Acta Cryst. (1972). B**28**, 1237

The Crystal Structure of α-Ni_7S_6

By M. E. Fleet

Department of Geology, University of Western Ontario, London, Ontario, Canada

(*Received* 28 *June* 1971)

α-Ni_7S_6 is orthorhombic with $a=3{\cdot}274\pm0{\cdot}001$, $b=16{\cdot}157\pm0{\cdot}007$, $c=11{\cdot}359\pm0{\cdot}004$ Å, space group *Bmmb*. The crystal structure has been determined on a synthetic single crystal by the application of a direct method of phase determination to data collected on a four-circle diffractometer and refined by full-matrix least squares to a residual index of 0·12. Based on $D_m=5{\cdot}36$ g.cm^{-3}, the unit-cell content is 22·5 Ni, 19·3 S. There are three non-equivalent S sites and five non-equivalent Ni sites per unit cell. Four of the Ni sites are in square pyramidal coordination with S and one is in tetrahedral coordination. The Ni is distributed to give occupancies of approximately 0·94 to two of the pyramidal sites and approximately 0·47 to the remaining sites. Each Ni site is related to at least one neighbouring Ni site by an interatomic distance similar to that of metallic Ni (2·492 Å) and, as such, the pyramidal and tetrahedral sites have similarities with the Ni site in millerite (NiS) and heazlewoodite (Ni_3S_2) respectively. It is apparent that metallic (Ni–Ni) bonding has been significant in stabilizing all three of these structures.

Introduction

The most recent comprehensive investigation of the Ni–S binary system indicates the existence of two stable phases of approximate composition Ni_7S_6 (Kullerud & Yund, 1962), designated as α-Ni_7S_6, which is stable between 400 °C and 573 °C, and as β-Ni_7S_6, which is stable below 400 °C. There is considerable disagreement in the earlier literature as to the ideal compositions of these two phases (Kullerud & Yund, 1962); they have been reported variously as Ni_6S_5, Ni_7S_6 and Ni_9S_8. The limits of solid solution within the α-Ni_7S_6 phase are unknown but the available data suggest that a small excess of Ni can be tolerated; solid solution within the low-temperature polymorph is even more restricted. This study is concerned only with the α-Ni_7S_6 phase.

Lundqvist (1947) in a single-crystal Weissenberg study on a phase assumed to have a composition Ni_6S_5 (equivalent to α-Ni_7S_6) found it to be orthorhombic with $a=11{\cdot}24$, $b=16{\cdot}59$, $c=3{\cdot}28$ Å, space group *Bb*2*m*, or *B*2*mb* or *Bbmm*. The density was estimated to be 5·60 g.cm^{-3}, which yielded a cell content of $Ni_{24}S_{20}$. However, the X-ray diffraction pattern of α-Ni_7S_6 did not agree with the pattern calculated from the cell data of Lundqvist (Kullerud & Yund, 1962).

Experimental

About 1·0 gm of Ni_7S_6 was synthesized by heating an appropriate mixture of Ni sponge and S crystals in an evacuated silica-glass tube at 504 °C for 9 days; the Ni sponge was reduced with hydrogen at 900 °C before use. Kullerud & Yund (1962) have shown that this composition homogenizes very readily under the conditions used in the present synthesis. Furthermore, X-ray powder diffraction studies indicated that the possible non-equilibrium products, high-temperature NiS, Ni_3S_2 and β-Ni_7S_6, were not observable and those diffraction lines not affected by the grinding procedure (below) were quite sharp. The material synthesized, then, appeared to be homogeneous and its composition was that of the bulk composition of the starting reagents.

The product of the synthesis was massive and in the form of a plug. This was crushed in a percussion mortar and fragments within the size range 0·01 mm to 0·2 mm in diameter were isolated by sieving. The appearance of this material in polished section was similar to the description of Kullerud & Yund (1962). Although many of the grains were twinned there were several large rectangular fragments within the sample examined which appeared to be untwinned, single crystals. For this reason several crystal fragments were examined by single-crystal diffraction procedures. The fragment selected for study appeared to be a single crystal; it was an irregular, but approximately equidimensional, solid bounded by plane surfaces with a calculated volume of $0{\cdot}3\times10^{-6}$ cm^3.

Preliminary single-crystal work essentially confirmed the earlier data of Lundqvist (1947). α-Ni_7S_6 is orthorhombic with $a=3{\cdot}274\pm0{\cdot}001$, $b=16{\cdot}157\pm0{\cdot}007$, $c=11{\cdot}359\pm0{\cdot}004$ Å; the lattice parameters were determined by least-squares refinement of 12 centred reflexions measured on a four-circle diffractometer. The systematic absences are hkl with $h+l\neq2n$ and $hk0$ with $k\neq2n$, which are consistent with the space groups *Bm*2*b* (C_{2v}^{12}), *Bbm*2 (C_{2v}^{16}) and *Bmmb* (D_{2h}^{17}). It was considered advantageous to switch the a and c parameters relative to the cell described by Lundqvist (1947) to facilitate structural correlation with β-Ni_7S_6. Preliminary single-crystal data for β-Ni_7S_6 show that it is tetragonal with $a=9{\cdot}343\pm0{\cdot}012$, $c=11{\cdot}250\pm0{\cdot}018$ Å; these parameters were determined with four-circle diffractometer data. However, the unit cell used in the present study for α-Ni_7S_6 is unconventional and the transformation matrix for conversion to the conventional cell of Lundqvist (1947) is:

$$\begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix}.$$

Some difficulty was encountered in indexing Jagodzinski powder camera films of α-Ni_7S_6. Comparison with the single-crystal film data showed that several reflexions, especially 200, were very diffuse on the powder film. This is most likely a result of the disruption of the structure on grinding, and accounts for the poor agreement between the crystallographic data of Lundqvist (1947) and those of Kullerud & Yund (1962). Experiments with a high temperature powder camera, in which the powdered sample is contained within a sealed evacuated capillary, showed that the diffuse reflexions are restored to their normal relative intensity on heating for two to three hours at temperatures within the stability field for the phase.

The observed density of α-Ni_7S_6 is $5{\cdot}36 \pm 0{\cdot}02$ g.cm^{-3}. This value was obtained using a Berman balance with toluene as a density medium; the estimate of the precision of the determination is based on triplicate measurements on two grains, 22 and 34 mg in weight. The corresponding unit-cell content is 22·5 Ni and 19·3 S.

The X-ray intensity data for the structure analysis were taken on a Picker FACS 1 four-circle diffractometer system at the University of Western Ontario. All *hkl* reflexions with $2\theta \leq 70°$ were measured using a scintillation detector, Zr-filtered Mo $K\alpha$ ($\lambda = 0{\cdot}7107$ Å) radiation and the 2θ scan technique: 40 second stationary background counts and peakbase widths of 2·5° 2θ (uncorrected for dispersion). The resulting data were processed by a data correction routine which removed space group extinctions and corrected for background, Lorentz and polarization effects, and absorption, and assigned standard deviations (σ) to the corrected data based on the summed variances of the counting rates of the peaks and associated backgrounds. Transmission factors for the absorption correction were calculated by gaussian integration of the volume elements using a value for the linear absorption coefficient of 186·4 cm^{-1}. The crystal was oriented with the c axis parallel to the φ axis. The calculated transmission factors varied from 0·33 for 301 to 0·44 for 17,17. Each reflexion whose intensity was less than the associated background plus one standard deviation was given zero intensity. The final data list contained 786 reflexions of which 222 were unobserved.

Crystal structure investigation

The structure factor data were processed for Wilson statistics by program *FAME* (R. B. K. Dewar, Illinois Institute of Technology, Chicago).

Statistical analysis of the normalized structure factors suggested a centric distribution; the structure was assumed to be centrosymmetric with the probable space group *Bmmb*. Preliminary consideration of the structure reveals that all atoms must be in special positions with $x = 0$ or $\frac{1}{2}$ to maximize the intensity of 200 which is the strongest reflexion. Furthermore, the structure has a mirror plane parallel to (100) and, with $a = 3{\cdot}274$ Å, any other location but the mirror planes would result in unacceptably small S–S distances, compared to the S–S distances of related compounds.

The phases of those structure factors with $E \geq 1{\cdot}5$ were assigned by a reiterative application of Sayre's equation using program *REL*1 (adapted from Long, Ph.D. Thesis, UCLA, 1965). The solution with the

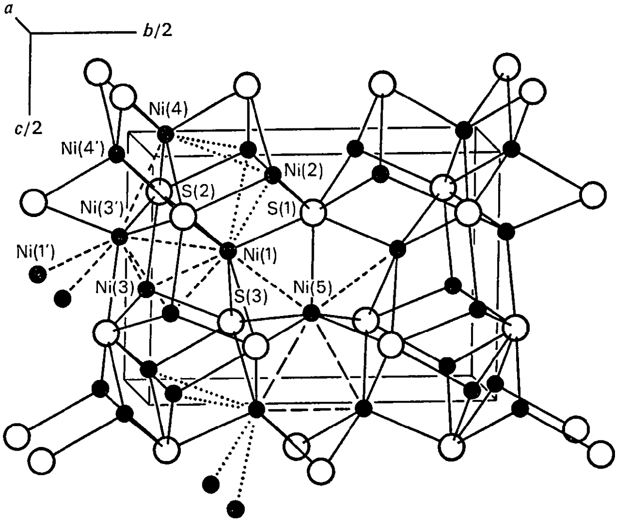


Fig. 1. Part of the unit cell of α-Ni_7S_6; S: large circles, Ni: small, full circles. Selected Ni–Ni bonds are indicated by broken lines; bonds between sites with occupancies greater than 0·92: large dashes, bonds to or from sites with occupancies less than 0·52: small dashes, bonds greater than 2·6 Å: stipples.

Table 1. *Positional parameters, anisotropic thermal parameters* ($B_{11} = 8\pi^2\bar{U}^2_{11}$ *etc.*) *and occupancies with their standard deviations in parentheses*

	Occupancy	x	y	z	B_{11}	B_{22}	B_{33}
S(1)—4(c)	1·000	$\frac{1}{2}$	$\frac{1}{4}$	0·1418 (7)	1·64 (40)	5·94 (71)	0·17 (26)
S(2)—8(f)	0·985 (16)	0	0·0450 (3)	0·1207 (4)	1·52 (24)	1·21 (21)	0·73 (18)
S(3)—8(f)	0·945 (16)	0	0·1527 (4)	0·3858 (6)	3·36 (34)	0·53 (20)	1·76 (23)
Ni(1)–8(f)	0·436 (10)	$\frac{1}{2}$	0·1277 (4)	0·2162 (6)	2·23 (33)	0·72 (26)	1·18 (24)
Ni(2)–8(f)	0·919 (10)	0	0·1728 (2)	0·0399 (2)	0·80 (12)	1·23 (13)	0·91 (10)
Ni(3)–8(f)	0·518 (10)	0	0·0289 (4)	0·3164 (4)	1·95 (27)	1·67 (26)	0·53 (18)
Ni(4)–8(f)	0·459 (9)	0	0·0346 (4)	0·4805 (5)	1·18 (26)	1·48 (26)	0·89 (22)
Ni(5)–4(c)	0·965 (20)	$\frac{1}{2}$	$\frac{1}{4}$	0·3448 (4)	2·32 (24)	2·42 (24)	0·53 (15)

Table 2. *Observed and calculated structure factors*

K	L	F_o	F_c	K	L	F_o	F_c	K	L	F_o	F_c	K	L	F_o	F_c	K	L	F_o	F_c	K	L	F_o	F_c	K	L	F_o	F_c
H = 0				10	0	256	275		11	110	107		3	30	11		4	72	76		6	68	64		5	99	98
					2	26	13		13	33	35		5	139	141		6	125	124		8	44	45		7	31	27
0	2	75	76		4	124	123		15	96	105		7	106	104		8	34	14	20	0	30	24		9	47	48
	4	91	73		6	55	54	2	1	139	144		9	21	9		10	40	31		4	92	89	13	3	24	2
	6	149	163		8	81	91		3	74	69		11	54	50		12	63	57		8	66	59		5	83	85
	8	45	38		12	44	46		5	223	219		15	29	25		14	29	12	21	2	46	49		7	69	68
	10	50	43	11	2	36	18		7	13	4	14	1	77	78	5	2	33	28	24	0	52	48		11	36	31
	12	121	128		4	54	50		9	135	133		3	20	18		4	29	19					14	1	51	46
	14	65	61		6	115	123		11	45	43		5	60	68		6	226	231	H = 3					5	43	36
	16	36	22		8	77	85		15	66	64		11	71	78		8	105	112						11	43	52
1	2	10	4		10	20	10		17	30	26		13	36	33		10	33	29	0	1	26	39	15	1	35	22
	4	118	117		12	50	48	3	1	145	153		15	31	28		12	24	13		3	44	54		3	32	26
	6	175	180	12	0	31	3		3	120	120	15	1	58	55		14	63	58		5	60	59		5	42	36
	8	27	21		2	74	87		5	162	167		3	39	31	6	0	107	115		7	47	15	16	1	47	42
	10	89	91		4	36	36		7	35	29		5	71	64		2	104	114		9	62	60		3	26	2
	12	28	29		6	24	11		9	74	82		9	30	28		4	93	91		11	76	69		7	35	29
	14	45	49		8	35	31		13	32	20		11	28	23		6	33	31		13	33	32	17	1	54	55
	18	31	25		10	120	115		17	27	29	16	1	71	78		8	47	42		15	35	33		3	36	33
2	0	26	21		16	48	48	4	1	53	28		3	26	15		10	37	20	1	1	20	16		9	32	33
	2	28	25	13	2	36	48		3	148	156		5	22	3		12	69	70		3	74	80	18	1	60	51
	4	65	62		4	140	148		5	90	86		7	53	54		14	81	85		5	87	91		5	34	26
	6	12	13		6	44	45		7	14	9		9	24	22	7	2	41	40		7	21	34	19	7	42	42
	8	21	4		8	58	56		9	81	84		11	40	38		4	95	103		9	26	22	20	3	55	46
	10	150	157		10	32	23		11	38	34		13	29	25		6	32	19		11	64	60				
	12	21	9		14	29	22		13	46	38	17	1	95	99		8	63	66		13	29	20	H = 4			
	14	48	50	14	0	189	191	5	1	26	9		3	59	53		10	30	29		15	54	63				
	16	79	88		2	66	72		3	132	142		5	28	14		12	40	39	2	1	62	71	0	0	159	201
3	2	51	51		4	33	27		5	23	13		9	53	50		16	57	51		3	51	50		2	48	41
	4	65	69		6	96	98		7	36	29		11	51	45	8	2	124	136		5	107	112		6	32	45
	6	64	65		8	27	21		9	93	94	18	1	83	75		4	48	40		9	70	72		12	59	55
	8	50	45		10	56	56		11	85	83		3	22	25		6	33	30		11	31	22	1	4	47	39
	10	24	15		12	27	24		13	31	27		5	46	41		12	51	49		15	44	42		6	44	49
	12	59	58		14	42	36		17	63	65	19	5	36	35		14	69	69	3	1	68	68		8	31	22
	16	27	22	15	2	106	107	6	1	42	32		7	70	66	9	2	72	68		3	59	57		10	32	38
	18	30	25		4	35	36		3	176	192		9	28	22		4	37	9		5	82	82	2	2	40	10
4	0	86	91		8	26	31		5	31	24		11	47	43		6	49	48		7	36	9		4	36	6
	2	30	25		10	80	76		7	54	53	20	1	28	24		8	89	88		9	47	47		10	57	57
	4	104	113		12	41	38		9	54	56		3	75	68		10	37	27	4	1	69	25	3	2	24	10
	6	180	188		14	55	57		11	81	87		5	39	40		12	63	57		3	66	71		6	34	25
	8	21	10	16	0	40	42		13	34	38		11	40	24		14	26	26		5	61	46		8	29	22
	10	47	49		2	41	53		17	31	32	21	3	34	26	10	0	186	192		9	50	45	4	0	29	26
	12	83	79		4	28	26	7	1	262	280		7	81	74		2	38	12		13	27	25		4	38	34
	14	25	15		8	26	21		3	138	147		9	38	37		4	92	88	5	1	38	7		6	53	47
	16	26	19		10	57	53		5	15	5	22	1	46	42		6	44	38		3	75	61		8	37	14
	18	30	35		14	60	59		7	139	145		3	27	15		8	69	68		5	20	7	5	6	105	106
5	2	45	24	17	2	32	28		9	118	125		5	27	31		12	34	35		7	34	28		8	55	54
	4	50	47		4	23	17		11	82	80	23	7	32	25	11	2	40	6		9	56	50	6	0	42	52
	6	308	323		6	28	32	8	1	116	116	24	1	43	39		4	50	38		11	52	50		2	52	55
	8	144	155		8	43	49		3	27	21		5	31	33		6	90	89	6	1	37	32		4	54	46
	10	45	43	18	0	30	26		5	23	17	25	1	37	36		8	69	66		3	85	91		8	29	26
	12	20	11		2	60	59		7	60	60		3	32	22		12	41	38		5	32	14	7	2	24	24
	14	74	78		6	61	50		9	51	51					12	0	23	2		7	28	25		4	47	51
	18	40	44		10	32	23		11	79	82	H = 2					2	58	63		9	42	36		8	35	31
6	0	163	172		12	46	45		13	75	76						4	28	18		11	61	58	8	2	62	59
	2	150	165	19	2	48	53	9	1	19	4	0	0	485	509		6	26	7	7	1	134	136		4	30	19
	4	126	126		4	24	27		3	55	44		2	72	61		8	32	29		3	82	87	9	2	30	21
	6	45	48		6	76	75		5	28	20		4	48	25		10	96	91		7	80	82		4	32	9
	8	57	53		8	56	52		7	29	23		6	110	109	13	2	29	30		9	78	80		6	32	33
	10	42	36		10	29	24		9	43	36		8	41	32		4	104	108		11	60	52		8	31	43
	12	94	91	20	0	34	23		11	80	85		10	44	36		6	34	40	8	1	71	70	10	0	77	79
	14	93	109		4	113	117		13	62	64		12	103	101		8	51	47		3	22	10		2	30	9
7	2	53	51		8	84	78		15	65	69		14	57	50		10	24	19		5	27	6		4	41	33
	4	133	144	21	2	57	67	10	1	18	8	1	4	89	83	14	0	146	147		7	31	26		8	28	29
	6	23	34		10	45	42		3	29	35		6	122	119		2	60	58		9	32	22	11	2	29	8
	8	87	95	23	2	28	25		5	22	20		8	34	25		4	25	20		11	54	53		4	34	22
	10	36	33	24	0	58	57		7	26	22		10	74	70		6	76	71		13	51	49		6	39	42
	12	50	55	25	2	74	66		9	44	39		14	43	40		10	48	43	9	3	43	20		8	32	35
	14	30	28						11	28	27	2	0	19	11	15	2	84	80		5	39	12	12	2	34	31
	16	66	59	H = 1				11	1	30	26		2	47	20		4	27	28		7	24	13	13	4	46	53
8	0	16	25						3	44	42		4	51	34		6	22	7		9	38	20	14	0	82	79
	2	183	200	0	1	53	49		5	102	103		6	19	9		10	60	58		11	53	48		2	35	37
	4	57	58		3	116	115		7	68	66		8	22	10		12	32	27		13	43	39		6	41	32
	6	46	44		5	111	117		9	21	5		10	116	117	16	0	29	31	10	3	23	20	15	2	43	36
	12	64	60		7	48	47		11	49	56		14	41	37		2	39	39		7	33	11	16	4	33	2
	14	86	86		9	129	121		13	45	37		16	66	69		4	31	15		11	33	17				
	16	33	33		11	110	108		15	33	33	3	2	43	30		6	27	11	11	1	27	14	H = 5			
9	2	105	111		13	31	29	12	1	102	104		4	44	43		10	47	40		3	28	23	1	5	46	42
	6	58	54		15	61	47		3	66	61		6	50	48	17	2	30	25		5	62	59	2	5	36	42
	8	119	122	1	1	40	44		5	165	175		8	43	37		6	23	25		7	47	27	4	1	43	18
	10	39	38		3	170	170		7	47	46		10	22	11		8	29	36		11	28	28	7	1	51	48
	12	77	75		5	165	169		9	73	78		12	48	41	18	2	54	46		13	31	24		3	32	39
	14	38	32		7	42	44		15	51	51	4	0	55	58		6	48	38	12	1	57	60	8	1	30	33
	16	32	21		9	44	30	13	1	33	30		2	27	16	19	2	37	38		3	46	47				

largest consistency index (0·98) proved to be the correct one. A value of the conventional residual index (R) of 0·39 was obtained using atomic sites as indicated by the strongest peaks on E maps prepared for $x=0$ and $\frac{1}{2}$. F_o and F_o-F_c Fourier syntheses suggested a few minor changes in the predicted structure and resulted in a lowering of the residual R to 0·27.

In the structure which emerged (Fig. 1) the S sites are arranged in alternate planes, parallel to the a axis, with $x=0$ and $\frac{1}{2}$. The S planes form a zigzag arrangement in the **b** direction, with a plane of symmetry at $y=\frac{1}{4}$ and $\frac{3}{4}$. In projection down the a axis, the S substructure would have a near sixfold symmetry. In each unit cell there are three non-equivalent S sites, two in 8(*f*) and one in 4(*c*). However, the observed density suggests that there are only 1·22 S atoms per asymmetric unit and, if these are distributed randomly over the available S sites (*i.e.* assuming random disorder of the S), the S occupancy is approximately 0·97. There are five non-equivalent Ni sites per unit cell, three fivefold coordinated (square pyramidal) with S in 8(*f*), one fivefold coordinated (pyramidal) in 4(*c*) and one tetrahedrally coordinated in 8(*f*). There are only 1·41 Ni atoms per asymmetric unit, again insufficient for the sites available. On the basis of the intensities of Fourier peaks the Ni was distributed to give occupancies of 0·94 to the 4(*c*) site and to one of the pyramidal 8(*f*) sites, and occupancies of 0·47 to the remaining three sites. Moving the Ni from the tetrahedral site to the adjacent pyramidal site increased the residual R to 0·42 and left a significant peak at the tetrahedral site on a F_o Fourier map. Thus, the structure with all of the Ni in pyramidal sites did not appear to be a plausible one.

The structure was refined further by full-matrix least-squares refinement using program *RFINE* (L. Finger, Geophysical Laboratory, Washington). *RFINE* minimizes the function $\sum w(|F_o|-|F_c|)^2$, where $w=1/\sigma^2$, F_o is the observed and F_c the calculated structure factor, and calculates a conventional residual index, $\sum||F_o|-|F_c||/\sum|F_o|$ and a weighted residual index, $[\sum w(|F_o|-|F_c|)^2/\sum wF_o^2]^{1/2}$. The scattering curve for Ni^{2+} was taken from Cromer & Mann (1968) and that for S^{2-} computed for a nine-parameter fit from data in *International Tables for X-ray Crystallography* (1962); the anomalous dispersion coefficients of Cromer (1965) for Ni and S were included. Isotropic and anisotropic thermal parameters and occupancies were added successively to the refinement. The occupancy of the S(1) site was held constant at 1·0, because it increased to a value slightly greater than unity when refined. The values of the conventional and weighted residual indices obtained for the 564 non-zero intensities used are isotropic 0·151 and 0·147, anisotropic 0·118 and 0·122 and anisotropic with occupancies 0·116 and 0·117. These values reflect the large number of weak reflexions in the data used. For the final value of the conventional residual index reported, the residual indices were calculated for eight equal intervals of F_o for all the reflexions used; the value for the lowest interval was 0·190 and that for the average of the other seven intervals was 0·057. A similar analysis in terms of ranges of $\sin^2\theta/\lambda^2$ showed that the residual indices were distributed evenly over all eight intervals. According to the procedure for testing weighted residuals (Hamilton, 1965), the value of the residual index for the refinement including occupancies is significant, compared to that using anisotropic thermal parameters only, at the 0·005 level. The occupancies, positional and anisotropic thermal parameters, and associated standard deviations for this refinement are given in Table 1.

The refinement was terminated when the changes to the positional and thermal parameters were in the sixth places and the changes to the occupancies were in the fifth places and the ratios of the changes in the parameters to the errors in the parameters were less than 0·005. The observed and calculated structure factors reported (Table 2) do not include the data for the unobserved reflexions; of these, the numbers within the F_c intervals 0 to 9, 10 to 19, 20 to 29 and 30 to 39 were 106, 90, 23 and 3 respectively, and the largest value of F_c was 34 for 563. The refined structure was checked with F_o and $F_o - F_c$ Fourier maps; no significant residual peaks were detected.

Discussion

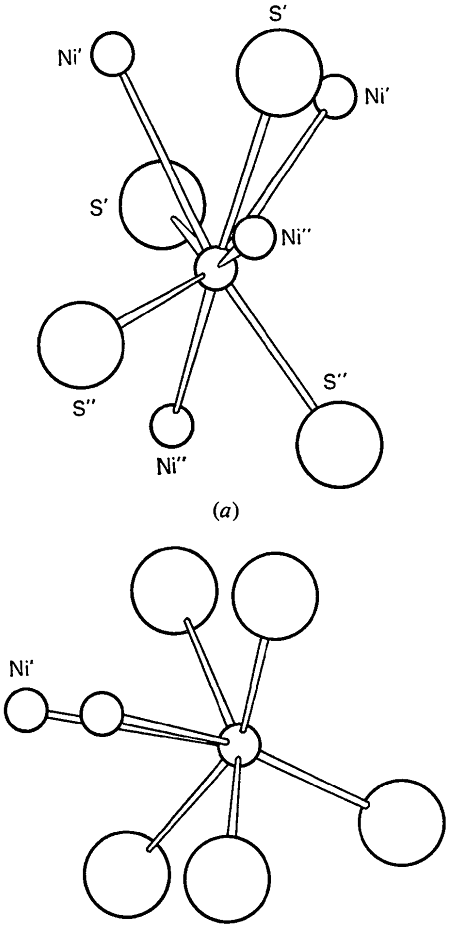
Although the structure presented so far is one in which the atoms are randomly disordered within the sites indicated, there is an indication that some long range order has occurred. Zero-level, *c*-axis precession films of α-Ni_7S_6 generally show weak superstructure reflexions with non-integral spacings in the **a*** direction. Such reflexions are characteristic of the development of long range order patterns within certain alloy and alloy-like crystals, for example the antiphase domains predicted for Cu_3Au (Fujiwara, 1957). The non-integral superstructure reflexions indicate that the ordering occurs along [100] and, although ordering may occur within all sites, we can argue that it must occur, to some extent, within the Ni(3) and Ni(4) sites. The refined occupancies of these are 0·52 and 0·46 respectively. Each Ni(4) site is symmetry-related to an equivalent site with an interatomic distance of only 1·20 Å, the sites being associated in pairs, so that adjacent sites cannot be occupied. Further, to maximize the distance between adjacent Ni(4) atoms, the sites would tend to be filled so that alternate sites are occupied in adjacent unit cells to give an interatomic distance of 3·49 Å. Now each Ni(3) sites is related to a Ni(4) site by an interatomic distance of 1·87 Å. Again, this distance is prohibitive so that the occupancy of the Ni(4) sites controls that of the Ni(3) sites; specifically when the primed Ni(4) site is occupied the primed Ni(3) site will be vacant (Fig. 1). The control on the Ni(1) site, limiting its occupancy to 0·44, is less obvious. However, the large number of possible nearest-neighbour Ni atoms surrounding it must have an adverse effect on its site preference.

Of course the non-stoichiometry of both S and Ni is predicated on the density determination. The calculated density for a unit-cell content of 20 S is 5·56 g.cm^{-3}. This study has demonstrated that the ideal composition of this phase is not Ni_7S_6, indeed an 'ideal' composition may not exist. The structure could accommodate the composition Ni_6S_5 (cell content 24 Ni, 20 S) assuming complete occupancy of all sites except Ni(1), Ni(3) and Ni(4), for which Ni(1)=0·5 and Ni(3)+Ni(4)=1·0. However, the thermochemical evidence suggests that this composition is unstable. This instability might be attributable to the crowded environments of most of the Ni sites, and especially of the Ni(1) site, in the filled structure.

Some calculated interatomic distances of interest are given in Table 3; the superscripts refer to Fig. 1. The anion polyhedra, though slightly distorted, are regular in their essential features. In addition to the Ni–S bonds within each polyhedron, each Ni site is related to at least one neighbouring Ni site by a bond distance similar to that of metallic Ni (2·492 Å) and it can be

Table 3. *Selected interatomic distances* (Å) *with their standard deviations in parentheses*

S(1)—S(1)	3·274 (1)	Ni(2)–S(1)	2·361 (4)
S(1)—S(2)	3·702 (5)	Ni(2)–S(2)	2·259 (6)
S(1)—S(3)	3·582 (8)	Ni(2)–S(3)	2·419 (5)
S(1)—S(3′)	3·305 (9)	Ni(2)–Ni(2)	2·495 (7)
S(2)—S(2)	3·274 (1)	Ni(2)–Ni(4)	2·849 (6)
S(2)—S(2′)	3·104 (10)	Ni(2)–Ni(5)	2·543 (5)
S(2)—S(2′)	3·664 (9)	Ni(3)–S(2)	2·238 (7)
S(2)—S(3)	3·478 (8)	Ni(3)–S(2′)	2·149 (5)
S(2)—S(3′)	3·581 (7)	Ni(3)–S(3)	2·150 (9)
S(3)—S(2′)	3·590 (8)	Ni(3)–Ni(3′)	2·414 (8)
S(3)—S(3)	3·274 (1)	Ni(3)–Ni(4′)	2·526 (9)
S(3)—S(3)	3·144 (12)	Ni(4)–S(2′)	2·378 (6)
Ni(1)–S(1)	2·149 (8)	Ni(4)–S(2)	2·290 (6)
Ni(1)–S(2)	2·375 (6)	Ni(4)–S(3)	2·190 (9)
Ni(1)–S(3)	2·560 (7)	Ni(5)–S(1)	2·307 (9)
Ni(1)–Ni(2)	2·687 (6)	Ni(5)–S(3)	2·317 (4)
Ni(1)–Ni(3)	2·554 (7)		
Ni(1)–Ni(3′)	2·558 (10)		
Ni(1)–Ni(5)	2·457 (7)		



(*a*)

(*b*)

Fig. 2. Ni coordination in (*a*) heazlewoodite (Ni_3S_2), (*b*) millerite (NiS); S: large circles, Ni: small circles.

concluded only that these distances represent full metal bonds. In addition, the Ni(1), Ni(2) and Ni(4) sites are related to adjacent Ni sites by distances of 2·6 to 2·9 Å, and these must represent weaker, but still significant, metal–metal interactions. The complete nearest-neighbour environments about the Ni sites are indicated for selected sites in Fig. 1. Because of the incomplete occupancy of all of the sites, the actual nearest-neighbour environment of any of the Ni atoms cannot be predicted.

The Ni_7S_6 composition is transitional between that of heazlewoodite (Ni_3S_2) and millerite (NiS). The Ni environment in the structures of both of these minerals is indicated in Fig. 2(*a*) and (*b*). The relevant interatomic distances are given in Table 4 for which the sources of the data are as follows: heazlewoodite, cell parameters: Peacock (1947), positional parameters: Westgren (1938); millerite: Alsén (1925). The Ni in heazlewoodite is coordinated to four S atoms, tetrahedrally arranged, and four Ni atoms. The Ni in millerite is coordinated to five S atoms, and two Ni atoms; the S polyhedron approximates a pyramidal configuration in which the fifth S is offset. The Ni–S bonds for α-Ni_7S_6 are within the range exhibited by millerite and heazlewoodite and the Ni–Ni distances suggest full metal bond formation. Allowing for the uncertainty in predicting the exact coordination of the Ni in α-Ni_7S_6, it is apparent that there is a good correlation between the configurations of the pyramidal and tetrahedral Ni sites in α-Ni_7S_6 and the Ni sites in millerite and heazlewoodite respectively. Clearly, metallic (Ni–Ni) bonding has been significant in stabilizing all three of these structures.

Table 4. *Nearest-neighbour interatomic distances* (Å) *in heazlewoodite and millerite*

Heazlewoodite		Millerite	
Ni–S	2·29	Ni–S	2·19
Ni–S′	2·27	Ni–S′	2·39
Ni–Ni′	2·49	Ni–S″	2·43
Ni–Ni″	2·52	Ni–Ni′	2·53

This work was supported by a National Research Council of Canada operating grant.

References

ALSÉN, N. (1925). *Geol. Fören. Stockholm Förh.* **47**, 19.

CROMER, D. T. (1965). *Acta Cryst.* **18**, 17.

CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A**24**, 321.

FUJIWARA, K. (1957). *J. Phys. Soc. Japan*, **12**, 7.

HAMILTON, W. C. (1965). *Acta Cryst.* **18**, 502.

International Tables for X-ray Crystallography (1962), Vol. III. Birmingham: Kynoch Press.

KULLERUD, G. & YUND, R. A. (1962). *J. Petrol.* **3**, 126.

LUNDQVIST, D. (1947). *Ark. Kemi Min. Geol.* **24**A, No. 21, 1.

PEACOCK, M. A. (1947). *Univ. Toronto Studies, Geol. Ser.* **51**, 59.

WESTGREN, A. (1938). *Z. anorg. Chem.* **239**, 82.

Acta Cryst. (1972). B**28**, 1241

Polymorphism of Barium Monoferrite, $BaFe_2O_4$

BY S. MERIANI

Istituto di Chimica Applicata dell'Università di Trieste, via Valerio 2, *Trieste, Italy*

(*Received* 6 *January* 1971 *and in revised form* 11 *October* 1971)

$BaFe_2O_4$ undergoes polymorphic transitions at 800°C and 1000°C. The resulting phases are: γ-$BaFe_2O_4$, stable up to 800°C, orthorhombic with $a=5\cdot387$, $b=19\cdot056$ and $c=8\cdot458$ Å; β-$BaFe_2O_4$, stable from 800°C to 1000°C, orthorhombic pseudo-hexagonal with $a=5\cdot463$, $b=9\cdot461$ $(a\sqrt{3})$ and $c=8\cdot710$ Å; α-$BaFe_2O_4$, stable above 1000°C, hexagonal with $a=5\cdot458$ and $c=9\cdot016$ Å, space group $P6_322$ with two formula units per unit cell, isomorphous with $BaAl_2O_4$. By quenching the β phase a new metastable β' phase, orthorhombic, with $a=5\cdot442$, $b=9\cdot325$ and $c=8\cdot670$ Å, has been obtained at room temperature.

Introduction

Interest in the phase equilibrium diagrams of the alkaline earth ferrites prompted us to examine previously reported data concerning both symmetry and cell dimensions of barium monoferrite, $BaFe_2O_4$.

Single-crystal data (Okazaki, Mori & Mitsuda, 1963) showed that the actual unit cell is orthorhombic, with $a=19\cdot05$, $b=5\cdot398$ and $c=8\cdot448$ Å; these results were confirmed also in an investigation of $BaAl_{2-x}Fe_xO_4$ solid solutions (Do Dinh & Bertaut, 1965).

A hexagonal symmetry, with $a=5\cdot51$ and $c=8\cdot44$ Å, was suggested by other authors (Winkler, 1965; Glasser & Dent Glasser, 1963; Okazaki, Mori & Kanamaru, 1961).

Differential thermal analysis (Ziolowski, 1962) suggested that $BaFe_2O_4$ undergoes plymorphic transi-