	6
5	46*	47
6	39*	26
7	47*	60
8	0*	2
9	40*	35
10	0*	7
14 k 3		
0	238	237
1	134	121
2	0*	14
3	129	132
4	0*	27
5	90	95
6	215	215
7	130	122
8	27*	2

Column 8

k	F_o	F_c
9	107	111
14 k 4		
0	62	61
1	24*	11
2	16*	2
3	37*	28
4	31*	8
5	0*	8
6	56	55
7	0*	12
8	23*	5
14 k 5		
0	257	248
1	27*	34
2	48*	39
3	0*	6
4	57	54
5	16*	27
6	229	224
14 k 6		
0	18*	9
1	15*	42
2	0*	11
3	0*	16
15 k 0		
1	48*	46
3	284	281
5	0*	23
15 k 1		
0	45*	25
1	35*	7
2	0*	12
3	33*	19
4	23*	13
5	38*	7
6	20*	23
15 k 2		
0	107	103
1	0*	17
2	95	99
3	119	105
4	111	112
5	32*	11
15 k 3		
0	50*	35
1	0*	11
2	0*	17
3	47*	50

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 $\frac{1}{2}\%$ 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 BUERGER (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 $10^0/_0$ significance level. Sets V and VI are the data from crystal 2 refined in space groups $Pcmn$ and $Pc2_1n$ 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 2σ (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 $1.5e/Å^3$ 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 Å relative to the two sulfur atoms not on the mirror plane, and there is a displacement of about 0.2 Å along the c direction between sulfur layers in adjacent wurtzitic slabs.

Figure 2a shows the geometry around the two atoms Cu and S(1) on the mirror plane and Fig. 2b 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_0 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.
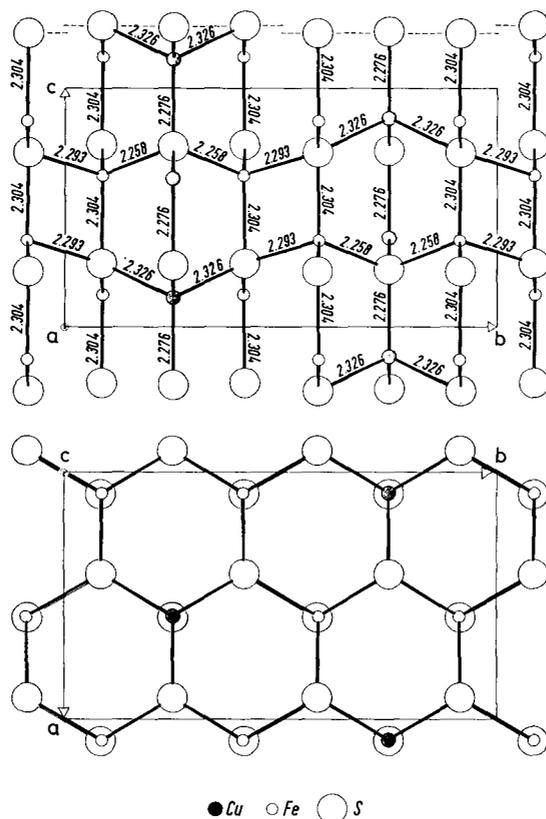
Fig. 1. The structure of cubanite projected down the a and c axes. The upper diagram also illustrates the relative displacement in the c direction of the close-packed sulfur layers between adjacent wurtzitic slabs $b/2$ wide

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 ± 0.02 Å, is significantly less than the mean given previously 2.34 ± 0.09 Å (Fleet, 1970). The values given here agree better with those given by Azaroff and Buerger (1955): Cu—S(1) = 2.29₂, mean Cu—S = 2.31 ± 0.04 Å. The mean Cu—S distance, 2.30₅ Å, compares very well with that recently found in chaclopyrite, 2.302(1) Å (Hall and Stewart, 1973) and the Fe—S distance in chalcopyrite, 2.257(1) Å, is in good agreement with the two shorter Fe—S distances in cubanite.
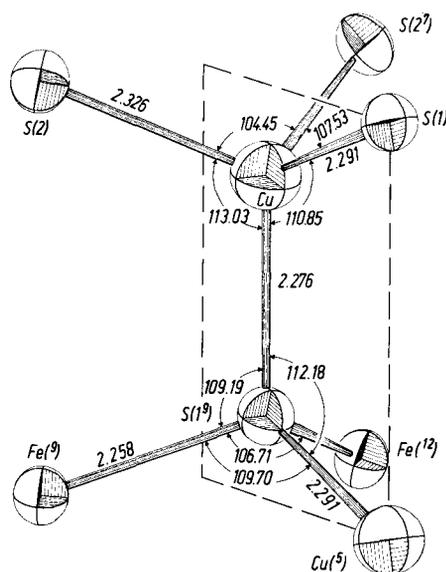
Fig. 2a. Bond lengths and angles around Cu and S(1), the atoms on the mirror plane, which is shown as the broken line

The two Fe—S bonds to the two sulfur atoms, 2.304(1), 2.293(1) Å, 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) Å. 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 Fe—S(2) bonds, a shortening of the S(2)—S(2) distances, and a decrease in the S(2)—Fe—S(2) angle. The two Fe—S bonds are longer, as noted above, the S(2)—S(2) tetrahedral-

edge distance is decreased to 3.642(1) Å, compared with the mean of the other five edges $3.73_7 + 0.02$ Å [2].

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 attached[3] to $S(2)^9$, i.e., $S(2)^9$—Cu^9, $S(2)^9$—Fe^9, 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 Fe^9—$S(2)^9$ 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.

leave $Fe\text{—}S(1)^2$ as a short bond, $Fe\text{—}S(2)$ as an unchanged bond, and $S(2)^9\text{—}Cu^9$ as a long bond. Indeed, in this study it is found that $Fe\text{—}S(1)^2$ is the shortest iron-sulfur bond, that $Fe\text{—}S(2)$ is longer, and that $S(2)^9\text{—}Cu^9$ is the longest of the copper-sulfur bonds in the structure. Furthermore, the decrease of the $S(2)\text{—}S(2)$ tetrahedral edge is reflected in an increase in the $S(2)\text{—}Cu\text{—}S(1)^9$ angle to $113.03(3)°$ over the expected tetrahedral value. Finally, the reasons for the difference in bond lengths of the two *longer* $Fe\text{—}S(2)$ bonds, $Fe\text{—}S(2)^9$: 2.304 Å, $Fe\text{—}S(2)^{11}$: 2.293 Å, can be found in considering the pseudo hexagonal close-packed sulfur matrix, in which distortions *within* a close-packed layer should be more difficult than a distortion which causes a slight separation of the close-packed layers. This is reflected in the shorter length of the $Fe\text{—}S(2)^{11}$ bond, nearly in the plane of the close-packed sulfur layer, and the longer $Fe\text{—}S(2)^9$ distance, the latter being normal to the sulfur layer.

In the present study, the mean Cu—S distance is found to be longer than the mean Fe—S distance, although there is an overlap in the individual distances, because of the distorted geometry at the shared tetrahedral edge. This means that it is not possible to identify positively the metal sites in more complex copper-iron sulfides, using the criterion of the bond lengths alone, without recourse to considering the spatial interrelationship of the metal-sulfur tetrahedra. The bond lengths and angles are given in Table 2 and Figs. 1 and 2. They are based upon the figures given in Data Set V, Table 1. The set of nonbonded sulfur-sulfur distances, across the corners of the coordination tetrahedra, is also given in Table 2.

The thermal parameters, given in Table 1 and illustrated graphically in Fig. 2, do not indicate any large anisotropy, and such anisotropy as is present is difficult to correlate to the features of the structure. However, as found in chalcopyrite (HALL and STEWART, 1973), the mean isotropic temperature factors of the sulfur atoms, $<B> = 0.96$ Å², are about 8% higher than that of iron, $B = 0.89$ Å², while that of copper, 1.38 Å², is about 60% higher than that of iron. The corresponding figures for the temperature factors found in chalcopyrite are 1.00, 0.92, 1.48 Å². On the basis of x-ray analysis, it is not possible to decide between possible oxidation states for Fe, but the refinement appears to indicate that the centrosymmetric space group *Pcmn* is correct; this implies that the two Fe atoms across the centre of symmetry are in identical oxidation states, at least on a time-average basis. GREENWOOD and WHITFIELD (1968) had earlier suggested, on the basis

of their Mössbauer spectra, that the odd electron per formula unit was being exchanged rapidly between the iron atoms, but other Mössbauer spectra at $4\,^{\circ}\mathrm{K}$ (IMBERT and WINTENBERGER, 1967; TOWNSEND *et al.*, 1973) have *not* shown any further splitting of lines compared with the room-temperature spectra. This precludes the idea of rapid electron exchange and favours the idea of identical oxidation states for iron at all times, though it does not answer the fundamental question as to the location or function of the odd electron per formula unit. The author feels that the problem of the location of this odd electron is still unresolved, though the suggestion of HULLIGER (1968) that it is in an incomplete d band thus accounting for the electrical conductivity of cubanite, seems reasonable. TOWNSEND *et al.* (1973) have recently reported that cubanite is an n-type semiconductor, thus giving further weight to HULLIGER's suggestion.

Conclusion

The final parameters for the present structure refinement, listed in Table 1, Data Set V, have yielded a set of bond lengths and angles that are considerably more accurate than those from previous work, and that are of comparable precision to those from the recent work on chalcopyrite. No attempt is made to rationalize the bonding within this structure in terms of the d orbitals of Fe and Cu, but this has already been discussed at some length by HULLIGER (1968), by KNOP *et al.* (1970) and by FLEET (1970, 1972). The distortions from tetrahedral geometry around the metal atoms are consistent with an Fe—Fe repulsion, rather than with a long Fe—Fe bond involving the dz^2 orbitals, as suggested by FLEET (1970). The space-group ambiguity has been studied, and despite the evidence of the Hamilton test, it is felt that the original assignment to the centric space group is correct.

Acknowledgements

References

L. V. Azaroff and M. J. Buerger (1955), Refinement of the structure of cubanite, $CuFe_2S_3$. Amer. Mineral. 40, 213—225.

W. L. Bond (1951), Making small spheres. Rev. Sci. Instr. 22, 344—345.

M. J. Buerger (1945), The crystal structure of cubanite, $CuFe_2S_3$, and the coordination of ferromagnetic iron. J. Amer. Chem. Soc. 67, 2056.

M. J. Buerger (1947), The crystal structure of cubanite. Amer. Mineral. 32, 415—425.

W. R. Busing (1970), Least squares refinement of lattice and orientation parameters for use in automatic diffractometry. *Crystallographic computing* (F. R. Ahmed, Ed.), Munksgaard, Copenhagen, 319—330.

L. J. Cabri and S. R. Hall (1972), Mooihoekite and haycockite, two new copper-iron sulphides and their relationship to chalcopyrite and talnakhite. Amer. Mineral. 57, 689—708.

L. J. Cabri, S. R. Hall, J. T. Szymański and J. M. Stewart (1973), On the transformation of cubanite. Can. Mineral. 12, 33—38.

D. T. Cromer and D. Libermann (1970), Relativistic calculation of anomalous scattering factors for x-rays. J. Chem. Physics 53, 1891—1898.

D. T. Cromer and J. B. Mann (1968), X-ray scattering factors computed from numerical Hartree-Fock wave functions. Acta Crystallogr. A24, 321—324.

G. Donnay, L. M. Corliss, J. D. H. Donnay, N. Elliott and J. M. Hastings (1958), Symmetry of magnetic structures: Magnetic structure of chalcopyrite. Physic. Rev. 112, 1917—1923.

M. E. Fleet (1970), Refinement of the crystal structure of cubanite and polymorphism of $CuFe_2S_3$. Z. Kristallogr. 132, 276—287.

M. E. Fleet (1972), A note on the oxidation state of iron in cubanite. Can. Mineral. 11, 901—902.

E. J. Gabe and T. O'Byrne (1970), An absorption correction program for the PDP-8. Amer. Crystallogr. Ass. Summer Meeting, Ottawa. Abstr. Paper A4.

N. N. Greenwood and H. J. Whitfield (1968), Mössbauer effect studies on cubanite ($CuFe_2S_3$) and related iron sulphides. J. Chem. Soc. [London] A, 1697—1699.

S. R. Hall and E. J. Gabe (1972), The crystal structure of talnakhite, $Cu_{18}Fe_{16}S_{32}$. Amer. Mineral. 57, 368—380.

S. R. Hall and J. F. Rowland (1973), The crystal structure of synthetic mooihoekite, $Cu_9Fe_9S_{16}$. Acta Crystallogr. B29, 2365—2372.

S. R. Hall and J. M. Stewart (1973), The crystal structure refinement of chalcopyrite, $CuFeS_2$. Acta Crystallogr. B29, 579—585.

W. C. Hamilton (1965), Significance tests on the crystallographic R factor. Acta Crystallogr. 18, 502—510.

F. Hulliger (1968), Crystal chemistry of the chalcogenides and pnictides of the transition elements. Structure and bonding. 4, 83—229

P. Imbert and W. Wintenberger (1967), Etudes des propriétés magnétiques et des spectres d'absorption par l'effet Mössbauer de la cubanite et de la sternbergite. Bull. Soc. franç. Mineral. Cristallogr. 90, 299—303.

C. K. Johnson (1965), U.S. Clearinghouse Fed. Sci. Tech. Inform. Rep. ORNL-3794.

O. Knop, C. Huang and F. W. Woodhams (1970), Chalcogenides of the transition elements, VII. A Mössbauer study of pentlandite. Amer. Mineral. **55**, 1115.

A. C. Larson (1970), The inclusion of secondary extinction in least-squares refinement of crystal structures. In: *Crystallographic computing*, Ed. F. R. Ahmed, Munksgaard, Copenhagen.

S. C. Nyburg, G. A. Ozin and J. T. Szymański (1971), The crystal and molecular structure of bismuth trichloride. Acta Crystallogr. B**27**, 2298—2304.

M. A. Peacock and G. M. Yatsevitch (1936), Cubanite from Sudbury, Ontario. Amer. Mineral. **21**, 55—62.

J. M. Stewart, G. Kruger, H. Ammon, C. H. Dickinson and S. R. Hall (1972), The x-ray system of crystallographic programs for any computer. U. Maryland Comp. Sc. Tech., Report TR-192.

J. T. Szymański (1974), The crystal structure of high-temperature $CuFe_2S_3$. Z. Kristallogr. **140**, 240—248.

Y. Tomiie and C. H. Stam (1958), Calculation of atomic scattering factors using Slater wave functions: sodium to calcium. Acta Crystallogr. **11**, 126—127.

M. G. Townsend, J. L. Horwood and J. R. Gosselin (1973), On the weak ferromagnetism of orthorhombic $CuFe_2S_3$. Canad. J. Physics **51** 2162—2165.