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The Crystal Structure of Maucherite ($Ni_{11}As_8$)

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Abstract

X-ray diffraction patterns of maucherite ($Ni_{11}As_8$) indicate the presence of a tetragonal supercell with $a = 6.8724(4)$ Å, $c = 21.821(1)$ Å, space group $P4_12_12$, $Z = 4$; the subcell is also tetragonal with $a' = a/2$, $c' = c$, space group $I4_1/amd$, $Z = 1$. The crystal structure has been determined using X-ray intensity data collected from a synthetic maucherite crystal on a four-circle diffractometer and refined to an R value of 0.063. The structure contains six non-equivalent Ni atoms per unit cell, five in square pyramidal coordination with As in equipoint position 8*b* and one in a stretched octahedral coordination in equipoint position 4*a*. The As polyhedra form single chains of trigonal prisms arranged so that the prism faces contribute to the square pyramidal Ni sites. Alternate prisms share a face with a prism from an adjacent chain; the site which includes the shared face is vacant to account for the unusual stoichiometry of maucherite. Each Ni is coordinated to four or five neighboring Ni atoms with Ni-Ni distances of 2.48 Å to 2.87 Å. The shorter distances arise through shared pyramidal faces and shared As polyhedral prisms; the longer ones arise through shared pyramidal-octahedral faces and shared pyramidal edges. It is suggested that 3*d* electron σ bonding between these related Ni atoms supplements the Ni-As σ bonds. The principal features of the maucherite structure have counterparts in the crystal structures of α-Ni_7S_6 and millerite (NiS).

Introduction

Maucherite ($Ni_{11}As_8$) is found associated with niccolite (NiAs), rammelsbergite ($NiAs_2$) and para-rammelsbergite ($NiAs_2$) in nickel-cobalt-native silver deposits as exemplified at Eisleben, Thuringia, Germany (the type locality) and Cobalt, Ontario, Canada.

Most of the present crystallographic data on maucherite were obtained by Peacock (1940) who, confirming earlier work by Laves (1935), reported that single crystal X-ray diffraction patterns indicate a well-developed pseudocell (subcell) which is tetragonal with $a = 3.42$ Å, $c = 21.83$ Å and space group $I4_1/amd$ (D_{4h}^{19}) but that the real unit cell, also tetragonal, is defined by a doubling of the a-axis, giving $a = 6.84$ Å, $c = 21.83$ Å, space group $P4_12_12$ (D_4^4) or $P4_32_12$ (D_4^8). However, the reflections characteristic of the supercell are diffuse and smeared into hk bands of continuous radiation (Peacock, 1942). On the basis of chemical analyses of several natural samples, Peacock (1940) established the composition as $Ni_{11}As_8$; small amounts of Co and S substitute for Ni and As respectively. A measured density of 8.00 gm cm^{-3} indicated $Z = 4$, and Peacock argued that the structure must contain four vacancies in the Ni sites per unit cell.

Laves (1935) showed that a synthetic Ni_3As_2 composition was crystallographically equivalent to maucherite, but systematic phase chemistry on the binary system later indicated that the stability region of synthetic maucherite was very narrow and restricted to $Ni_{11}As_8$ (Heyding and Calvert, 1957). Yund (1961) confirmed the chemical and crystallographic equivalence of natural maucherite and the synthetic phase synthesized below 700°C. X-ray powder diffraction patterns of the product quenched from above 700°C contain several additional reflections; however, a phase transition in the temperature range 650° to 800°C was not indicated by differential thermal analyses. $Ni_{11}As_8$ melts incongruently at 830° ± 5°C to niccolite plus liquid.

Experimental

A crystal structure determination on natural maucherite was not possible because of the diffuse nature of the superstructure reflections in all the specimens examined to date. Thus it was decided to attempt synthesis of a maucherite in which these reflections were sharp. Clearly, the existence of the diffuse reflections in the natural product indicates that maucherite attempts further long-range order at low temperatures, so that the synthetic material should be annealed at a temperature higher than that at which this long-range order is initiated but at or below 700°C to prevent the formation of the possible metastable phase reported by Yund (1961).

About 1.0 gm of $Ni_{11}As_8$ was synthesized by heating an appropriate mixture of purified Ni sponge, previously reduced with hydrogen at 900°C, and As powder in an evacuated silica-glass tube placed in a horizontal tube furnace. Initially, the charge was heated at 795°C for 11 days to attempt complete reaction of the starting reactants, then annealed at 696°C for five days. However, the product contained NiAs and Ni in addition to $Ni_{11}As_8$. Homogenization was completed by preparing a second charge from the ground products of the first synthesis and heating this at 825°C for one day, and 790°C for six days, then annealing it at 692°C for three days. The charge was allowed to cool to room temperature in the furnace. 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 material appeared homogeneous in polished section examination and the individual fragments were generally monocrystalline. The crystal fragment selected for study was bounded by plane surfaces, with a near-rhombic habit, and had a calculated volume of 0.1 $\times 10^{-6}$ cm^3.

A preliminary single crystal study on a precession camera confirmed the fragment to be a single crystal with reflections characteristic of the supercell sharp and distinct. The existing crystallographic data on maucherite were confirmed also: the subcell is tetragonal with the systematic absences hkl with $h+k+l \neq 2n$, $hk0$ with $h \neq 2n$ and hhl with $2h + l \neq 4n$, consistent with the space group $I4_1/amd$ (D_{4h}^{19}), and the supercell is tetragonal with the systematic absences $00l$ with $l \neq 4n$ and $h00$ with $h \neq 2n$, consistent with the enantiomorphic space groups $P4_12_12_1$ (D_4^4) and $P4_32_12$ (D_4^8). The lattice parameters of the supercell, determined by least-squares refinement of 12 centered reflections measured on a four-circle diffractometer with Zr-filtered MoKα ($\lambda = 0.7107$ Å) radiation, are $a = 6.8724(4)$ Å, $c = 21.821(1)$ Å. These data compare quite well with the parameters reported by Heyding and Calvert (1957; $a = 6.868(4)$ Å, $c = 21.80(2)$ Å) and Yund (1961; $a = 6.867(2)$ Å, $c = 21.80(1)$ Å) for synthetic maucherite, both sets of data being determined from powder patterns.

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 non-equivalent hkl reflections with $2\theta \leq 65°$ were measured using a scintillation detector, Zr-filtered MoKα ($\lambda = 0.7107$ Å) radiation and the 2θ scan technique: 40 second stationary background counts, peak-base widths of 2.0° 2θ (uncorrected for dispersion) and a scanning rate of 0.5° per minute. The resulting data were processed by a data correction routine which corrected for background, Lorentz and polarization effects, and absorption. Transmission factors for the absorption correction were calculated by the analytical method of de Meulenaer and Tompa (1965) using a value for the linear absorption coefficient of 463.5 cm^{-1}. The crystal was oriented with the a-axis parallel to the ϕ axis. The calculated transmission factors varied from 0.14 for 017 to 0.20 for 021. Standard deviations (σ) were calculated from the expression $\sigma = 1/2\ [1/LpT \cdot (\sigma_p^2 + \sigma_{b1}^2 + \sigma_{b2}^2 + (0.02I)^2)/I]^{1/2}$, where Lp is the Lorentz-polarization factor, T is the transmission factor, σ_p, σ_{b1} and σ_{b2} are, respectively, the standard deviations for the counting rates of the peak and backgrounds and I is the background-corrected peak intensity. Each reflection whose intensity was less than the associated background plus 3σ was given zero intensity. The final data list contained 1178 reflections of which 713 were 'unobserved.' The large number of 'unobserved' reflections is attributed to the manner in which the superstructure is developed from the substructure; there is, for example, a structural extinction for hkl with $h \neq 2n$ and $h + k = 2n$.

Crystal Structure Investigation

The true cell of maucherite is defined by a noncentrosymmetric superstructure. The crystal structure investigation was initiated by a determination of the structure of the subcell, in the expectation that the positional data for the disordered basic structure could be expanded into an ordered arrangement which would account for the X-ray diffraction intensity distribution of the supercell.

The crystal structure of the subcell is centrosymmetric; the space group $I4_1/amd$ being uniquely defined by the systematic absences. The structure factors were converted to normalized structure factors (E's) using program FAME (R. B. K. Dewar, Illinois Institute of Technology, Chicago) and the phases of those normalized structure factors with $E \geq 1.5$ were assigned by a reiterative application of Sayre's equation using program REL1 (adapted from Long, 1965, and further modified by the author to accommodate space group $I4_1/amd$). Atomic positions taken from E maps, prepared from the solution with the largest consistency index (0.81), lead directly to a value of the conventional residual index of 0.30.

The structure was improved following an F_0 Fourier analysis and refined further by full-matrix, least-squares refinement using program RFINE (L. Finger, Geophysical Laboratory, Washington), which minimizes the function $\Sigma\ w\ (|F_0| - |F_c|)^2$, where $w = 1/\sigma^2$, F_0 is the observed and F_c the calculated structure factor, and calculates a conventional residual index, $\Sigma\ ||F_0| - |F_c|\ | / \Sigma\ |F_0|$ and a weighted residual index, $[\Sigma\ w\ (|F_0| - |F_c|)^2 / \Sigma\ wF_0^2]^{1/2}$. The scattering curves for Ni^{2+} and As were taken from Cromer and Mann (1968) and real and imaginary components of the anomalous dispersion coefficients for Ni and As were from Cromer (1965). The refinement converged, giving values of the conventional and weighted residual indices of 0.047 and 0.053; the final positional and isotropic thermal parameters are given in Table 1.

The unit cell content of the subcell is $Ni_{11}As_8$. The

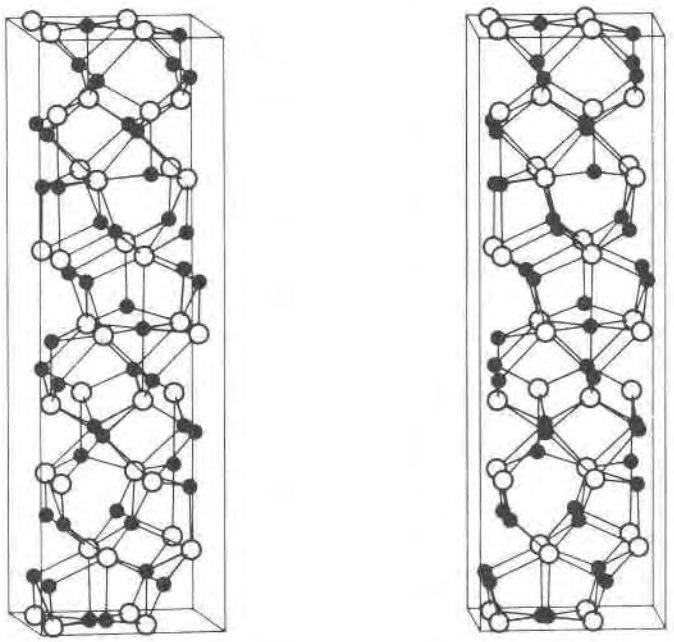

FIG. 1. Stereoscopic view of the crystal structure of maucherite; Ni: small full circles. As: large open circles.

structure analysis has shown that four As are ordered in the As(1) sites and that the remaining four As are disordered among the As(2) sites, with an occupancy of 0.5. All of the Ni are in disordered positions, with eight Ni in Ni(3) sites, occupancy 0.5, two Ni in Ni(1) sites, occupancy 0.25, and one Ni in Ni(2) sites, occupancy 0.25.

The crystal structure of the superstructure was developed by expanding the positional data of the subcell, with a suitable change in origin, to conform to the non-centrosymmetric space group $P4_12_12$. Initially, several trial structures giving reasonable Ni coordinations with unit site occupancies were attempted. Comparison of these resulted in a set of ordered sites which satisfied the general features of the diffraction intensity distribution of the supercell. The agreement between the observed and calculated structure factors was improved following analysis of F_0 Fourier maps. These ordered sites and the subcell sites they are related to are given in Table 2. The superstructure contains six non-equivalent Ni atoms per unit cell of which five, Ni(1), Ni(3), N(4), N(5) and Ni(6) in 8*b* equipoint positions, are in square pyramidal coordination with As, and one, Ni(2) in 4*a*, is in a stretched octahedral coordination with As (Fig. 1). The As polyhedra form single chains of trigonal prisms arranged so that the prism faces contribute to the square pyramidal Ni sites (Fig. 2).

The positional and thermal parameters were refined using program RFINE. Initially, constraints were added to relate the parameters of Ni(4), Ni(5), and Ni(6) to those of Ni(3), of As(2) and As(3) to

TABLE 1. Positional and Thermal Parameter for Subcell*

TABLE 1. POSITIONAL AND THERMAL PARAMETERS FOR SUBCELL*

Site	Equipoint position	Site occupancy	x	y	z	B
Ni(1)	8e	0.25	0	3/4	0.1076(6)	0.64(17)
Ni(2)	4a	0.25	0	3/4	1/8	0.98(39)
Ni(3)	16h	0.5	0	0.1292(9)	0.2033(1)	0.44(5)
As(1)	4b	1.0	0	1/4	3/8	0.46(5)
As(2)	8e	0.5	0	1/4	0.9980(2)	0.39(6)

*Estimated standard deviations (in parentheses) refer to the last decimal place cited. Thus 0.64(17) means an esd of 0.17 whereas 0.1076(6) indicates an esd of 0.0006.

TABLE 2. Approximate Positional Parameters for Maucherite

TABLE 2. APPROXIMATE POSITIONAL PARAMETERS FOR MAUCHERITE

Site	Equivalent subcell site	Equipoint position	x	y	z
Ni(1)	Ni(1)	8b	1/8	3/8	0.269
Ni(2)	Ni(2)	4a	3/8	3/8	0
Ni(3)	Ni(3)	8b	1/8	0.565	0.172
Ni(4)	Ni(3)	8b	5/8	0.565	0.172
Ni(5)	Ni(3)	8b	3/8	0.685	0.078
Ni(6)	Ni(3)	8b	7/8	0.685	0.078
As(1)	As(1)	4a	1/8	1/8	0
As(2)	As(1)	4a	5/8	5/8	0
As(3)	As(1)	8b	5/8	1/8	0.0
As(4)	As(2)	8b	7/8	3/8	0.123
As(5)	As(2)	8b	1/8	7/8	0.127

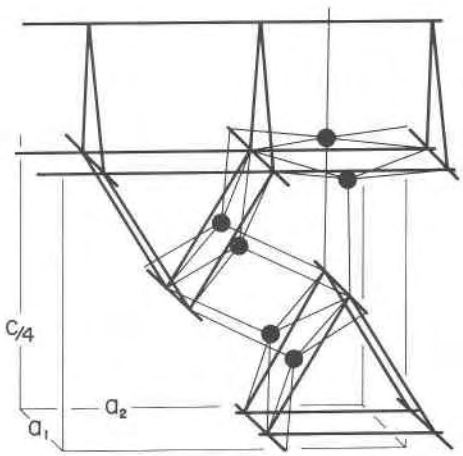

FIG. 2. Intersecting chains of trigonal prisms of As atoms in the maucherite structure; Ni: small full circles.

those of As(1), and of As(5) to those of As(4) (Table 2). The values of the conventional and weighted residual indices thus obtained for isotropic thermal motion are 0.130 and 0.098 respectively. The refinement was continued by removing the inter-site positional constraints and finally converged on values of the conventional and weighted residual indices of 0.078 and 0.063 respectively. Convergence was assumed when the changes to the positional parameters were in the sixth places and the changes in the thermal parameters 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 positional and isotropic thermal parameters are given in Table 3, and the observed and calculated structure factors are given in Table 4. The isotropic thermal parameters were constrained as in the initial stage of the refinement. In unconstrained refinement the thermal parameter of Ni(3) and Ni(6) refined to negative values. Attempts at constrained anisotropic refinement resulted in negative B_{33} parameters for Ni(3) and Ni(6). Furthermore, the motions of the remaining atoms were virtually isotropic and the reductions in the residual indices were not significant. The correlation coefficients for those positional parameters related through common subcell sites are given in Table 5 and indicate a high interdependency for these parameters.

TABLE 3. Refined Positional and Thermal Parameters for Maucherite*

Site	x	y	z	B
Ni(1)	0.125(2)	0.373(2)	0.2686(3)	0.66(9)
Ni(2)	3/8	3/8	0	0.43(13)
Ni(3)	0.120(3)	0.569(2)	0.1734(4)	0.35(4)
Ni(4)	0.608(2)	0.562(2)	0.1710(5)	0.35(4)
Ni(5)	0.372(3)	0.683(2)	0.0805(4)	0.35(4)
Ni(6)	0.871(3)	0.690(2)	0.0770(4)	0.35(4)
As(1)	0.120(2)	0.120(2)	0	0.43(5)
As(2)	0.635(2)	0.635(2)	0	0.43(5)
As(3)	0.635(2)	0.129(2)	0.0004(2)	0.43(5)
As(4)	0.877(2)	0.382(2)	0.1250(2)	0.32(5)
As(5)	0.121(2)	0.869(2)	0.1289(2)	0.32(5)

*Standard deviations in parentheses

Discussion

The crystal structure of maucherite has a substructure of As polyhedra in the form of single chains of trigonal prisms arranged so that alternate prisms share a face with a prism from an adjacent chain (Fig. 2). The shared faces lie in planes normal to the *c*-axis at $z = 0$, ¼, ½ and ¾. The 44 Ni atoms per unit cell are accommodated in six non-equivalent positions, five in square pyramidal coordination with As and one in a stretched octahedral coordination with As. There are 40 unshared prism faces of the As polyhedra per unit cell and each of these contributes to the square pyramidal sites so that the base of each square pyramid is formed on one As polyhedral unit and the apex is formed on a neighboring unit. The four octahedral sites per unit cell are formed from a square planar arrangement of As within the planes of shared prism faces, at $z = 0$, ¼, ½ and ¾, and from more distant As in polyhedral units immediately above and below these planes. The possible metal sites formed about the shared faces themselves are vacant. Thus, the 44 Ni atoms per unit cell are located in 44 discrete structural positions. The structure specifically accommodates the composition of the compound, $Ni_{11}As_8$, and is not a non-stoichiometric variant of an established or hypothetical A_3B_2 structure as suggested earlier (Peacock, 1940). The establishment of $Ni_{11}As_8$ as a stoichiometric compound largely accounts for its restricted range in composition (Yund, 1961).

Some relevant interatomic distances and bond angles are given in Table 6 and 7 respectively (the atom identification labels are consistent with the usage in Figure 3; atoms marked by an asterisk are located in adjacent unit cells). The Ni-As bond distances range from 2.28 Å to 2.54 Å; the stretched Ni-As bond distance in the octahedral site is 2.64 Å. The shorter distances tend to be to the apical As in the square pyramidal coordinations. These values may be compared to a Ni-As bond distance of 2.439

TABLE 4. Observed and Calculated Structure Factors for Maucherite

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	K L F_o F_c	K L F_o F_c
H = 0	26 155 170	14 78 81	22 61 22	7 66 59	12 155 159		14 78 76	6 67 62
	27 139 140	15 122 117	24 71 61		13 112 115	3 1 44 40	15 109 111	8 478 488
	4 010891243	16 96 67	25 86 111	H = 2	14 86 85	2 48 22	16 128 110	10 137 128
0 8 549 539	2 231 234	19 67 48	26 66 62		15 107 106	18 74 98	9 1 63 28	12 78 82
12 686 685	4 82 79	20 66 33	29 74 88	2 2 391 391	16 113 134	19 77 75	2 63 31	14 80 73
16 665 643	6 55 48	8 0 514 507	30 88 103	6 9161021	17 148 143	20 82 47		16 318 299
20 388 391	8 596 599	2 256 261	32 76 94	10 436 430	18 74 67	24 83 59	H = 4	9 6 77 51
24 612 651	10 234 231	3 56 52	3 0 43 59	18 572 577	20 66 88	27 80 79		H = 5
1 4 52 33	12 331 305	4 89 95	4 47 45	22 179 182	28 74 29	4 1 109 110	4 0 738 767	
5 85 74	14 123 116	8 466 470	7 44 54	28 70 7	6 2 400 405	2 167 171	4 133 136	517 63 63
6 147 135	16 537 534	10 269 273	18 96 94	30 193 182	4 251 255	3 191 188	8 606 632	18 83 65
7 197 181	18 86 97	14 148 144	19 75 55	3 0 380 372	6 360 357	4 172 173	12 76 75	19 74 45
8 166 161	20 175 173	16 348 338	20 72 76	1 358 352	8 183 188	5 154 153	16 443 453	6 6 63 59
9 79 76	22 145 148	18 122 132	25 63 43	2 335 326	10 324 339	6 122 119	24 308 310	7 146 141
10 63 74	24 435 455	19 59 17	26 89 85	3 283 273	12 93 101	7 74 65	5 2 65 63	8 191 185
11 145 138	27 63 17	9 5 64 54	4 5 65 58	4 183 178	14 209 204	9 61 63	3 79 77	9 235 233
12 139 131	30 85 87	7 68 22	6 65 74	5 81 77	16 231 213	10 104 115	4 100 112	10 198 204
13 98 96	5 2 87 90	8 68 15	7 113 130	6 51 27	18 251 237	11 90 105	5 102 100	11 146 157
14 65 70	3 111 104	10 1 153 160	8 135 130	9 53 48	20 77 80	13 77 73	6 118 114	12 107 101
18 120 126	4 114 117	3 87 93	9 66 93	12 68 64	22 100 102	14 130 134	7 132 133	13 102 97
19 131 143	5 128 125	5 240 237	10 59 61	13 75 76	24 107 116	15 175 179	8 152 153	16 100 93
20 70 62	6 180 165	7 119 117	11 125 118	16 121 114	26 150 161	16 155 161	9 106 97	17 117 125
23 58 27	7 170 172		12 110 109	17 204 211	7 0 153 139	17 106 98	11 86 86	18 66 53
26 64 19	8 171 175	H = 1	14 56 46	18 203 214	1 132 134	24 70 48	12 88 104	714 64 18
2 1 52 44	9 122 120		17 57 46	19 163 167	2 143 145	25 87 107	13 108 109	8 5 77 60
3 147 130	11 96 110	1 0 42 34	18 78 103	20 168 173	3 142 141	26 140 153	14 109 112	7 84 88
5 653 686	12 113 112	2 42 35	19 91 108	21 165 166	4 116 117	27 155 125	15 88 77	8 97 96
7 153 145	13 141 125	6 59 55	29 71 43	22 147 159	9 72 60	5 0 53 40	16 72 73	H = 6
9 421 416	14 146 146	13 50 18	519 65 52	23 120 131	10 85 66	11 49 11	18 87 110	
11 580 565	15 111 100	17 88 95	23 69 49	24 123 142	11 64 54	19 63 59	19 111 112	6 2 403 391
13 371 358	17 88 87	18 96 97	25 67 47	25 140 147	16 87 51	26 69 48	20 85 71	6 83 70
15 251 229	18 155 139	19 86 44	26 68 78	26 84 85	17 126 133	27 77 63	24 74 78	10 279 281
17 283 290	19 117 133	20 59 80	6 1 80 88	27 63 49	18 119 119	6 0 218 214	6 1 156 175	14 281 284
19 303 312	20 90 70	23 64 45	2 76 86	30 58 15	19 76 90	1 216 223	3 255 252	17 57 39
21 163 179	25 83 53	27 86 104	3 58 87	4 1 116 104	20 97 102	2 212 219	5 226 218	19 58 5
23 273 292	27 67 51	32 65 19	6 56 65	3 122 121	21 83 87	3 176 183	7 68 38	7 0 96 96
29 373 407	6 1 252 264	2 0 130 121	7 114 126	5 289 270	22 69 80	4 109 112	11 74 93	1 103 102
3 1 115 116	3 139 142	1 131 130	8 187 180	7 110 110	8 1 111 95	5 76 60	13 125 142	2 130 121
2 224 218	5 448 447	2 114 115	9 200 204	9 220 206	3 214 209	16 71 82	15 69 62	3 107 91
3 275 273	7 206 215	3 73 78	10 171 190	11 431 430	7 199 203	17 146 150	19 251 247	4 72 85
4 240 235	8 56 52	5 47 45	11 134 132	13 422 422	11 238 243	18 168 164	20 64 43	5 75 64
5 207 206	11 116 111	6 89 86	12 102 105	19 142 157	13 350 345	19 114 130	21 281 291	6 67 53
6 157 155	13 90 58	7 168 168	16 131 114	21 169 174	15 114 124	20 115 111	22 58 11	10 75 37
7 62 68	15 80 77	8 267 262	17 155 143	23 196 184	9 0 116 114	21 121 118	7 1 67 77	11 70 44
9 110 103	17 134 130	9 344 335	18 119 104	25 80 73	1 127 140	22 113 131	2 82 89	14 59 28
10 149 151	19 394 373	10 307 296	23 65 37	26 64 31	2 92 110	23 102 111	3 101 101	8 1 80 76
11 116 105	21 328 320	11 223 214	25 76 77	27 204 182	7 65 65	24 106 101	10 69 83	3 264 250
13 69 74	25 94 115	12 141 139	711 58 53	29 273 271	8 114 95	25 78 110	11 91 91	5 58 35
14 160 155	7 2 104 112	13 88 78	19 64 44	5 6 79 81	9 120 112	8 1 79 63	14 76 75	7 90 94
15 238 231	3 114 122	14 76 67	21 59 26	7 182 179	10 2 239 230	2 74 107	15 104 101	9 86 86
16 206 199	4 65 64	15 64 74	816 64 27	8 271 271	4 181 154	3 106 103	16 84 68	H = 7
17 132 132	9 64 59	16 162 160	10 0 67 56	9 336 340	6 178 170	4 117 108	8 0 325 317	
24 64 58	10 92 96	17 188 186	2 66 45	10 284 282		5 84 80	2 102 124	7 2 64 22
25 95 118	11 91 85	18 129 134	3 66 59	11 226 220	H = 3	11 80 59	4 125 131	7 65 18

Å (computed from the lattice parameter data of Yund, 1961) in stoichiometric niccolite (NiAs), in which the Ni is coordinated octahedrally with As, and also to a Ni-As bond distance range of 2.359 Å to 2.392 Å in pararammelsbergite ($NiAs_2$, Fleet, 1972b), in which the Ni is again coordinated octahedrally with As. The values for the nearest As-As distances, those within the As polyhedral units, range from 3.21 Å to 3.54 Å. The As-As distances between the As polyhedral units, forming both the edges of the pyramidal faces and the inclined edges of the octahedral site, range from 3.62 Å to 3.90 Å. Comparative data for niccolite are 3.619 Å, for As-As normal to the *c*-axis, and 3.272 Å, for As-As inclined to the *c*-axis; for pararammelsbergite nonbonded As-As distances range from 3.129 Å to 3.575 Å.

The Ni atoms are in close proximity to each other in the maucherite strutcure; the nearest Ni-Ni distances range from 2.48 Å to 2.87 Å. There are four neighboring Ni atoms about the Ni(1), Ni(2), Ni(4) and Ni(6) sites and five about the Ni(3) and Ni(5) sites. The shortest Ni-Ni distances arise through shared pyramidal faces (2.51 Å and 2.53 Å) and through shared trigonal prisms of As atoms (2.48 Å to 2.65 Å). The shared pyramidal-octahedral faces give Ni-Ni distances of 2.69 Å and 2.75 Å, and shared pyramidal edges give Ni-Ni distances of 2.69 Å to 2.87 Å.

The unusual five-fold, square pyramidal, coordination of Ni in maucherite is found also in the structures of millerite (NiS) and of α-Ni_7S_6 (Fleet, 1972a). In the trigonal millerite structure, the S atoms form single chains of trigonal prisms oriented parallel to the *c*-axis as do the As atoms in the maucherite structure; the square pyramids are formed on the prism faces with the apical S atoms slightly offset from adjacent chains. The shared trigonal prisms permit each Ni to have two Ni neighbors with interatomic distances of 2.53 Å. The

TABLE 5. Correlation Coefficients (r) for Related Superstructure Positional Parameters

	r	r	r
	x-Ni(3)	x-Ni(4)	x-Ni(5)
x-Ni(4)	0.121		
x-Ni(5)	-0.204	0.409	
x-Ni(6)	0.553	0.032	0.384
	y-Ni(3)	y-Ni(4)	y-Ni(5)
y-Ni(4)	-0.735		
y-Ni(5)	0.661	-0.547	
y-Ni(6)	-0.547	0.657	-0.746
	z-Ni(3)	z-Ni(4)	z-Ni(5)
z-Ni(4)	-0.511		
z-Ni(5)	-0.561	0.271	
z-Ni(6)	0.282	-0.582	-0.513
	x-As(1)	x-As(2)	x-As(3)
x-As(2)	-.005		
x-As(3)	0.444	-0.437	
y-As(3)	-0.385	0.336	0.193
	x-As(4)	y-As(4)	x-As(5)
y-As(4)	0.114		
x-As(5)	-0.813	-0.047	
y-As(5)	-0.152	-0.631	0.126
	z-As(4)		
z-As(5)	0.490		

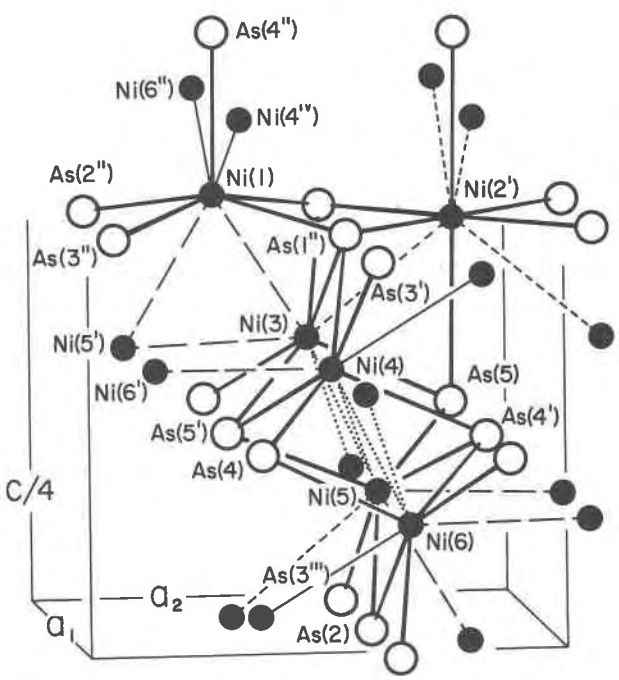

FIG. 3. Nearest-neighbor Ni environments in maucherite; Ni-Ni bonds indicated by shared pyramidal faces: full lines; shared trigonal prisms of As atoms: long dashes; shared pyramidal-octahedral faces: short dashes; shared pyramidal edges: stipples.

TABLE 6. Interatomic Distances in Maucherite

Atoms*		Distance (Å)**	Atoms*		Distance (Å)**
Ni(1)	- As(1'')	2.47(1)	As(1'')	- As*(3')	3.54(1)
	- As*(2'')	2.46(1)		- As(3'')	3.335(0)
	- As*(3')	2.54(2)		- As(4'')	3.668(7)
	- As(3'')	2.39(2)			
	- As(4'')	2.322(5)	As*(2'')	- As*(3')	3.39(2)
				- As(3'')	3.48(2)
Ni(2')	- As(1'')	2.48(1)		- As(4'')	3.639(6)
	- As*(2'')	2.524(9)			
	- As*(3')	2.46(1)	As*(3')	- As(4'')	3.67(1)
	- As(5)	2.643(5)			
			As(3'')	- As(4'')	3.63(1)
Ni(3)	- As(1'')	2.47(2)			
	- As*(3')	2.45(1)	As(1'')	- As(5)	3.62(1)
	- As*(4)	2.36(2)			
	- As(5)	2.28(1)	As*(2'')	- As*(3')	3.48(2)
	- As(5')	2.52(2)		- As(5)	3.66(1)
Ni(4)	- As(1'')	2.36(1)	As*(3')	- As(5)	3.57(1)
	- As*(3')	2.51(1)			
	- As(4)	2.44(1)	As(3'')	- As(5)	3.65(1)
	- As(4')	2.42(1)			
	- As(5')	2.33(1)	As(1'')	- As(5')	3.30(1)
Ni(5)	- As(2)	2.54(1)	As(5)	- As(5')	3.87(2)
	- As(3''')	2.46(2)			
	- As(4')	2.40(2)	As(1'')	- As(3')	3.34(1)
	- As(5)	2.39(2)		- As(4')	3.668(7)
	- As(5')	2.33(1)			
			As(3')	- As(4)	3.21(1)
Ni(6)	- As(2)	2.37(2)		- As(4')	3.63(1)
	- As*(3''')	2.47(2)			
	- As(4)	2.36(1)	As(4)	- As(4')	3.86(2)
	- As(4')	2.40(2)			
	- As*(5)	2.40(2)	As(4)	- As(5')	3.426(0)
Ni(1)	- Ni(3)	2.48(1)	As(4')	- As(5')	3.90(2)
	- Ni(4'v)	2.53(2)			
	- Ni(5')	2.53(1)	As(2)	- As(3''')	3.48(2)
	- Ni(6'')	2.51(2)		- As(4')	3.214(9)
				- As(5')	3.66(1)
Ni(2')	- Ni(3)	2.69(1)			
	- Ni*(5')	2.75(1)	As(3''')	- As(5)	3.25(1)
Ni(3)	- Ni(5)	2.79(2)	As(2)	- As*(3''')	3.39(2)
	- Ni(5')	2.65(2)		- As(4)	3.639(6)
	- Ni*(6)	2.835(7)			
			As*(3''')	- As(4)	3.67(1)
Ni(4)	- Ni(5)	2.688(8)			
	- Ni(6)	2.87(1)	As(4)	- As*(5)	3.75(2)
	- Ni(6')	2.56(2)			

*Atoms marked by asterisks are located in adjacent unit cells
**Standard deviations (in parentheses) refer to the last decimal place cited

orthorhombic structure of α-Ni_7S_6 is more complex. The Ni is distributed among five non-equivalent sites. These include one tetrahedral site, with a site occupancy of approximately 0.5, and four square pyramidal sites, two with site occupancies of approximately 1.0 and two with site occupancies of approximately 0.5 (Fleet, 1972a). Twelve of the 20 S atoms per unit cell are organized into chains of trigonal prisms parallel to the *a*-axis at $y = \frac{1}{4}$ and $\frac{3}{4}$. The prism faces contribute to the two square pyramidal sites which have near unit occupancy. Each Ni site has several possible Ni neighbors: the Ni atoms in square pyramidal coordination are related through shared pyramidal faces, shared trigonal prisms of S, and shared pyramidal edges, so that, as in the maucherite structure, there is a range of observed Ni-Ni distances, from 2.457 Å to 2.849 Å.

During the early stages of this investigation, a

TABLE 7. Bond Angles in Maucherite

Atoms* forming angle			Angle**	Atoms* forming angle			Angle**
As(1'')	-Ni(1)	-As*(2'')	161.0(3)°	As(1'')	-Ni(4)	-As(3')	86.4(5)°
		-As*(3')	89.9(5)			-As(4)	152.6(7)
		-As(3'')	86.6(5)			-As(4')	100.1(6)
		-As(4'')	99.8(4)			-As(5')	89.4(5)
As*(2'')	-Ni(1)	-As*(3')	85.6(6)	As(3')	-Ni(4)	-As(4)	80.8(5)
		-As(3'')	91.7(5)			-As(4')	95.0(6)
		-As(4'')	99.1(4)			-As(5')	154.4(7)
As*(3')	-Ni(1)	-As(3'')	161.0(3)	As(4)	-Ni(4)	-As(4')	105.0(4)
		-As(4'')	98.2(5)			-As(5')	91.9(3)
As(3'')	-Ni(1)	-As(4'')	100.8(5)	As(4')	-Ni(4)	-As(5')	110.6(5)
As(1'')	-Ni(2')	-As*(2'')	180.0(0)	As(2)	-Ni(5)	-As(3''')	88.2(5)
		-As*(3')	91.5(4)			-As(4')	81.1(7)
		-As(5)	89,8(3)			-As(5)	152.6(6)
						-As(5')	97.3(6)
As*(2'')	-Ni(2')	-As*(3')	88.5(4)				
		-As(5)	90.2(3)	As(3''')	-Ni(5)	-As(4')	149.0(6)
						-As(5)	84.2(7)
As*(3')	-Ni(2')	-As*(3'')	177.0(7)			-As(5')	99.2(7)
		-As(5)	88.8(3)				
				As(4')	-Ni(5)	-As(5)	92.1(4)
As*(3'')	-Ni(2')	-As(5)	91.3(3)			-As(5')	111.0(7)
As(5)	-Ni(2')	-As(5'v)	179.6(5)	As(5)	-Ni(5)	-As(5')	109.9(6)
As(1'')	-Ni(3)	-As*(3')	91.9(4)	As(2)	-Ni(6)	-As*(3''')	89.0(4)
		-As*(4)	153.1(6)			-As(4)	100.6(7)
		-As(5)	99.1(7)			-As(4')	84.8(7)
		-As(5')	82.7(7)			-As*(5)	155.3(7)
As*(3')	-Ni(3)	-As*(4)	83.7(7)	As*(3''')	-Ni(6)	-As(4)	98.8(6)
		-As(5)	98.0(7)			-As(4')	153.0(6)
		-As(5')	154.6(6)			-As*(5)	83.6(8)
As*(4)	-Ni(3)	-As(5)	107.8(7)	As(4)	-Ni(6)	-As(4')	108.2(6)
		-As(5')	90.0(4)			-As*(5)	103.8(6)
As(5)	-Ni(3)	-As(5')	107.5(5)°	As(4')	-Ni(6)	-As*(5)	91.1(4)°

*Atoms marked by asterisks are located in adjacent unit cells.
**Standard deviations (in parentheses) refer to the last decimal place cited.

specimen of natural maucherite from Eisleben, Thuringia, was examined, although the examination was limited by an inability to obtain single crystal fragments. The virtual crystallographic equivalence of synthetic $Ni_{11}As_8$ and natural maucherite was confirmed. Also, in agreement with earlier workers (Peacock, 1940; Jagodzinski and Laves, 1948), $0kl$ superstructure reflections are smeared in the c^*-axis direction. However, the diffraction maxima are centered in the same relative positions and are of the same relative intensity as in the synthetic product. In addition, the $hk0$ superstructure reflections are replaced by diffuse areas of satellite diffraction in the form of small crosses centered on the positions of the original reflections.

The diffuse satellite reflections indicate that maucherite attempts further long-range ordering processes at low temperature, the full development of which is inhibited by very slow reaction rates. The ordering may be due to a modulation of the structure. However, this modulation cannot be unidirectional in the c-axis direction, since satellite reflections are observed for $hk0$ reflections as well as for $0kl$ reflections. The diffuse nature of the satellite reflections suggests that the modulation must have a variable periodicity. It is difficult to predict the actual structural expression of the ordering, although one might expect a further rationalization of the Ni-Ni interactions involving, in part, the development of two square pyramidal sites from the stretched octahedral site of the Ni(2) atoms, one site being occupied in any instance and the modulation being based on the sequence of occupancy of the two sites.

The unit cell composition of maucherite is $Ni_{44}As_{32}$. The structure requires 224 Ni-As σ bonds per unit cell; compared to the assumed single Ni-As bond distances for octahedral coordination in pararammelsbergite, most of these σ bonds must have either unit or near-unit bond numbers. The outer electron configuration of Ni is $3d^8 4s^2$ and that of As is $4s^2 4p^3$. The molecular orbital bonding theory would require that the $4s$ electrons on the Ni atoms and the $4s$ and $4p$ electrons on the As contribute to the Ni-As σ bonding scheme; these total 248 electrons per unit cell, far fewer than required for 224 full σ bonds. The remaining electrons must be supplied by the $3d$ electrons on the Ni atoms. Of these, the d_{xy}, d_{xz} and d_{yz} orbitals are poorly disposed to contribute to the Ni-As σ bonds, and the $3d$ electron contribution can be made only via the axially oriented $d_{x^2-y^2}$ and d_{z^2} orbitals. On the isolated atom these are doubly degenerate and carry one electron each. However, in maucherite the short Ni-Ni distances indicate strong positive interactions between the d_{xy}, d_{xz} and d_{yz} orbitals which project through the pyramidal and octahedral edges. The interaction of the orbitals projected between the Ni atoms related through shared pyramidal edges will be σ bonding in character since the orbitals overlap end-on. However, orbitals between the Ni atoms related through shared pyramidal faces, shared trigonal prisms of As atoms, and shared pyramidal-octahedral faces will interact obliquely. Although the site symmetries of the Ni atoms related by shared trigonal prisms of As atoms would permit π bonding between those orbitals normal to the bonding plane, π bonding possibilities for the other Ni-Ni bonds are limited. It seems logical, then, to argue that, as in parkerite ($Ni_3Bi_2S_2$) where the Ni atoms are related at moderately short distances through shared octahedral faces (Fleet, unpublished data), all of the d_{xy}, d_{xz} and d_{yz} orbital interactions are σ bonding in character, the oblique orbital interactions giving rise to fractional bent σ bonds. Alternatively, one might invoke a hybridization of

these orbitals on each Ni to allow direct bonding orbitals between the related Ni atoms. The d_{xy}, d_{yz} and d_{xz} orbitals are triply degenerate on the isolated atom and carry two electrons each, but a σ bonding role must require fewer electrons. If, say, two of these are added to the $d_{x^2-y^2}$ and d_{z^2} orbitals, allowing a maximum contribution of four $3d$ electrons per Ni atom to the Ni-As σ bonds, the remaining four $3d$ electrons may be distributed among the bonding and antibonding Ni-Ni σ orbitals such that for the shorter Ni-Ni bonds, which are similar to the bond distance in metallic Ni (2.492 Å), a greater proportion would be bonding and for the longer distances relatively more would be antibonding. There are now 424 electrons for the Ni-As σ bonds; the discrepancy of 24 electrons per unit cell must reflect some degree of partial bond formation; for example, the stretched Ni(2)-As(5) bonds would represent bond numbers of about 0.5.

Acknowledgments

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