

= Mn < Re. The  $X-M-X$  angles increase in the order  $X = \text{Cl} < \text{Br} < \text{I}$ , where  $M = \text{Mn}$  and in the order  $\text{Re} < \text{Mn}$  where  $X = \text{I}$ , entirely as expected based on covalent radii. The  $M-\text{CO}$  distances for the carbonyl groups *cis* to  $X$  in  $[\text{M}_2\text{X}_2(\text{CO})_8]$  differ significantly from the  $M-\text{CO}$  distances *trans* to  $X$ ; in every case the *cis* bonds are longer as anticipated based on the known *trans*-influences of the groups involved. The  $\text{C}-\text{O}$  bond lengths shorten as  $M-\text{C}$  lengthens owing to less effective back bonding from manganese. Unfortunately, comparisons of  $M-\text{CO}$  bond distances as  $X$  is varied are hindered by the low accuracy of the bond lengths for  $[\text{Mn}_2\text{Br}_2(\text{CO})_8]$ , whose structure was solved from photographic data. The nonbonded  $\text{Mn}\cdots\text{Mn}$  distances in  $[\text{Mn}_2\text{X}_2(\text{CO})_8]$  (all > 3.5 Å) are significantly longer than the  $\text{Mn}-\text{Mn}$  distance of 2.923 (3) Å in  $[\text{Mn}_2(\text{CO})_{10}]$  (Dahl & Rundle, 1963) confirming the absence of any metal-metal interaction.

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## Structure of Synthetic Perryite, $(\text{Ni,Fe})_8(\text{Si,P})_3$

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**Abstract.**  $(\text{Ni}_{0.97}\text{Fe}_{0.03})_8(\text{Si}_{0.79}\text{P}_{0.21})_3$ ,  $M_r = 550$ , trigonal,  $R3c$ , hexagonal axes,  $a = 6.640$  (2),  $c = 37.982$  (7) Å,  $V = 1450.3$  (7) Å<sup>3</sup>,  $Z = 12$  [96 Ni(Fe) and 36 Si(P) per unit cell],  $D_x = 7.63$  (1) Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 31.07$  mm<sup>-1</sup>,  $F(000) = 3194$ ,  $T = 295$  K, final  $R = 0.027$ ,  $wR = 0.019$  for 333 independent reflections. The structure was found to be isomorphous with that of  $\text{Pd}_8\text{Sb}_3$ , and also a stacking variant of  $\text{Ni}_{31}\text{Si}_{12}$  and  $\text{Pd}_5\text{Sb}_2$  structures.

**Introduction.** In the highly reduced stony meteorites, *i.e.* enstatite chondrites and enstatite achondrites, it has been known that a nickel silicide mineral called perryite occurs as thin rims around and as thin

lamellae within metallic nickel-iron grains. The chemical composition of perryite as determined by electron probe microanalysis is Ni 75.5–83.7, Fe 1.7–9.4, Si 9.7–15.0 and P 2.4–5.2 wt% (Fredriksson & Henderson, 1965; Okada, Keil & Taylor, 1988; Reed, 1968; Wai, 1970).

Natural perryite crystals in meteorites which are usually less than 20  $\mu\text{m}$  are too small to be used for single-crystal structure analysis. This is the main reason why the crystal structure and the accurate chemical formula of perryite have not been clarified. We synthesized the crystal by melting the materials, the composition obtained is almost the same as that of perryite in the Norton County enstatite achondrite

(Okada *et al.*, 1988). The chemical composition of the synthetic crystal was determined to be Ni 82.5, Fe 2.4, Si 12.2 and P 3.7 wt% by electron probe microanalysis. Weissenberg photographs showed that all of the synthetic crystals examined exhibited twinning on the (0001) plane of the hexagonal lattice in the same way as perryite crystals in Norton County enstatite achondrite. Both the synthetic and meteoritic perryites show the same X-ray powder diffraction patterns. In this work, the structure analysis of synthetic perryite was performed using a twinned crystal. As a result, the ideal formula of perryite was determined to be  $(\text{Ni,Fe})_8(\text{Si,P})_3$ .

**Experimental.** A twinned synthetic crystal, of size  $0.18 \times 0.12 \times 0.04$  mm, was used for the X-ray study. Since the twin operation was the (0001) mirror, the two components had a common hexagonal lattice. Lattice parameters were determined by the least-squares refinement of 20 reflections ( $18 < 2\theta < 25^\circ$ ). Intensities were measured on a Rigaku automated four-circle diffractometer (AFC-4) with graphite-monochromated Mo  $K\alpha$  radiation by the  $\omega$  scan methods within the range  $0 < 2\theta < 55^\circ$ ,  $-7 \leq h \leq 7$ ,  $-7 \leq k \leq 7$ ,  $-48 \leq l \leq 48$ . Three standard reflections showed variations in intensities of less than 2%. 5448 reflections with  $|F_o| \geq 3\sigma(|F_o|)$  were observed. Intensities were corrected for Lorentz and polarization factors. The absorption was corrected by the semi-empirical method of North, Phillips & Mathews (1968), because the geometrical arrangement of twin components within the specimen was unknown; the absorption correction factors for  $|F_o|$  ranged from 1.0 to 2.86.

Owing to the twinning, the observed intensity data consisted of two components, the major component satisfying the obverse reflection condition ( $-h + k + l = 3n$ ) and the minor one satisfying the reverse reflection condition ( $h - k + l = 3n$ ). The intensity ratio of the minor to major components was determined to be 0.166 (1) by comparing intensities of equivalent reflections of both components. Only the major component was used for the subsequent structure analysis. Since the two components overlapped for the reflections with  $l = 3n$ , these intensities were corrected for the contribution of the minor component using the above ratio. After averaging equivalent reflections, 334 unique reflections were obtained with  $R_{\text{int}} = 0.019$ .

From the additional reflection condition of  $h\bar{h}0l$ :  $l = 2n$ , the possible space group was either  $R3c$  or  $R\bar{3}c$ , but the subsequent structure analysis showed that  $R3c$  was the correct one. The structure was solved by *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) and refined by the full-matrix least-squares method based on  $|F_o|$  with anisotropic temperature factors for all

atoms. At the final stage of refinement, the reflection 300 which was highly affected by extinction was excluded from the data set. The function minimized was  $\sum w(|F_o| - |F_c|)^2$ , where  $w = 1/\sigma(F_o)^2$ . The final  $R$ ,  $wR$  and  $S$  values were 0.027, 0.019 and 2.67, respectively.  $(\Delta/\sigma)_{\text{max}}$  in the final refinement was 0.09 for  $y$  of the Si(P)2' atom. Maximum and minimum peaks in the final difference Fourier synthesis were 1.86 and  $-1.76 \text{ e } \text{Å}^{-3}$ , respectively. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV), and the values used in the refinement were the mean values calculated according to the chemical composition. All calculations were performed on a FACOM M-780 computer of this Institute using a *UNICS-III* program system (Sakurai & Kobayashi, 1979).

**Discussion.** The final  $R$  and  $wR$  values are reasonably low, considering that the structure analysis was carried out using a twinned crystal. The crystal structure of synthetic perryite,  $(\text{Ni,Fe})_8(\text{Si,P})_3$ , was found to be isomorphous with that of  $\text{Pd}_8\text{Sb}_3$  ( $R3c$ ,  $a = 7.615$  and  $c = 43.03 \text{ Å}$ ; Wopersnow & Schubert, 1976). The final atomic parameters of synthetic perryite are listed in Table 1.\* As can be seen in Table 1, the structure is approximately centrosymmetric, *i.e.* it approximately conforms to the centrosymmetric space group  $R\bar{3}c$ . The maximum displacement from centrosymmetry is  $0.182 (10) \text{ Å}$  for Si(P)2' in synthetic perryite. The coordination numbers and the interatomic distances of synthetic perryite are listed in Table 2. The coordination numbers of Ni(Fe) atoms range from 11 to 14, and those of the Si(P) atoms from 8 to 12. The Ni(Fe) atoms are coordinated with both Ni(Fe) and Si(P) atoms, whereas the Si(P) atoms are coordinated with only Ni(Fe) atoms.

In view of the fact that nickel silicide of  $M_8X_3$  type has not been observed in the phase diagram of the Ni-Si system at 1 atm (Ellner, Heinrich, Bhargava & Schubert, 1979), the minor Fe and P components in synthetic perryite are probably essential to stabilize the structure by partially replacing the major Ni and Si atoms, respectively.

Fig. 1(a) shows the atomic arrangements of the eight kinds of fundamental layers which construct the layer structure of synthetic perryite. Each layer consists of only one atomic species, Ni(Fe) or Si(P), with the same  $z$  value. The three  $X$  and  $Y$  layers are related by the  $3_1$  screw axis, whereas the corresponding  $X_i$  and  $Y_i$  ( $i = 1, 3$ ), and  $Z1$  and  $Z2$  layers are related by the  $c$  glide. Fig. 1(b) shows the crystal

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53898 (6 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic parameters of synthetic perryite

Positional parameters are multiplied by  $10^5$  with e.s.d.'s in parentheses. The equivalent isotropic temperature factor is defined by

$$B_{\text{eq}} = (4/3) \sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{eq}}(\text{\AA}^2)$	
Ni(Fe)1	18( <i>b</i> )	33210 (19)	41179 (20)	5036 (5)	0.56
Ni(Fe)1'	18( <i>b</i> )	-33113 (19)	-42293 (19)	-5419 (5)	0.45
Ni(Fe)2	18( <i>b</i> )	33605 (22)	3622 (20)	1668 (5)	0.46
Ni(Fe)2'	18( <i>b</i> )	-33858 (19)	-3086 (19)	-1831 (4)	0.27
Ni(Fe)3	6( <i>a</i> )	0	0	21671 (7)	0.23
Ni(Fe)3'	6( <i>a</i> )	0	0	-22059 (8)	0.63
Ni(Fe)4	6( <i>a</i> )	0	0	5766 (8)	0.43
Ni(Fe)4'	6( <i>a</i> )	0	0	-6164 (8)	0.45
Si(P)1	18( <i>b</i> )	34898 (78)	1845 (73)	8147 (22)	0.48
Si(P)2	6( <i>a</i> )	0	0	15565 (17)	0.13
Si(P)2'	6( <i>a</i> )	0	0	-16045 (19)	0.81
Si(P)3	6( <i>a</i> )	0	0	0 (44)	0.20

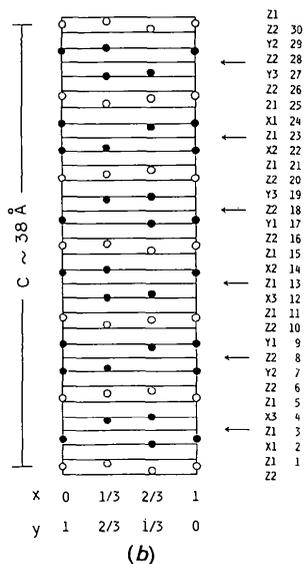
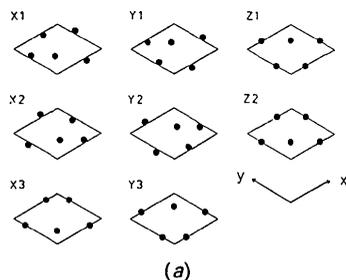


Fig. 1. Structure of synthetic perryite. (a) Atomic arrangements of the eight kinds of fundamental layers. The filled circles indicate Ni(Fe) or Si(P) atoms. (b) Projection along the  $[\bar{1}\bar{1}20]$  axis. Each fundamental layer is shown by a horizontal line. The arrows indicate the fundamental layers consisting of Si(P) atoms; the other layers consist of Ni(Fe) atoms. The filled and open circles are the interstitial Ni(Fe) and Si(P) atoms on the threefold axes, respectively.

structure of synthetic perryite projected along the  $[\bar{1}\bar{1}20]$  direction. The structure consists of 30 fundamental layers stacked along the *c* axis with inter-layer spacings of approximately  $c/30$ . In addition,

Table 2. Coordination numbers and interatomic distances of synthetic perryite

	Coordination numbers	Interatomic distances (Å)		
		Minimum	Maximum	
Ni(Fe)1	14	[10Ni(Fe), 4Si(P)]	2.319 (6)	2.924 (3)
Ni(Fe)1'	14	[10Ni(Fe), 4Si(P)]	2.281 (6)	2.791 (2)
Ni(Fe)2	13	[9Ni(Fe), 4Si(P)]	2.214 (5)	2.756 (2)
Ni(Fe)2'	13	[9Ni(Fe), 4Si(P)]	2.263 (5)	2.729 (2)
Ni(Fe)3	11	[7Ni(Fe), 4Si(P)]	2.319 (7)	2.523 (2)
Ni(Fe)3'	11	[7Ni(Fe), 4Si(P)]	2.284 (8)	2.577 (2)
Ni(Fe)4	13	[9Ni(Fe), 4Si(P)]	2.190 (17)	2.632 (3)
Ni(Fe)4'	13	[9Ni(Fe), 4Si(P)]	2.341 (17)	2.710 (3)
Si(P)1	12	[12Ni(Fe)]	2.281 (6)	3.015 (6)
Si(P)2	10	[10Ni(Fe)]	2.299 (5)	2.417 (2)
Si(P)2'	10	[10Ni(Fe)]	2.296 (3)	2.477 (2)
Si(P)3	8	[8Ni(Fe)]	2.214 (5)	2.341 (17)

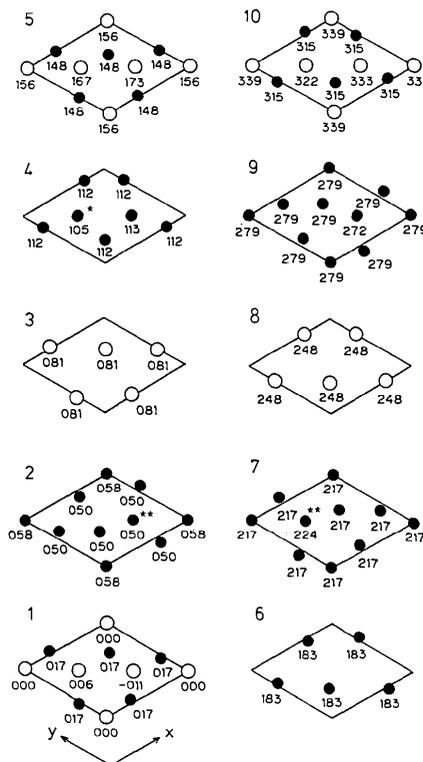


Fig. 2. Structure of synthetic perryite projected along the *c* axis. The filled and open circles indicate Ni(Fe) and Si(P) atoms, respectively. The numbers denote the *z* values multiplied by  $10^3$ .

there are interstitial atoms between the fundamental layers; they lie on the threefold axes as indicated with *x* and *y* coordinates in Fig. 1(b). The structures from layers 11 to 20 and from layers 21 to 30 are related to that from layers 1 to 10 by the  $3_1$  screw axis.

The 30 fundamental layers may be divided into six blocks, each consisting of five fundamental layers, ZXZXZ or ZYZYZ, as shown in Fig. 1(b). Si(P) atoms are located on the middle layer of each block and also between the layers at the block boundaries. Ni(Fe) atoms are located on the remaining fun-

damental layers and also on interstitial sites approximately  $\pm$  one layer apart from each middle layer.

The structure of synthetic perryite is closely related to that of  $\text{Ni}_{31}\text{Si}_{12}$  ( $P321$ ,  $a = 6.67$  and  $c = 12.28$  Å; Frank & Schubert, 1971). The  $c$ -axis length of  $\text{Ni}_{31}\text{Si}_{12}$  is approximately one third that of synthetic perryite, and the atomic arrangements in the unit cell of  $\text{Ni}_{31}\text{Si}_{12}$  are similar to those in one third of the unit cell of synthetic perryite (Fig. 2), which contains 32 Ni(Fe) atoms and 12 Si(P) Atoms. The interstitial Ni(Fe) atom marked with an asterisk in layer 4 of Fig. 2 is absent in  $\text{Ni}_{31}\text{Si}_{12}$  with significant displacements of the surrounding atoms.

In a similar way, the structure of synthetic perryite is also related to that of  $\text{Pd}_5\text{Sb}_2$  ( $P6_3cm$ ,  $a = 7.606$  and  $c = 13.863$  Å; El-Boragy, Bhan & Schubert, 1970). In this case, the unit-cell content is  $\text{Pd}_{30}\text{Sb}_{12}$ , and the two interstitial Ni(Fe) atoms marked with double asterisks in layers 2 and 7 of Fig. 2 are absent with significant displacements of the surrounding atoms. Thus, the structure of synthetic perryite  $(\text{Ni,Fe})_8(\text{Si,P})_3$ , which is isomorphous with that of

$\text{Pd}_8\text{Sb}_3$ , is a stacking variant of  $\text{Ni}_{31}\text{Si}_{12}$  and  $\text{Pd}_5\text{Sb}_2$  structures.

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## CoAPO-21, a Cobalt-Doped Aluminophosphate Related to AlPO<sub>4</sub>-21

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**Abstract.**  $\text{Co}_{0.12}\text{Al}_{5.88}\text{P}_6\text{O}_{24}(\text{OH})_2 \cdot \text{C}_2\text{H}_{10}\text{N}_2 \cdot 2\text{H}_2\text{O}$ ,  $M_r = 867.7$ , monoclinic,  $P2_1/n$ ,  $a = 8.992$  (3),  $b = 17.760$  (8),  $c = 8.359$  (4) Å,  $\beta = 105.39$  (4)°,  $U = 1287.0$  Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 2.24$  g cm<sup>-3</sup>,  $\lambda = 0.895$  (5) Å,  $\mu = 14.7$  cm<sup>-1</sup>,  $F(000) = 871.4$ ,  $R = 0.061$  for 1163 observed reflections, recorded with an area-detector diffractometer. The framework structure is similar to that of AlPO<sub>4</sub>-21 [Parise & Day (1985). *Acta Cryst.*

**C41**, 515–520], with 4-, 5- and 6-coordinate aluminium atoms;  $\text{Co}^{2+}$  replaces tetrahedral  $\text{Al}^{3+}$  ions, and the 6-coordinate  $\text{Al}^{3+}$  has one water molecule as ligand (in addition to 5 framework O atoms). In the channels, the C and N atoms of the ethylenediamine molecule were located; the molecules are disordered, and occupy two mutually exclusive positions related by an inversion centre.

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