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THE CRYSTAL STRUCTURE OF ANTIMONIAN HAUCHECORNITE FROM WESTPHALIA

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ABSTRACT

Hauchecornite, $Ni_9(Bi_{1.3}Sb_{0.7})S_8$, from the type locality of the Friedrich mine, Westphalia is tetragonal, $a = 7.300(3)$, $c = 5.402(2)$Å; $D_{meas} = 6.35 - 6.47$, $D_{calc} = 6.58$ g/cm^{-3}; $Z = 1$; space group *P4/mmm*. The structure was solved by the heavy atom method from 271 symmetry-independent reflections with $F_0^2 > 3\sigma F_0^2$ collected on a Picker four-circle FACS-1 diffractometer using Mo$K\alpha$ ($\lambda = 0.71069$Å) radiation. Crystal-boundary and Φ absorption corrections were applied to the data and the structure was refined by full-matrix least-squares using anisotropic temperature factors to an *R* value of 0.067 ($R_w = 0.115$). The structure consists of double Ni(2)—S ribbons linked by Bi—Ni(1) chains, all parallel to [001]. *M*(0.7Sb + 0.3Bi) sites occur along the line of intersection of four double ribbons. Bi and Ni(1) are octahedrally coordinated. Ni(2) is in distorted square-planar coordination with 4S. The *M* site is coordinated by 8Ni(2). The closest Ni—Ni distances in the double ribbons are 2.639, 2.674 and 2.728Å, suggesting orbital interaction.

INTRODUCTION

The generally accepted composition $Ni_9(Bi,Sb)_2S_8$, of hauchecornite from the type locality at the Friendrich mine, Westphalia was established by Peacock (1950) on the basis of a single crystal *x*-ray study applied to the original analyses reported by Scheibe (1888, 1893). Gait & Harris (1972) have recently discovered slightly differing chemical varieties from other localities and proposed the formula $Ni_9(Bi,X)_2S_8$ in which X = Sb, As or Te, as best representing the known analyses.

Peacock (1950) confirmed the tetragonal symmetry originally proposed for the mineral and obtained the cell dimensions $a = 7.29$, $c = 5.40$Å on a crystal chosen from Harvard Mineralogical Museum specimen No. 89710 from the Friedrich mine. His Weissenberg photographs indicated no systematically-absent reflections although the condition, 00*l* present only with *l* even, was found to be excluded only by a "very very weak" 003 reflection. The photographs showed the Laue symmetry 4/*mmm* and hence the probable space groups *P4/mmm*, *P422*, *P4mm*, $P\bar{4}2m$ and $P\bar{4}m2$ were indicated. From this group Peacock eliminated *P4mm* because examination of the morphology of crystals on an optical goniometer showed the presence of several tetragonal dipyramids which are incompatible with the point group 4*mm*. Gait & Harris (1972) reported that the *x*-ray powder patterns of arsenian and tellurian varieties of haucheconite included two weak reflections which could only be indexed on a cell with doubled *a* and *c* dimensions. These reflections were not present on Peacock's powder films of Westphalian (antimonian) hauchecornite and are not listed by Berry & Thompson (1962) for material from the same locality.

The original density measurements in Scheibe (1888, 1893) range from 6.35 to 6.47 g/cm^{-3}. Peacock (1950) measured 6.36 g/cm^{-3}, on a 17 mg crystal, with a torsion balance.

EXPERIMENTAL

The present study was made on Peacock's crystal — a square plate measuring respectively, 0.29 × 0.29 × 0.13 mm along the *a* and *c* axes. The dominant form is {001}. Before proceeding to the collection of intensity data, long-exposure Cu$K\alpha$ and Mo$K\alpha$ Weissenberg and precession films were prepared in search of evidence for a doubling of Peacock's cell, for the presence of Renninger reflections and as a test of the diffraction symbol. The 00*l* row was further probed with an 80 hour Mo$K\alpha$ exposure of the (*h*0*l*) reciprocal plane. This work supported Peacock's choice of cell and Laue symmetry. Although we could find no trace of the 003 reflection reported by Peacock, we did observe a faint 001 reflection whose existence was later confirmed by several scans across the peak position on a four-circle Picker diffractometer. Thus hauchecornite from the Friedrich mine in Westphalia has no systematically missing *x*-ray reflections. In general, however, intensities of reflections with $h + k + l = 2n$ are stronger than those for which the sum is odd, suggesting a pseudo-body centering arrangement of the Bi atoms in the structure.

The cell parameters were calculated from the 2θ values of a number of high angle axial reflections measured on the Picker diffractometer. Standard deviations were calculated by hand in the usual way. This gave $a = 7.300(3)$, $c = 5.402(2)$ Å and these values were subsequently used in calculating the bond lengths and angles.

Table 1 shows the results of calculating the cell contents of this cell for the measured density 6.47 g/cm^{-3} and the best available analyses for Westphalian hauchecornite. The values are very close to $Ni_9(Bi_{1.3}Sb_{0.7})S_8$ and since the calculated density, 6.58 g/cm^{-3}, is in reasonably good agreement with the measured values, this formula was used in the determination of the structure.

A total of 289 symmetry-independent reflections were collected on a Picker four-circle FACS-1 diffractometer with Mo$K\alpha$ radiation ($\lambda = 0.71069$ Å) in the θ-2θ scan mode over the range $0.02 \leq (\sin\theta)/\lambda \leq 0.70$, using a 0.5° min^{-1} scan rate and a 100 s background count on each side of the peak. The data were scaled by reference to two standard reflections monitored throughout the collection and corrected for Lorentz, polarization and both Φ and crystal-boundary absorption (μMo$K\alpha$ = 354.2 cm^{-1}) factors, yielding 271 reflections with $F_o^2 > 3\sigma F_o^2$ which were taken to be observed. The values of minimum and maximum absorption corrections were 586 and 4913.

TABLE 1. THE CELL CONTENTS OF HAUCHECORNITE FROM THE FRIEDRICH MINE WESTPHALIA

	Weight per cent				Atoms in the unit cell				
	1	2	3	4	5		6		7
Ni	45.054	45.883	45.26	46.8	8.65	8.83	8.94	9.00	9
Co	0.704	0.82	0.76	0.3	0.14		0.06		
Fe	0.271	0.17	0.22		0.04				
Pb	0.03								
Bi	24.508	23.72	24.00	22.3	1.29	1.98	1.20	1.95	1.3 2
Sb	6.738	6.226	6.45	7.8	0.59		0.72		0.7
As	0.895	0.45	0.67	0.2	0.10		0.03		
S	22.879	22.625	22.64	22.6	7.92		7.92		8
	101.079	99.894	100.00	100.0					

1,2. Analyst Hesse (in Scheibe 1893) on material composed wholly of crystal fragments with bright fracture surfaces and no traces of impurities or alteration; measured density 6.47 g/cm^3.

3. Average of 1 and 2 recalculated to sum 100% after subtracting as PbS 0.03% Pb in 1.

4. Gait & Harris (1972); microprobe analysis on the same specimen (HM 89710) that yielded Peacock's crystal.

5,6. Atoms in the unit cell calculated from 3 and 4, respectively, for a cell with a=7.300, c=5.402Å and a density of 6.47 g/cm^3.

7. $Ni_9(Bi_{1.3}Sb_{0.7})S_8$; idealized cell contents for hauchecornite from Westphalia.

DETERMINATION AND REFINEMENT OF THE STRUCTURE

The distribution of E values indicated the presence of a centre of symmetry and consequently the centrosymmetric space group $P4/mmm$ was chosen for the determination.

A three-dimensional Patterson map and a similar map based on $(E^2 - 1)$ coefficients suggested that Bi was located at (0,0,0,) and $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$. Structure factor calculations for these two positions gave $R = 0.68$ (where R is defined as: $\Sigma|\,|F_o| - |F_c|\,|/\Sigma|F_o|$). The Ni and S positions were revealed by subsequent F_o Fourier maps calculated with successively refined phases. Isotropic refinement reached an R value of 0.121. The temperature factors of the two Bi positions were grossly different (0.58, 1.72). In the next step the multipliers for the two Bi positions were allowed to vary while the isotropic temperature factors were constrained to their mean value. This reduced the R value to 0.113 and indicated that the (0,0,0) position contained more scattering power than the $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ location. Consequently the $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ site (hereafter called the M site) was assigned all the Sb, giving it the composition $(Sb_{0.7}Bi_{0.3})$. Three cycles of refinement employing weighted averages of Sb and Bi scattering factors for the M site, anomalous dispersion corrections for all the atoms, anisotropic temperature factors and new weights based on a value $\sigma F_o = 0.095\,\overline{F_o} + 1.50 + 9.26/\overline{F_o}$ derived from a plot of $\overline{\Delta F_o}/\overline{F_o}$ vs $1/\overline{F_o}$ gave an R value of 0.076 (0.078 for all 289 reflections). Three reflections (004, 240, 550) which were observed on the films to be situated on strong Laue streaks, gave widely differing background counts on either side of the peak position. It was felt, therefore, that the net intensities were less accurately collected than the bulk of the data. With these reflections deleted from the final refinement the R value reduced to 0.067 and the value of $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2} = 0.115$. Atomic parameters and temperature factors are listed in Table 2; pertinent interatomic distances and angles are given in Table 3. The comparison of observed and calculated structure factors is given in Table 4.

TABLE 2. FRACTIONAL COORDINATES AND TEMPERATURE FACTORS

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	B(Å^2)
Bi	0	0	0	52(6)	52(6)	28(7)	0	0	0	0.93
$M(Sb_{0.7}Bi_{0.3})$	50000	50000	50000	45(8)	45(8)	58(10)	0	0	0	0.99
Ni(1)	0	0	50000	29(14)	29(14)	45(21)	0	0	0	0.82
Ni(2)	18076(46)	50000	25249(42)	84(6)	52(5)	51(10)	0	14(5)	0	1.22
S(1)	31274(92)	0	50000	27(10)	38(10)	23(16)	0	0	0	0.64
S(2)	26961(139)	26961(139)	0	33(13)	33(13)	30(16)	2(9)	0	0	0.66

Fractional coordinates x 10^5 and anisotropic thermal parameters x 10^4; values in parentheses are estimated standard deviations as obtained from the last cycle of least-squares refinement;

$T=\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$

The full matrix least-squares program XFLS (Ellison 1962) was used for the structure factor calculations and the refinement. The scattering factors for neutral atoms were taken from Cromer & Mann (1968). The anomalous dispersion corrections were made from the values computed by Cromer (1965). The standard deviations of interatomic distances and angles were calculated with the program ORFFE (Busing *et al.* 1964).

DISCUSSION OF THE STRUCTURE

The Bi atoms in the (0,0,0) positions in the structure are at the centre of a regular dipyramid consisting of 4S(2) in the (001) plane and 2Ni(1) on the vertical axis. The Ni(1) atoms occupy the (0,0,½) positions and are similarly octahedrally coordinated by 4S(1) in the (001) plane and by 2Bi in the (0,0,0) positions. Thus the two kinds of polyhedron are linked by —Bi—Ni(1)—Bi—Ni(1)— bonds into continuous chains parallel to *c*[001] (Fig. 1).

Ni(2) is in distorted square-planar coordination with 2S(1) and 2S(2) (Fig. 2). The Ni atom is 0.28Å out of the S plane. A prominent feature of the structure is the arrangement of the planar polyhedra into continuous zig-zag ribbons, along *c*[001], which occur in pairs by sharing

TABLE 3. INTERATOMIC DISTANCES AND ANGLES†

Coordinates of equivalent positions

i	x,y,z;	ii	$\bar{x},\bar{y},z$;	iii	$x,y,\bar{z}$;	iv	$\bar{x},\bar{y},\bar{z}$;
v	$\bar{x},y,z$;	vi	$x,\bar{y},z$;	vi	$\bar{x},y,\bar{z}$;	viii	$x,\bar{y},\bar{z}$;
ix	$\bar{y},x,z$;	x	$y,\bar{x},z$;	xi	$\bar{y},x,\bar{z}$;	xii	$y,\bar{x},\bar{z}$;
xiii	y,x,z;	xiv	$\bar{y},\bar{x},z$;	xv	$y,x,\bar{z}$;	xvi	$\bar{y},\bar{x},\bar{z}$.

Metal-atom polyhedra

Bi			$M(\mathrm{Sb}_{0.7}\mathrm{Bi}_{0.3})$		
S(2)	2.784(7)Å	4x	Ni(2)	2.687(3)Å	8x
Ni(1)	2.701(1)	2x			

Ni(1)			Ni(2)		
S(1)	2.283(7)	4x	S(1)	2.323(5)	2x
Bi	2.701(1)	2x	S(2)	2.260(8)	2x
			M	2.687(3)	1x

Sulphur-atom polyhedra

S(1)			S(2)		
Ni(1)	2.283(7)Å	]x	Bi	2.784(7)Å	]x
Ni(2)	2.323(5)	4x	Ni(2)	2.260(3)	4x

Closest Ni-Ni distances		Closest S-S distances	
Ni(2^{i})—Ni(2^{iii})	2.674(7)Å	S(1^{i})—S(1^{v})	2.735(8)Å
Ni(2^{i})—Ni(2^{ii})*	2.639(7)	S(2^{i})—S(2^{v})	3.364(8)
Ni(2^{i})—Ni(2^{iii})*	2.728(7)	S(1^{i})—S(2^{i})	3.357(8)

*atom located in adjacent cell

Interatomic angles

Ni(2^{iii})—*M*—Ni(2^{xi})	75.7(1)°	S(1^{i})—Ni(2)—S(1^{v})	72.1(1)
Ni(2^{i})—*M*—Ni(2^{ii})	120.3(1)	S(2^{i})—Ni(2)—S(2^{v})	96.1(1)
Ni(2^{i})—*M*—Ni(2^{iii})	59.7(1)	S(1^{i})—Ni(2)—S(2^{i})	94.2(1)
Ni(2^{i})—*M*—Ni(2^{xi})	104.3(1)		

†Estimated standard deviations in parentheses

Following Ni(1) ...... read 1X and Bi 1X

TABLE 4. Observed and calculated structure factors. →

L	FO	FC
H= 0, K= 0		
1	141	-114
2	608	463
3	72*	73
4	3499	2866
5	96*	-75
6	411	391
7	172	123
H= 0, K= 1		
0	32*	-71
1	842	783
2	991	997
3	535	616
4	49*	50
5	591	517
6	600	521
7	417	342
H= 0, K= 2		
0	1506	1391
1	685	-583
2	648	642
3	377	-389
4	758	935
5	268	-271
6	423	386
7	215	-173
H= 0, K= 3		
0	773	-713
2	2208	2265
3	443	464
4	366	-389
5	376	463
6	1189	1217
7	276	249
H= 0, K= 4		
0	2221	2240
1	123	86
2	925	924
3	132	144
4	1394	1585
5	46*	69
6	521	622
H= 0, K= 5		
0	59*	-56
1	475	481
2	256	262
3	414	429
4	46*	-50
5	281	338
6	195	172
H= 0, K= 6		
0	1761	1813
1	443	-453
2	120	-66
3	346	-358
4	1279	1357
5	313	-332
6	54*	84
H= 0, K= 7		
0	62*	89
1	533	515
2	890	953
3	406	416
4	85	115
5	420	423
H= 0, K= 8		
0	779	802
1	96	103
2	552	609
3	111	100
4	654	653
H= 0, K= 9		
0	342	-321
1	115	110
2	527	544
3	110	97
H= 0, K= 10		
0	807	827
1	177	-205
H= 1, K= 1		
0	528	468
1	97	163
2	1823	1881
3	104	116
4	398	377
5	175	157
6	1165	962
7	117	117
H= 1, K= 2		
0	1321	1210
1	1310	1192
2	690	-646
3	920	1004
4	654	780
5	673	702
6	336	-269
7	721	602
H= 1, K= 3		
0	1808	1795
1	213	-182
2	830	843
3	118	-107
4	1071	1227
5	99	-89
6	505	527
7	51*	-47
H= 1, K= 4		
0	646	651
1	790	768
2	200	-165
3	637	654
4	412	462
5	456	533
6	72	-66
H= 1, K= 5		
0	169	115
1	214	206
2	1354	1389
3	136	155
4	122	123
5	198	220
6	759	814
H= 1, K= 6		
0	158	146
1	529	542
2	445	467
3	469	481
4	124	137
5	383	399
6	299	315
H= 1, K= 7		
0	589	561
1	63	-59
2	746	794
3	126	-39
4	444	455
5	48*	-43
H= 1, K= 8		
0	431	437
1	523	539
2	362	-369
3	517	518
4	364	347
H= 1, K= 9		
0	568	578
1	39*	-29
2	477	485
3	43*	-28
H= 1, K= 10		
0	197	200
1	283	277
H= 2, K= 2		
0	511	317
1	743	654
2	2095	2223
3	422	456
4	279	286
5	491	496
6	1329	1183
7	326	294
H= 2, K= 3		
0	190	61
1	650	618
2	654	461
3	518	537
4	102	73
5	363	418
6	341	278
7	380	328
H= 2, K= 4		
0	656	165
1	197	-190
2	1112	1109
3	179	-158
4	293	152
5	70	-88
6	617	628
H= 2, K= 5		
0	1014	1012
1	970	992
2	530	-549
3	923	940
4	685	728
5	613	673
6	290	-278
H= 2, K= 6		
0	1049	1061
1	179	159
2	824	873
3	145	142
4	827	834
5	153	158
H= 2, K= 7		
0	222	239
1	351	350
2	285	-205
3	305	313
4	184	190
5	297	274
H= 2, K= 8		
0	249	-172
1	75	74
2	715	746
3	60	43
4	183	-130
H= 2, K= 9		
0	307	291
1	486	497
2	251	230
3	476	475
H= 2, K= 10		
0	409	390
H= 3, K= 1		
0	1818	1795
H= 3, K= 3		
0	2732	2791
1	346	-319
2	274	165
3	195	-199
4	1757	1964
5	209	-220
6	209	215
H= 3, K= 4		
0	225	57
1	628	625
2	935	930
3	501	507
4	141	93
5	437	470
6	570	575
H= 3, K= 5		
0	886	915
1	93	-86
2	644	676
3	97	-75
4	675	700
5	47*	-43
6	441	446
H= 3, K= 6		
0	445	-410
1	269	269
2	1020	1062
3	281	216
4	317	-268
5	241	222
H= 3, K= 7		
0	1205	1250
1	119	-118
2	436	457
3	109	-65
4	1023	998
5	123	-101
H= 3, K= 8		
0	152	138
1	421	428
2	243	232
3	411	398
4	135	124
H= 3, K= 9		
0	950	931
1	168	-181
2	160	156
H= 4, K= 4		
0	1049	934
1	214	180
2	1167	1196
3	197	204
4	738	732
5	141	147
6	782	767
H= 4, K= 5		
0	418	439
1	510	528
2	417	-417
3	496	492
4	316	324
5	377	381
H= 4, K= 6		
0	936	898
1	255	-252
2	368	380
3	214	-201
4	760	708
5	196	-191
H= 4, K= 7		
0	367	377
1	516	512
2	367	309
3	453	436
4	327	319
H= 4, K= 8		
0	318	249
1	163	165
2	729	749
3	153	147
H= 4, K= 9		
0	93	-56
1	172	170
2	172	142
H= 5, K= 5		
0	319	-97
1	308	291
2	1136	1139
3	229	221
4	48*	-70
5	306	287
H= 5, K= 6		
0	253	250
1	528	531
2	251	246
3	511	501
4	223	212
H= 5, K= 7		
0	229	225
1	70	-54
2	603	610
3	44*	-47
4	199	196
H= 5, K= 8		
0	350	337
1	430	434
2	453	-454
3	456	435
H= 6, K= 6		
0	1289	1306
1	107	-68
2	303	312
3	73	-49
4	1152	1062
H= 6, K= 7		
0	96	-88
1	208	174
2	397	372
3	178	142
H= 6, K= 8		
0	428	362
1	39*	-54
H= 7, K= 7		
0	651	634
1	39*	-25
2	551	532

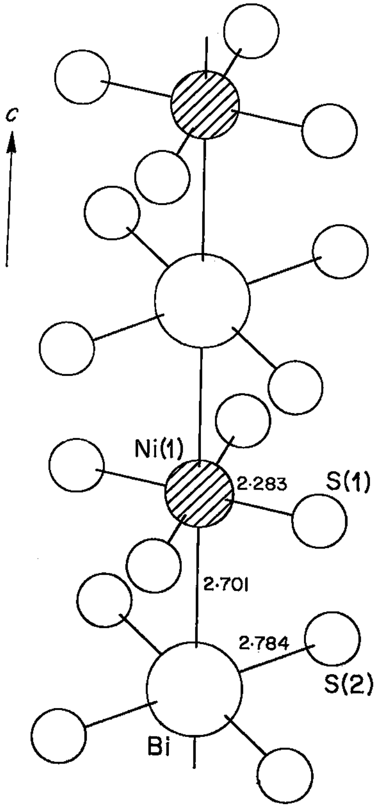

FIG. 1. Octahedrally-coordinated Ni(1) —Bi chains.

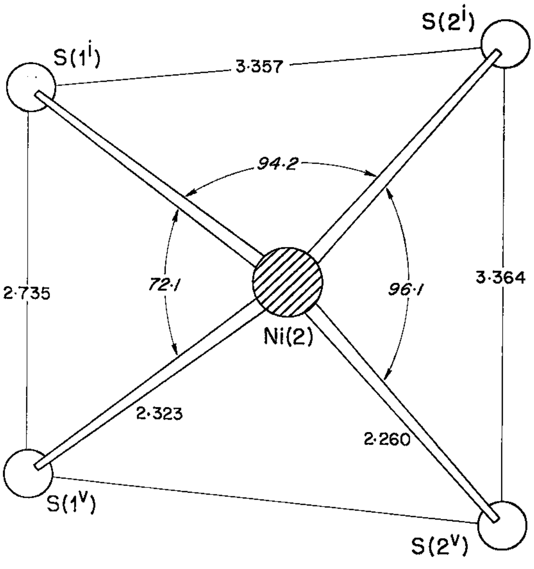

FIG. 2. Distorted square-planar coordination of S about Ni(2).

the S(1)—S(1) edges of the square polyhedra (Fig. 3). The closest Ni—Ni distances within the single ribbons are 2.674 and 2.728Å, and between the single ribbons, 2.639Å, as compared to 2.492Å in metallic nickel. The distances are so short as to suggest some orbital interaction and a contribution to the strength of the double ribbons.

The double Ni(2)—S ribbons are linked to the Bi—Ni(1) chains, and hence to neighbouring Ni(2)—S double ribbons along the two *a*-axis directions, by the sharing of S atoms, thereby producing a tightly knit three-dimensional structure (Fig. 4).

The *M* (0.7Sb + 0.3Bi) sites, in the (½,½,½) positions are situated along the line of intersection of four double ribbons (Fig. 4). The atoms in these sites are in eight-fold coordination with Ni(2) occupying the corners of a regular tetragonal prism (Fig. 5). If the relatively weak Ni(2)—*M* bonds are taken into account,

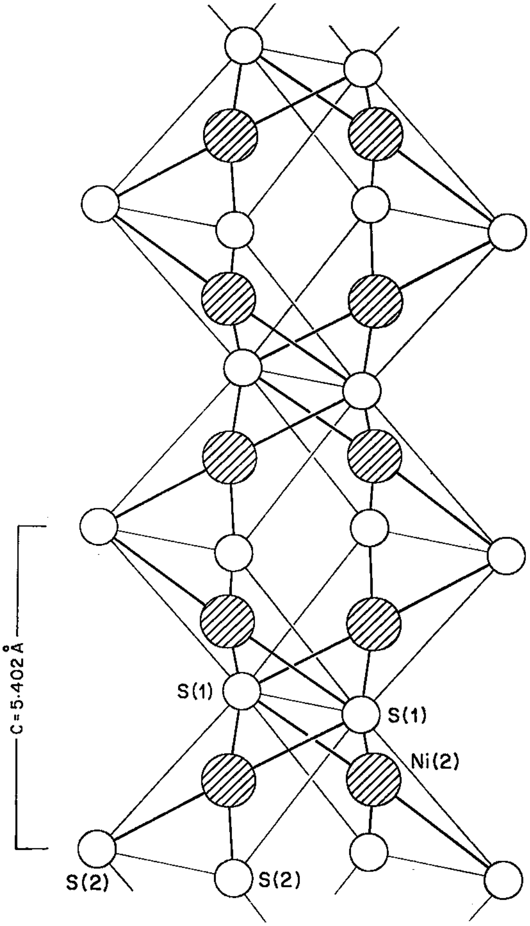

FIG. 3. Double Ni(2)—S ribbons.

the square-planar S coordination about Ni(2) becomes the base of a tetragonal pyramid with the *M* site at the vertex.

The eight-fold coordination of the *M* site by Ni suggests that the bonding of Sb and Bi in this position has considerable metallic character. The close agreement of the Ni—*M* distance, 2.687Å, with the Ni—Bi distance 2.71Å in the alloy NiBi (Hägg & Funke 1930) supports this view. The structure determination has shown that of the two Group V-element sites, (0,0,0) and $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$, the less metallic element Sb is ordered into the *M* site. Since the Ni(1)—Bi distance, 2.701Å, in the first site is not significantly greater than the Ni—*M* distance, geometrical considerations have no bearing on the ordering. Evidently the predominantly covalent bonding at the (0,0,0) sites to 4S as well as to 2Ni favours the presence of Bi over Sb.

All S atoms are coordinated by five metal atoms on the corners of a nearly regular tetragonal pyramid. In the S(1) pyramid, Ni(2) atoms occupy the base with Ni(1) at the vertex. Ni(2) atoms also occupy the base of the S(2) pyramid but Bi is situated at the vertex.

The atoms of the unit cell are arranged into four layers parallel to (001), at intervals of almost exactly $\frac{1}{4}c$. This layering evidently

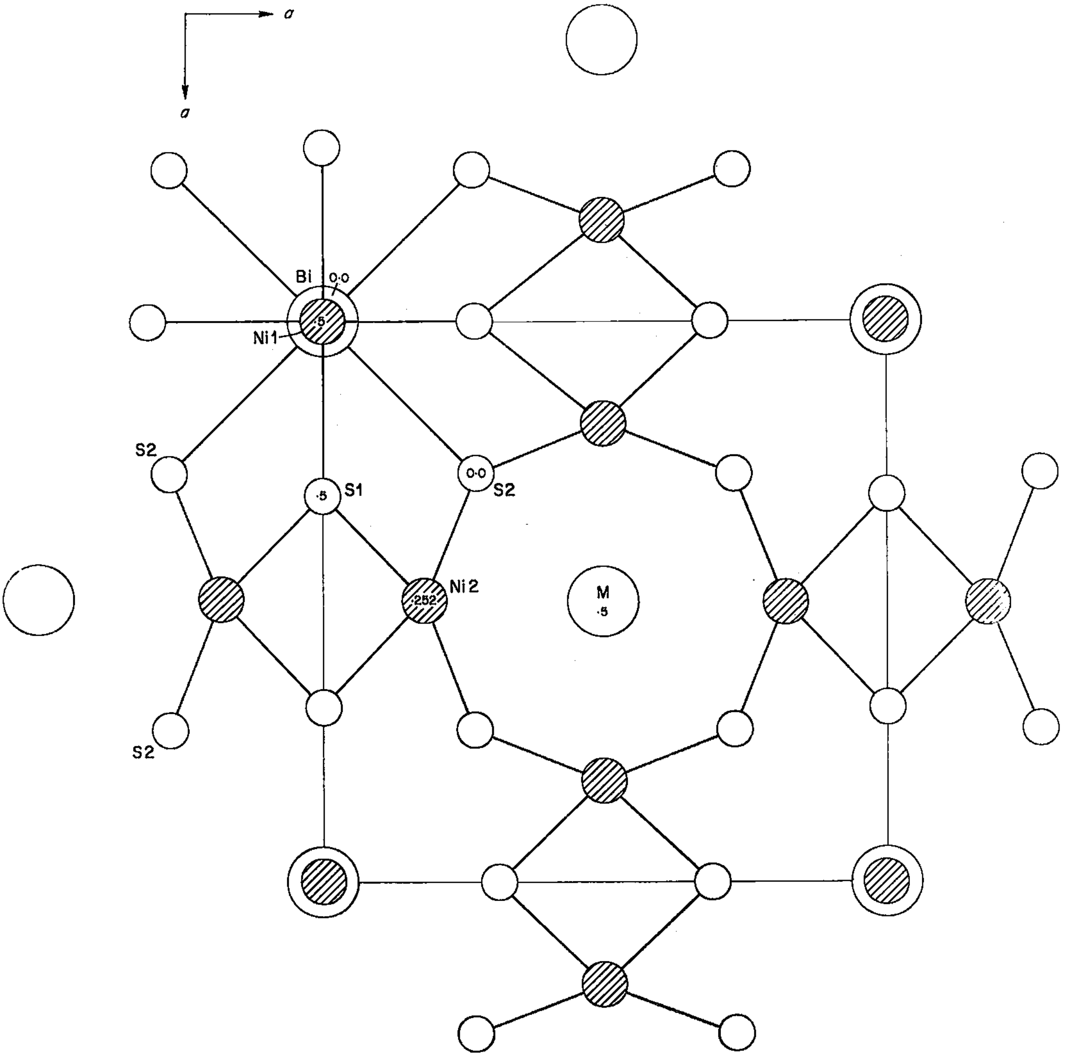

FIG. 4. Projection of the hauchecornite structure on (001). Numbers are fractional z coordinates. The coordination for only one Ni(1)—Bi chain is shown to emphasize the arrangement of the double Ni(2)—S ribbons and the *M* sites they enclose.

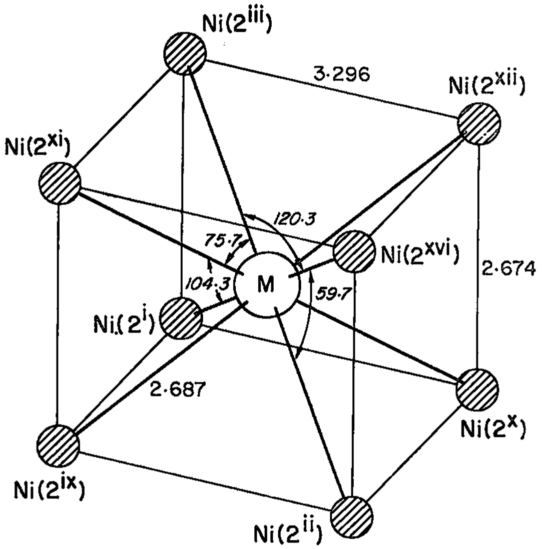

FIG. 5. Eight-fold coordination of Ni(2) about the $M(0.7Sb + 0.3Bi)$ site.

accounts for the dominant external form found on crystals. Another prominent set of atomic planes, parallel to the S(1)—S(2) planar polyhedra in the double ribbons, might be supposed to manifest itself as one of the external {*h*0*l*} forms measured by Peacock (1950). The planes make an angle of 53.9° with the horizontal. The most likely form, {201}, has a corresponding angle of 56.3° which is in poor agreement with this value.

The composition of hauchecornite represents an unusual combination of elements. Among minerals, only parkerite ($Ni_3Bi_2S_2$) has a similar composition. A bismuthian ullmannite, Ni(Sb, Bi)S, is known but the ratio Sb:Bi = 6.6:1 and therefore, bismuth is not an essential constituent of the mineral. The structure of parkerite has recently been solved and explained by Fleet (1973). It has little in common with the structure of hauchecornite. One point of similarity is the absence of TS_3 pyramids (in which $T =$ As, Sb, Bi) which Takéuchi & Sadanaga (1969) regard as the unit of structure that distinguishes a sulphosalt from a sulphide. According to this concept, hauchecornite and parkerite would not be classified as sulphosalts and this is in keeping with practice in reference works.

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