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THE CRYSTAL STRUCTURE OF ARSENOHAUCHECORNITE

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ABSTRACT

Arsenohauchecornite, $Ni_{18}Bi_3AsS_{16}$, is tetragonal *I4/mmm* (No. 139), with $Z = 2$, and cell parameters *a* 10.2711(2), *c* 10.8070(4) Å. This superstructure was refined using 404 observed $[I > 3\sigma(I)]$ reflections to residuals $R = 1.5\%$ and $R_w = 1.8\%$. The (001) layered structure is dominated by three different Ni coordination polyhedra, one octahedral and two cubic. The superstructure results from the ordering in the cubic polyhedra of Bi and As, which have very different mean bond-lengths (2.828 and 2.478 Å, respectively). Precise X-ray powder-diffraction data clearly reveal the *I* supercell.

Keywords: arsenohauchecornite, superstructure, ordering, X-ray, powder data, structure refinement.

SOMMAIRE

L'arsénohauchécornite $Ni_{18}Bi_3AsS_{16}$ est tétragonale, groupe spatial *I4/mmm* (no 139), avec $Z = 2$ et les paramètres *a* 10.2711(2), *c* 10.8070(4) Å. La surstructure a été affinée à partir de 404 réflexions observées $[I > 3\sigma(I)]$ jusqu'à un résidu $R = 1.5\%$, $R_w = 1.8\%$. La structure en feuillets (001) contient trois différents polyèdres de coordination du Ni, dont un est octaédrique et deux sont cubiques. La surstructure résulte de la mise en ordre du Bi et de l'As, qui possèdent des longueurs de liaison moyennes très différentes (2.828 et 2.478 Å, respectivement), dans les polyèdres cubiques. Des données précises de diffraction X (méthode des poudres) révèlent clairement la surmaille *I*.

(Traduit par la Rédaction)

Mots-clés: arsénohauchécornite, surstructure, mise en ordre, données de diffraction X (méthode des poudres), affinement de la structure.

INTRODUCTION

The authors began studies of arsenohauchecornite in 1970, at which time it was considered to be an arsenian variety of hauchecornite. It later attained species status through the the work of Gait & Harris (1980). The present authors have now confirmed that the true cell of this mineral is a multiple of the 7.3 × 5.4 Å tetragonal *P* cell of Peacock (1950), and of the Kocman & Nuffield (1974) cell for hauchecornite. Gait & Harris (1972, 1980) adopted a 14.6 × 10.8 Å *P* cell for both these minerals, but the present work shows that this larger cell is in fact an *F* cell which, convention requires, be rotated 45° to give a 10.3 × 10.8 Å *I* cell, the one regarded by us as correct for arsenohauchecornite. Possible space-groups are *I4/mmm*, *I*422, *I4mm*, $I\bar{4}2m$, and $I\bar{4}m2$. The formula used to transform the cell of Peacock (1950) and Kocman & Nuffield (1974) to the present one is $1\bar{1}0/110/002$. This larger *I* cell of arsenohauchecornite has a unit-cell content *Z* of $4[Ni_{8.9}Fe_{0.3}Co_{0.1})_{\Sigma 9.3}Bi_{1.0}(As_{0.7}Bi_{0.5})_{\Sigma 1.2}S_8]$ (see Gait & Harris 1972), as opposed to $Z = 1$ for the small *P* cell. Although the present authors did solve the substructure of arsenohauchecornite at the earlier date, we were unsuccessful in determining the (true) superstructure. Our efforts were pre-empted by the solution of the (sub)structure of hauchecornite by Kocman & Nuffield (1974), which matched our substructure of arsenohauchecornite, and our project was discontinued. An interest in solving the 'superstructure' prompted our further investigation of arsenohauchecornite.

CRYSTAL-STRUCTURE ANALYSIS OF ARSENOHAUCHECORNITE

Experimental details

Intensity data for the present structure-determination of arsenohauchecornite were collected twice on the same crystal fragment of holotype material from the Vermilion mine, Sudbury District, Ontario (Royal Ontario Museum specimen #M29208). The initial set of intensities was collected using a sphere 0.28 mm in diameter. This data set, collected on the Nicolet *R3m* four-circle diffractometer at the University of Manitoba, served to solve the structure and refine it to $R = 7.2\%$ and $R_w = 6.4\%$. To refine the structure to a more satisfactory *R* value, the sphere was ground to 0.13 mm, and a larger data-set collected. The greatly improved results are described here in detail. Intensity data

TABLE 1. POSITIONAL COORDINATES AND THERMAL PARAMETERS (Å^2) IN ARSENOHAUCHECORNITE

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	U_{eq}
Ni(1)	1/2	0	0	0.78(8)	0.78(8)	0.94(7)	0	0	0	0.66(6)
Ni(2)	0.14501(6)	0.14501	0.37922(8)	1.01(3)	1.01	0.81(4)	0.07(3)	-.04(2)	-.04	0.75(2)
Ni(3)	0.17109(6)	0.17109	0.12524(8)	0.88(3)	0.88	0.87(4)	0.14(3)	0.14(2)	0.14	0.69(2)
Bi(1)	1/2	0	1/4	0.89(2)	0.89	0.79(2)	0	0	0	0.64(1)
Bi(2)	0	0	0	0.98(3)	0.98	1.02(4)	0	0	0	0.78(2)
As	0	0	1/2	0.63(6)	0.63	0.99(10)	0	0	0	0.59(5)
S (1)	0.3493(2)	0.1613(2)	0	0.52(7)	0.57(7)	0.76(5)	0.09(5)	0	0	0.48(5)
S (2)	0.2287(2)	0	0.2415(2)	0.84(7)	0.69(7)	0.85(6)	0	0.08(6)	0	0.63(5)

* U_{ij} values X100

TABLE 2. SELECTED INTERATOMIC DISTANCES (Å) AND BOND ANGLES IN ARSENOHAUCHECORNITE

			Ni(1) octahedron		
Ni(1)-Bi(1)	2.700(1)	x2	Bi(1)-Ni(1)-Bi(1)	180	
Ni(1)-S (1)	2.266(1)	x4	Bi(1)-Ni(1)-S (1)	90	x4
Mean	2.411		S (1)-Ni(1)-S (1)	86.12(6)	x2
			S (1)-Ni(1)-S (1)	93.88(6)	x2
			Ni(2) distorted cube		
Ni(2)-Ni(2)	2.609(2)		Ni(2)-Ni(2)-Ni(3)	91.03(4)	
Ni(2)-Ni(3)	2.769(1)		Ni(2)-Ni(2)-As	58.21(3)	
Ni(2)-Ni(3)	2.670(1)		Ni(2)-Ni(2)-S (1)	56.74(4)	x2
Ni(2)-As	2.476(1)		Ni(3)-Ni(2)-S (1)	53.24(4)	x2
Ni(2)-S (1)	2.379(2)	x2	As -Ni(2)-S (2)	100.28(4)	x2
Ni(2)-S (2)	2.273(2)	x2	S (1)-Ni(2)-S (1)	69.99(6)	
Mean	2.479		S (1)-Ni(2)-S (2)	93.39(5)	x2
			S (2)-Ni(2)-S (2)	93.83(7)	
			Mean	76.70	
			Ni(3) distorted cube		
Ni(3)-Ni(2)	2.769(1)		Ni(2)-Ni(3)-Ni(3)	88.97(3)	
Ni(3)-Ni(2)	2.670(1)		Ni(2)-Ni(3)-S (1)	56.81(5)	x2
Ni(3)-Ni(3)	2.706(2)		Ni(3)-Ni(3)-Bi(2)	61.42(3)	
Ni(3)-Bi(2)	2.828(1)		Ni(3)-Ni(3)-S (1)	53.55(3)	x2
Ni(3)-S (1)	2.277(2)	x2	Bi(2)-Ni(3)-S (2)	86.87(5)	x2
Ni(3)-S (2)	2.238(1)	x2	S (1)-Ni(3)-S (1)	73.61(5)	
Mean	2.537		S (1)-Ni(3)-S (2)	94.96(5)	x2
			S (2)-Ni(3)-S (2)	95.73(7)	
			Mean	75.34	
			Bi(1) octahedron		
Bi(1)-Ni(1)	2.700(1)	x2	Ni(1)-Bi(1)-Ni(1)	180	
Bi(1)-S (2)	2.786(2)	x4	S (2)-Bi(1)-S (2)	90	x4
Mean	2.757		Ni(1)-Bi(1)-S (2)	88.11(4)	x2
			Ni(1)-Bi(1)-S (2)	91.89(4)	x2
			Bi(2) cube		
Bi(2)-Ni(3)	2.828(1)	x8	Ni(3)-Bi(2)-Ni(3)	76.77(2)	x8
			Ni(3)-Bi(2)-Ni(3)	57.16(2)	x4
			Mean	70.23	
			As cube		
As -Ni(2)	2.476(1)	x8	Ni(2)-As-Ni(2)	73.89(2)	x8
			Ni(2)-As-Ni(2)	63.58(2)	x4
			Mean	70.45	

were collected at CANMET, Ottawa on an Enraf Nonius CAD–4 single-crystal diffractometer operated at 50 kV and 26 mA with graphite-monochromated Mo$K\alpha$ radiation. Data collection and structure determination were done using the NRCVAX package of computer programs (Gabe *et al.* 1985). A set of 25 reflections permutated four ways, $\pm h$ at $\pm 2\theta$ (*i.e.*, 100 reflections), was used to orient the crystal. Fifty-four reflections with 2θ values from 23 to 49° permutated as above (*i.e.*, 216 reflections) were used to refine the cell parameters: a 10.2711(2), c 10.8070(4) Å. Four asymmetric units ($hkl, \bar{h}\bar{k}\bar{l}, h\bar{k}l$ and $\bar{h}kl$, with $h \geq k$) of data were collected to $2\theta = 60°$ assuming an I lattice. Data reduction included background, scaling, Lorentz, and polarization spherical absorption corrections ($\mu = 380$ cm^{-1}). Of the 2037 measured intensities, 508 are independent, and 404 of these were observed [$I > 3\sigma(I)$].

Structure analysis

Phasing of a set of normalized structure-factors gave a unique E-map, with four major peaks corresponding to heavy-atom sites of the subcell structure previously determined in space group $P4/mmm$. This initial model refined in $I4/mmm$ to give a residual index $R = 3.4\%$. With the transformed sites and a series of difference-Fourier maps, all of the cation sites were found and assigned the correct scattering curve. There were three notable differences in the large supercell (denoted l) structure from that of the small subcell (denoted s); in addition to the cell transformation, there is a shift of origin $(0,0,0)_s \rightarrow (\frac{1}{2},0,\frac{1}{4})_l$, a new Ni site [$\text{Ni}(1)_s \rightarrow \text{Ni}(1)_l$, $\text{Ni}(2)_s \rightarrow \text{Ni}(2)_l$ and $\text{Ni}(3)_l$], and a new, distinct As site [$\text{Bi}_s \rightarrow \text{Bi}(1)_l$, $(\text{Sb,Bi})_s \rightarrow \text{Bi}(2)_l$ and As_l]. The sulfur sites are the same in both structures. These differences will be discussed in detail later. At this point in the structure analysis, the first data-set would not refine below $R = 7.2\%$ and $R_w = 6.4\%$ with anisotropic thermal parameters. As described above, the second data-set was used in the final stages of the least-squares refinement, with the last cycle calculated using the 404 observed reflections with 8 atoms, 36 parameters, a secondary extinction coefficient, and unit weights. Final R indices were $R = 1.5\%$ and $R_w = 1.8\%$. The final positional and thermal parameters are given in Table 1, and the bond lengths and angles in Table 2. Table 3, the observed and calculated structure-factors, has been submitted to the Repository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Canada KlA 0S2.

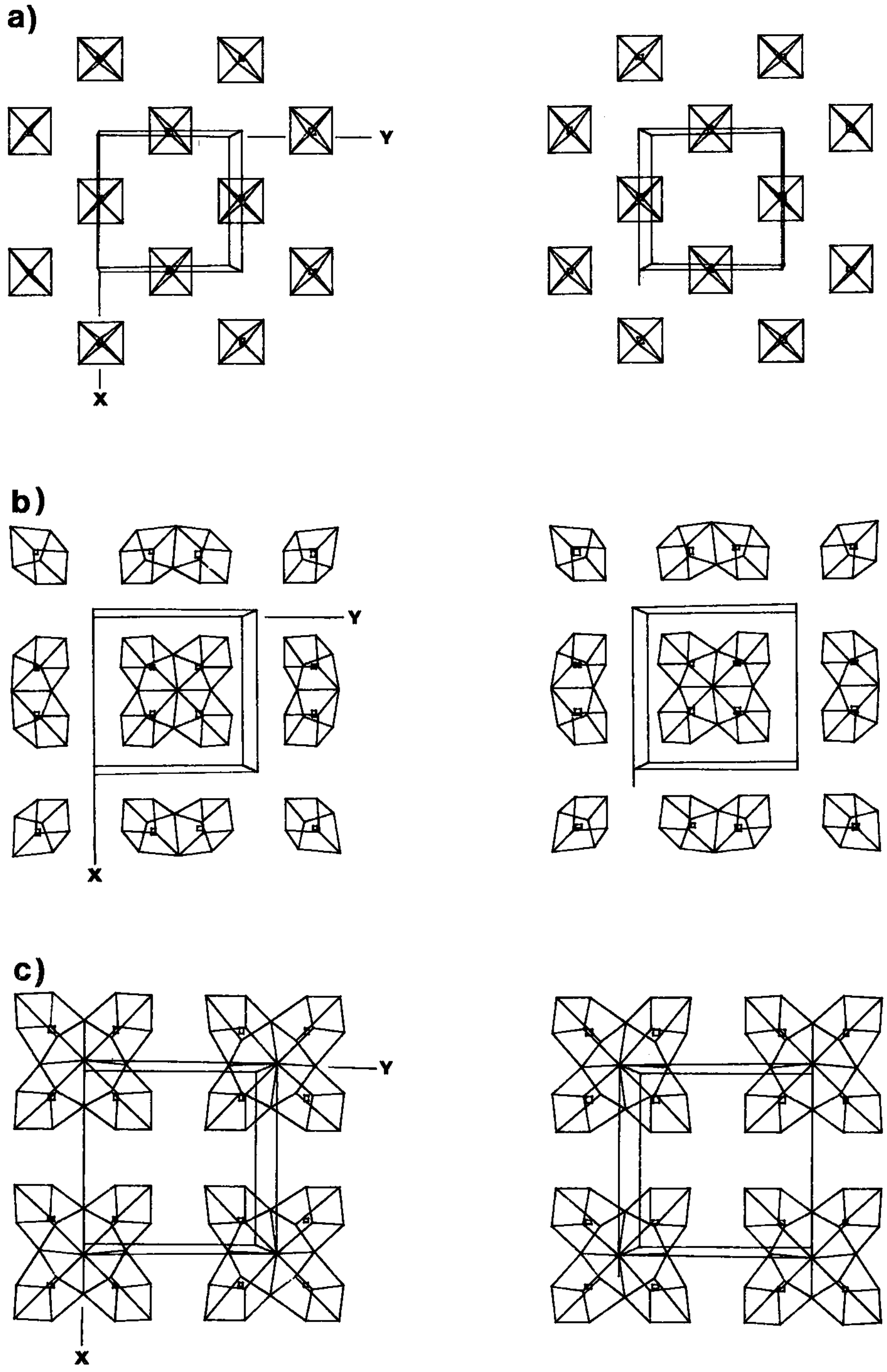

FIG. 1. Z-axis projections, stereoscopic view of the Ni coordination polyhedra in arsenohauchecornite; a) Ni(1) octahedra at $z = 0$, b) Ni(2) distorted cubes at $z = 0.121$, and c) Ni(3) distorted cubes at $z = 0.125$.

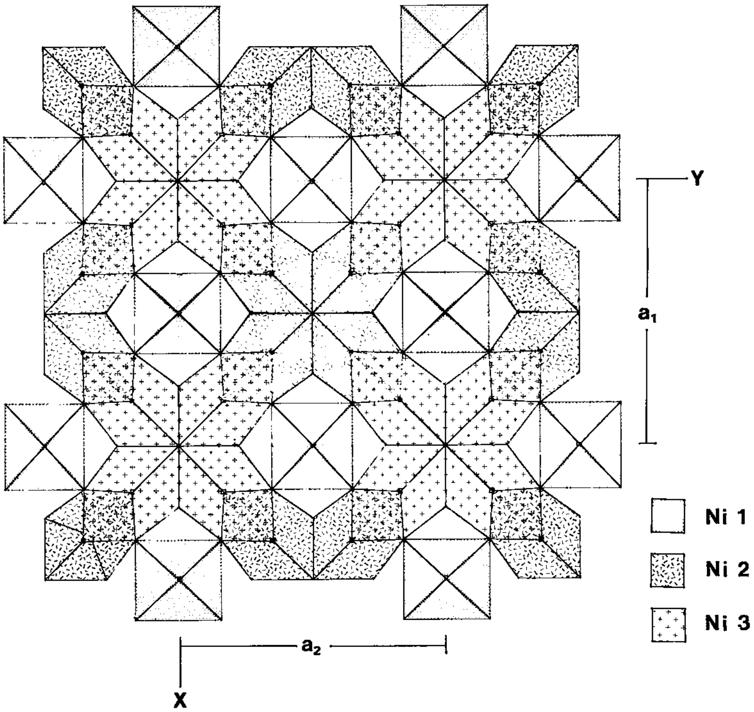

FIG. 2. *Z*-axis projection of the lower ¼ *c* showing a combination of the three Ni coordination polyhedra of Figure 1.

Description and discussion of the structure

The arsenohauchecornite structure consists of alternating layers of Ni atoms and S, Bi and As atoms, parallel to (001), at approximately one-eighth intervals of the *c* cell dimension. The structure is dominated by three different Ni coordination polyhedra, two of which are distorted cubes and the third, an octahedron. The Ni(1) octahedron has a plane of 4 S(1) atoms parallel to (001) and two apical Bi(1) atoms. The Ni(2) and Ni(3) sites are 8-coordinated distorted cubes. Although the latter two sites are similar, the Ni(2) site has a shorter mean bond-distance than the Ni(3) site (2.479 *versus* 2.537 Å). Both of these polyhedra contain a nearly square plane of 4 atoms, which is a diagonal within the distorted cube. In the Ni(2) polyhedron, the Ni(2)–S bonds are longer and the Ni–metal bonds shorter than those of the corresponding Ni(3) polyhedron. Of particular note is the short Ni(2)–As bond, 2.476 Å, as opposed to the Ni(3)–Bi(2) distance of 2.828 Å. For an ideal body-centered cubic coordination, the angle subtended by the central atom to each of the 8 corners is 70.53°. The mean bond-angles given in Table 2 for each of these 8 coordination angles in Ni(2) and Ni(3) are 76.70° and 75.34°, respectively, neither of which is close to the ideal value. Figure 1 shows three sets of *Z*-axis stereoscopic projections. Each projection set is one layer, and each contains only one Ni site. Figure 2 shows the three of these superimposed, and this represents the space filling Ni polyhedra for ¼ of the *c* repeat. The next ¼ of *c* would be very similar, but not identical, owing to the small but significant differences between the Ni(2) and Ni(3) polyhedra.

There are two different Bi sites. Bi(1) is octahedrally coordinated by 4 S(2) atoms in the (001) plane and 2 apical Ni(2) atoms with a mean bond-length of 2.757 Å. The Bi(2) site is very different, as it occupies the body center of a cube of Ni(3) atoms, with a bond length of 2.828 Å. The As site also occupies the center of a cube, but with Ni(2) atoms at a much shorter distance of 2.476 Å (Fig. 3). This segregation of the Bi and As atoms is the cause of the supercell structure. In Kocman & Nuffield (1974), these two sites, Bi(2) and As, were treated as one, the $(Sb_{0.7}Bi_{0.3})$ site, with a bond length of 2.687 Å, an average of what would have been observed for the superstructure of hauchecornite. The relevance of this feature of the superstructure of arsenohauchecornite to other members of the hauchecornite group is briefly discussed below.

X-ray powder data

Table 4 gives the X-ray powder-diffraction data for arsenohauchecornite from the same holotype specimen as that used for the structure analysis. The pattern was recorded on a Philips automated powder diffractometer (System 1710) with a curved-crystal monochromator, using Cu*K*α radiation, scan speed 0.6°2θ/min., chart recorder full-scale setting 5000 counts/s, speed 20 mm/°2θ, rate-meter time-constant 2 s, and a sampling interval of 4 s; Si powder (Diffraction Standard Reference Material 640a: Hubbard 1983) was added as an internal standard. The computer program of Appleman & Evans (1973) was used for refinement of the cell dimensions.

The data in Table 4 show that the large 'supercell' and the *I* lattice of arsenohauchecornite are clearly revealed by a good powder diffractogram. A comparison of the powder-derived unit-cell dimensions in Table 4 with those derived from the single-crystal diffractometer given earlier indicates differences several times greater than the (larger) error shown for the powder data. However, the differences are still only about 0.1%. Although the precision of the single-crystal diffractometer exceeds that of the powder diffractometer, the former lacks the accuracy of standardization achieved by the powder method.

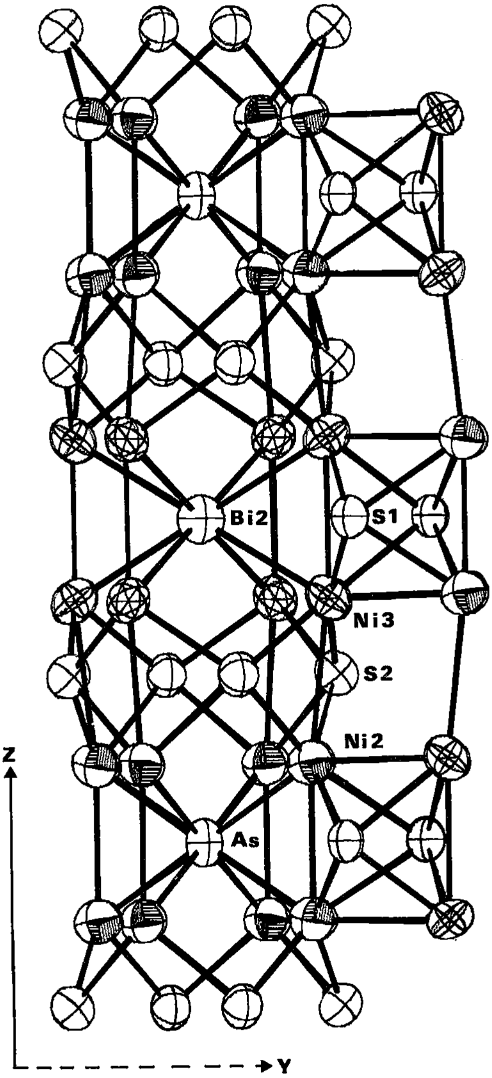

FIG. 3. An inclined *X*-axis projection (Y axis back 15°) of a portion of the arsenohauchecornite structure showing the Bi(2) and As polyhedral cubes and their effect on ordering along the *Z* axis. Ellipsoids have been selectively shaded to differentiate the types of atoms as labeled.

CONCLUSIONS

The superstructure of arsenohauchecornite is a result of the ordering of As and Bi into two different Ni-coordinated body-centered-cube sites. The much shorter As–Ni bond lengths, compared to the Bi–Ni bond lengths, create differences in the Ni polyhedra of the Ni(2) and Ni(3) sites and the coordinated Ni(2) and Ni(3) chains. The structural formula of arsenohauchecornite is thus ${}^{VI}Ni_4{}^{VIII}Ni_{16}{}^{VIII}Ni_{16}{}^{VI}Bi_4{}^{VIII}Bi_2{}^{VIII}As_2S_{16}S_{16}$, and the simplest formula $Ni_{18}Bi_3AsS_{16}$, with $Z = 2$.

For other members of the hauchecornite group,such as tučekite (Just & Feather 1978) and bismutohauchecornite (Just 1980), there is no possibility of a supercell similar to that observed in arsenohauchecornite, as there is only one large (periodic group VA) element in each, Sb and Bi, respectively. The covalent radii of Sb (1.38 Å) and Te (1.35 Å) are closer to that of Bi (1.46 Å) than As (1.19 Å); thus, a superstructure in hauchecornite or tellurohauchecornite, if it exists, would be less pronounced because the bond differences causing the superstructure would be minimal. At present there is insufficient material for single-crystal studies of tellurohauchecornite, but the authors have some indication of a polytype for hauchecornite, which is presently under investigation.

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TABLE 4. X-RAY POWDER DIFFRACTOMETER DATA FOR ARSENOHAUCHECORNITE

space group I4/mmm
a 10.277(1), *c* 10.816(1) A

* Reflections incompatible with the P4/mmm 7.3x5.4 A cell.

hkl	d_{calc},A	d_{obs},A	2θ(Cu)$_{obs}$	*I*/*I*$_0$
* 101	7.450	7.457	11.859	3
200	5.138	5.141	17.234	15
112	4.338	4.343	20.434	53
* 211	4.230	4.234	20.966	4
202	3.725	3.727	23.854	2
220	3.633	3.637	24.452	48
* 103	3.402	3.403	26.167	2
310	3.250	3.253	27.399	56
222	3.016	3.017	29.584	13
* 213	2.837	2.837	31.514	8
312	2.786	2.785	32.110	100
* 321	2.756	2.759	32.426	9
004	2.704	2.703	33.114	3
400	2.569	-	-	-
114	2.534	2.535	35.376	25
* 303	2.483	2.485	35.123	1
* 411	2.429	2.427	37.006	7
204	2.393	2.393	37.562	66
402	2.321	2.320	38.780	14
420	2.298	2.298	39.175	59
332	2.211	2.210	40.807	7
224	2.169	2.169	41.609	7
422	2.115	2.115	42.724	2
314	2.079	2.085	43.361	21
* 431	2.019	2.018	44.882	5
* 501	2.019			
512	1.889	1.888	48.151	9
404	1.863	1.862	48.868	48
440	1.817	1.816	50.188	32
334	1.804	1.804	50.552	48
* 433	1.786	1.785	51.123	3
* 503	1.786			
530	1.762	1.762	51.852	3
424	1.751	1.750	52.222	20
116	1.750			
600	1.713	1.712	53.464	35
* 523	1.687	1.686	54.355	1
532	1.676	1.675	54.743	13
226	1.615	1.614	57.000	3
316	1.576	1.576	58.520	17
444	1.508	1.508	61.424	7
* 435	1.490	1.490	62.253	1
* 505	1.490			
406	1.476	1.476	62.938	<1
604	1.447	1.446	64.353	1
336	1.446			
* 525	1.431	1.431	65.135	<1
* 633	1.410	1.409	66.259	2
712	1.404	1.404	66.559	11
552	1.404			
* 721	1.400	1.401	66.721	6
624	1.393	1.393	67.152	10
008	1.352	1.352	69.460	8
730	1.349	1.349	69.629	7
516	1.344	1.344	69.964	4
732	1.309	1.309	72.076	11
* 651	1.306	1.306	72.260	8
800	1.285	1.285	73.691	4
554	1.280	1.280	73.977	8
714	1.280			
* 741	1.266	1.266	74.926	3
* 811	1.266			
644	1.261	1.261	75.334	16
536	1.260			

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