TORARDI, C. C. & MCCARLEY, E. (1979). *J. Am. Chem. Soc.* **101**, 3963–3964.

TORARDI, C. C. & MCCARLEY, E. (1981). *J. Solid State Chem.* **37**, 393–397.

TORARDI, C. C. & MCCARLEY, E. (1986). *J. Less-Common Met.* **116**, 169–186.

VICAT, J., FANCHON, E., STROBEL, P. & QUI, D. T. (1986). *Acta Cryst.* **B42**, 162–167.

Crystalline Phases Related to the Icosahedral Al–Li–Cu Phase: a Single-Crystal X-ray Diffraction Study of the Hexagonal Z-Al$_{59}$Cu$_5$Li$_{26}$Mg$_{10}$ Phase

BY A. LE BAIL AND M. LEBLANC

Laboratoire des Fluorures, Faculté des Sciences, Université du Maine, route de Laval, BP 535, 72017 Le Mans CEDEX, France

AND M. AUDIER

Laboratoire de Thermodynamique et Physico-Chimie Métallurgiques, UA CNRS 29, BP 75 ENSEEG, 38402 Saint Martin d'Hères, France

(Received 14 December 1990; accepted 18 February 1991)

Abstract

Z phase, Al$_{0.59}$Cu$_{0.05}$Li$_{0.26}$Mg$_{0.10}$, $M_r = 23.35$, hexagonal, $P6_3/mmc$, $a = 14.116$ (3), $c = 28.235$ (6) Å, $V = 4873$ (3) Å^3, $Z = 272$, $D_x = 2.164$, D_m (by flotation) = 2.14 Mg m^{-3}, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 0.25$ mm^{-1}, $F(000) = 3013$, $T =$ room temperature, $R = 0.042$ for 1794 reflections. The hexagonal Z phase belongs to a family of intermetallics Al–Li–(Cu–Zn–Mg) which have relationships with the icosahedral Al–Cu–Li phase. By using a description proposed by Samson [*Structural Chemistry and Molecular Biology* (1968), edited by Rich & Davidson, pp. 687–717. San Franscisco: Freeman], a basic structural unit can be defined in the Z structure as an arrrangement of ten Friauf polyhedra which forms a half-Samson polyhedron. This polyhedron is directly related to the complete Samson polyhedron determined in the b.c.c. structure of R-Al$_5$CuLi$_3$. Such a result suggests that the Friauf polyhedron could be the only structural unit common to quasi-crystalline and related crystalline Al–Li–(Cu–Zn–Mg) phases.

Introduction

Research concerning the atomic structure of quasi-crystals has been carried out by different methods. The exact structural features of this state of matter are not yet fully understood and each approach to the atomic structure is in fact based on various assumptions.

One empirical method consists of performing a direct atomic decoration of the two basic cells of the icosahedral quasilattice, *i.e.* the prolate and oblate rhombohedra (Henley & Elser, 1986; Elswijk, de Hosson, van Smaalen & de Boer, 1988; Audier & Guyot, 1988a). In that case, it is assumed that such an icosahedral quasilattice, resulting from an irrational cut and projection operation from a six-dimensional periodic space (Elser, 1985; Duneau & Katz, 1985) constitutes the equivalent of a Bravais lattice for the quasicrystal. However, the main difficulty, which has not been resolved, is to reconcile the complicated matching rules (Katz, 1988) and inflation rules (Elser, 1985; Audier & Guyot, 1988b) of the icosahedral quasilattice rules with a unique decoration of each type of rhombohedron. Such an atomic decoration, respecting density and chemical composition, has been attempted for the icosahedral Al–Li–Cu phase (Guyot, Audier & de Boissieu, 1989), by considering an aggregation of atomic clusters, derived from those defined in the related cubic R-Al$_5$CuLi$_3$ phase (Cherkashin, Kripyakevich & Oleksiv, 1964; Audier, Pannetier, Leblanc, Janot, Lang & Dubost, 1988). Comparisons between calculated X-ray and neutron spectra and experimental crystal diffraction data (G. Heger & J. Pannetier, private communication; Janot, Pannetier, Sainfort, Dubost, Audier & Bouvaist, 1987) are only partially satisfactory: expressed in terms of a reliability factor ($R = \Sigma |F_{obs} - F_{calc}| / \Sigma |F_{obs}|$), values of 0.16 and 0.13 have been obtained for 56 X-ray reflections and 40 neutron reflections respectively. Better results have been obtained by using a method equivalent to the so-called direct methods of crystallography, where it is assumed that periodic schemes are recovered in six-dimensional space (de Boissieu, Janot, Dubois, Pannetier, Audier & Dubost, 1991). In that case, the

structure has been determined in six-dimensional space and both reliability factors have been found to be equal to 0·08 for the same experimental X-ray and neutron data sets. Although the quasicrystalline structure may be considered as fully described in a six-dimensional space with this second type of crystallographic approach, it appears rather difficult to analyse what are the different structural characteristics of the icosahedral phase when it is projected in our physical space. Nevertheless, a first analysis reveals that the local atomic arrangements in the six-dimensional quasicrystalline structure are directly derived from the atomic cluster of 160 atoms defined in the cubic R-Al$_5$CuLi$_3$ phase, thus confirming that quasicrystalline structures are well related to some structures of periodic phases.

Recently the icosahedral $T2$-Al$_6$CuLi$_3$ phase has been shown to be related, not only to the cubic R-Al$_5$CuLi$_3$ phase, but to several stable intermetallic compounds (Audier, Janot, de Boissieu & Dubost, 1989) whose chemical compositions are close to those of the b.c.c. R-Al$_5$CuLi$_3$ and icosahedral $T2$-Al$_6$CuLi$_3$ phases. Their identification has resulted from extensive metallurgical studies on the formation of several Al–Li–Cu–Mg, Al–Li–Zn and Al–Li–Zn–Cu alloys (Dubost, Bompard & Ansara, 1987; Dubost, Colinet & Ansara, 1988). Some physical chemistry characteristics of all these phases, denoted R, $T2$, Z, C and τ, are summarized in Table 1. Several relationships between these intermetallic compounds have been previously studied by transmission electron microscopy and neutron diffraction (Loiseau & Lapasset, 1986, 1987; Cassada, Shiflet & Poon, 1986; Audier, Sainfort & Dubost, 1986; Audier et al., 1989). However, the next step was to establish their crystallographic structures.

In this paper we present the results of a single-crystal X-ray diffraction study of the hexagonal Z phase and compare its structural characteristics with those of the b.c.c. R phase. Results on the crystallographic structure of the τ phase will be presented in a separate paper (Leblanc, Le Bail & Audier, 1991).

Experimental

Single crystals of the Z phase were prepared by slow solidification of the liquid, following a process similar to that used to grow triacontahedral grains of the icosahedral $T2$ phase (Dubost, Lang, Tanaka, Sainfort & Audier, 1986; Lang, Audier, Dubost & Sainfort, 1987). This procedure tends to reproduce natural geode formation and gives quite large single crystals (a few millimeters) which develop at the free internal surfaces of an ingot cavity.

For the X-ray diffraction study, a black crystal flake with approximate dimensions 0·20 × 0·15 × 0·15 mm was obtained by crushing a large hexagonal

facetted crystal and it was inserted in a glass capillary tube. Data were collected on a Siemens AED-2 four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation and a counter aperture of 4·0 mm. Lattice constants were obtained from 32 reflections measured in double step-scan mode at $\pm(2\theta \simeq 30°)$. Intensities were measured in the range $2\theta \le 90°$ with the ω–2θ step-scan technique in N steps of $\Delta\omega$ ($37 \le N \le 48$, $0·025 \le \Delta\omega \le 0·032°$, time per step = 2 s). The line profile was analysed (Clegg, 1981) and the equivalent isotropic linewidth was $\omega = (0·812 + 0·271\tan\theta)°$. The intensity variation of three standard reflections ($3\bar{5}6$, 602, $5\bar{5}4$) measured every hour was below 3%. A total of 10 331 reflections were collected in the range $0 \le h \le 24$, $0 \le k \le 19$, $0 \le l \le 56$. 1794 independent reflections were used for refinements ($|F| \ge 10\sigma(|F|)$ and $R_{int} = 0·030$.

Structure determination and refinement

The SHELXS86 program (Sheldrick, 1985; Robinson & Sheldrick, 1988) was used for the structure determination. Straightforward application of direct methods to the whole data set did not produce any convenient starting model. However, a solution including all 16 Al/Cu and Mg sites was obtained by limiting the resolution sphere to 1 Å (Sheldrick, 1990).

The structure refinements were performed using the SHELX76 program (Sheldrick, 1976). The refined parameters were scale factors, atomic coordinates and isotropic factors, assuming at the first stage that all the 16 sites were fully occupied by Al atoms. The scattering factors and anomalous-dispersion corrections were taken from International Tables for X-ray Crystallography (1974, Vol. IV, pp. 71, 148). An initial Al/Cu/Mg assignment was deduced from the thermal-parameter values, which were either quite normal, abnormally high or negative, suggesting five pure Al atom sites [Al(7) to Al(11)], five pure Mg atom sites [Mg(1) to Mg(3), Al(12), Al(13)] and six mixed Al/Cu sites, with one of them being half occupied [Al(6)]. After the refinement of the Al/Cu site occupancies, all the Li atoms were located from a difference Fourier map. Further refinements including all atoms with isotropic B factors led to $R = 0·062$ for 81 parameters. The final values of $R = 0·042$ and $wR = 0·043$ for 133 parameters were obtained with anisotropic thermal motion for the Al/Cu-, Al- and Mg-atom sites. The function minimized was $\Sigma w(F_o - F_c)^2$ with $w^{-1} = \sigma^2(F)$ based on $\sigma(F^2)$ as determined by counting statistics plus a contribution of $0·00032F^2$. $(\Delta/\sigma)_{max} = 0·010$, $(\Delta/\sigma)_{mean} = 0·001$. Final $\Delta\rho$ excursions $-1·0$ to $+0·7$ e Å^{-3}. No absorption or secondary-extinction corrections (tests showed negligible

effects). During the final refinements, chemical composition and distance considerations led to changing the initial assignments of two Mg-atom sites to Al-atom sites [Al(12) and Al(13)] in spite of their thermal parameters being clearly larger than those of the other Al atoms. Some Li-atom sites [Li(6) to Li(9)] had very low or negative isotropic thermal parameters and were allowed to be partly occupied by Mg atoms. Owing to the differences in atomic sizes, only possible distributions of Al/Cu or Li/Mg atoms were considered. Anisotropic thermal parameters were also refined for one of the Li/Mg-atom sites [Li(9)] on a general position, owing to the high Mg proportion (34%). Finally, 2·5% Cu were forced to occupy the Al(7) to Al(11) sites to fit the chemical composition $Al_{0.59}Cu_{0.05}Li_{0.26}Mg_{0.10}$ and specific weight 2·14 g cm^{-3} better (Audier et al., 1989). Thus, the total number of atoms per cell is 272, corresponding to a repartition of nearly 151 Al, 15 Cu, 73 Li and 33 Mg atoms; the resulting formula $Al_{0.59}Cu_{0.05}Li_{0.26}Mg_{0.10}$ gives the calculated specific weight 2·164 g cm^{-3}. The final parameters are listed in Table 2, the anisotropic thermal parameters in Table 3 and selected interatomic distances are given in Table 4.* It must be noted that six pairs among the 25 independent sites are quasi-related by a $c/2$ translation: Al(4)/Al(1), Al(5)/Al(11), Al(9)/Al(10), Al(12)/Al(13), Li(1)/Li(2), Li(5)/Li(8); one site shows this translation due to its unusual position [Li(6)]; moreover, five other sites show this quasi-translation due to their unusual coordinates ($z \simeq 0$ or $\frac{1}{2}$; $x \simeq y$; $x \simeq 0$): Li(3), Al(8), Al(7), Mg(3), Al(6). Thus, a few atoms are mainly responsible for all reflections with l odd since a subcell with $c/2$ is quasi-verified. This explains the huge number of weak reflections leading to the choice of $|F| \geq 10\sigma(|F|)$.

Description and comparison of the R and Z structures

The description of the hexagonal Z structure can be related to structural features exhibited by the b.c.c. R phase (Audier, Pannetier et al., 1988) which are briefly recalled hereafter. As illustrated in Fig. 1, Al, Cu and Li atoms in the R phase are distributed over shells centered around an origin (000 and $\frac{111}{222}$ in the structure of the R phase, space group $Im\bar{3}$). The successive shells are (a) an icosahedron of (Al, Cu) with an empty site at the origin, (b) a pentagonal dodecahedron of Li, which assembled with another icosahedron of (Al, Cu) forms a rhombic triacontahedron, (c) a truncated icosahedron of (Al, Cu) or so-called soccer ball which is slightly distorted

* Lists of structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53987 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Physical chemistry properties of intermetallic compounds found in the* Al–Li–Cu, Al–Li–Zn, Al–Li–Cu–Mg *and* Al–Li–Cu–Zn *alloy systems*

Phase	Chemical composition	Structure	Space group	Lattice parameters (Å)	Density (g cm^{-3})
R	$Al_{0.564}Cu_{0.116}Li_{0.32}$ $Al_{0.52}Cu_{0.15}Li_{0.25}Mg_{0.08}$	Cubic	$Im\bar{3}$	13·9056	2·46
T2	$Al_{0.57}Cu_{0.108}Li_{0.322}$ $Al_{0.60}Cu_{0.10}Li_{0.22}Mg_{0.08}$	Icosahedral	Point group only $m\bar{3}5$	$5.05\,\tau^{3n}$ $[\tau=(1+5^{1/2})/2]$ n any integer	2·47
Z	$Al_{0.59}Cu_{0.05}Li_{0.26}Mg_{0.10}$	Hexagonal	$P6_3/mmc$	$a=14.12$ $c=28.24$	2·14
C	$Al_{0.59}Cu_{0.036}Li_{0.35}Mg_{0.024}$	Tetragonal	$P4_2/mmc$ (probably)	$a\approx14$ $c\approx54.15$	2·0
T	$Al_{0.56}Zn_{0.11}Li_{0.33}$ $Al_{0.56}(Cu,Zn)_{0.11}Li_{0.33}$	Tetragonal	$P4_2/mmc$	$a=14.05$ $c=83.14$	2·33

Table 2. *Refined atomic coordinates, isotropic thermal parameters and site occupancies in* Z *phase* $Al_{0.59}Cu_{0.05}Li_{0.26}Mg_{0.10}$

	Site	x	y	z	$B(\text{Å}^2)$	Al or Li (%)	Cu or Mg (%)
Al(1)	12(k)	0·54526 (5)	2x	0·32584 (4)	0·98 (6)	66·4 (5)	33·6 (5)
Al(2)	4(f)	$\frac{1}{3}$	$\frac{2}{3}$	0·17146 (7)	1·48 (9)	56·1 (9)	43·9 (9)
Al(3)	12(j)	0·4844 (1)	0·33115 (1)	$\frac{1}{4}$	0·96 (8)	80·0 (5)	20·0 (5)
Al(4)	12(k)	0·56143 (6)	2x	0·82714 (5)	1·77 (8)	76·1 (5)	23·9 (5)
Al(5)	12(k)	0·60206 (6)	2x	0·40296 (5)	1·28 (8)	87·7 (5)	12·3 (5)
Al(6)	12(k)	0·0624 (1)	2x	0·50066 (9)	1·1 (1)	42·8 (5)	7·2 (5)
Al(7)	24(l)	0·00008 (9)	0·18824 (9)	0·84533 (3)	0·88 (6)	97·5	2·5
Al(8)	24(l)	0·35629 (9)	0·33523 (9)	0·70282 (3)	0·93 (6)	97·5	2·5
Al(9)	12(k)	0·22499 (7)	2x	0·94995 (5)	1·15 (8)	97·5	2·5
Al(10)	12(k)	0·22388 (7)	2x	0·45698 (5)	1·25 (8)	97·5	2·5
Al(11)	12(k)	0·60147 (7)	2x	0·91184 (5)	1·00 (8)	97·5	2·5
Al(12)	12(k)	0·8788 (1)	2x	0·42614 (9)	3·3 (1)	100	—
Al(13)	12(k)	0·8796 (1)	2x	0·92769 (9)	2·9 (1)	100	—
Mg(1)	4(e)	0	0	0·2009 (1)	1·1 (1)	—	100
Mg(2)	6(h)	0·2521 (2)	2x	$\frac{1}{4}$	1·9 (2)	—	100
Mg(3)	12(k)	0·55460 (8)	2x	0·49522 (7)	1·5 (1)	—	100
Li(1)	6(h)	0·1303 (6)	2x	$\frac{1}{4}$	1·3 (2)	100	—
Li(2)	4(e)	0	0	0·4039 (7)	2·0 (3)	100	—
Li(3)	4(f)	$\frac{1}{3}$	$\frac{2}{3}$	0·9979 (6)	1·4 (3)	100	—
Li(4)	6(h)	0·1204 (6)	2x	$\frac{1}{4}$	1·3 (2)	100	—
Li(5)	12(k)	0·2110 (5)	2x	0·1448 (4)	1·8 (2)	100	—
Li(6)	12(i)	0	0·2976 (6)	0	1·9 (2)	91 (1)	9 (1)
Li(7)	4(f)	$\frac{1}{3}$	$\frac{2}{3}$	0·8077 (4)	1·8 (3)	83 (2)	17 (2)
Li(8)	12(k)	0·7919 (4)	2x	0·3423 (3)	1·8 (2)	93 (1)	7 (1)
Li(9)	24(l)	0·0008 (3)	0·3812 (3)	0·4037 (1)	1·6 (2)	66 (1)	34 (1)

Table 3. *Anisotropic* ($\text{Å}^2 \times 10^4$) *temperature factors in* Z *phase* $Al_{0.59}Cu_{0.05}Li_{0.26}Mg_{0.10}$

	Site	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Al(1)	12(k)	125 (4)	127 (5)	121 (5)	$2U_{13}$	-2 (2)	$\frac{1}{2}U_{22}$
Al(2)	4(f)	179 (7)	U_{11}	203 (10)	0	0	$\frac{1}{2}U_{11}$
Al(3)	12(j)	107 (6)	110 (6)	144 (5)	0	0	51 (5)
Al(4)	12(k)	151 (5)	194 (7)	343 (8)	$2U_{13}$	-63 (3)	$\frac{1}{2}U_{22}$
Al(5)	12(k)	157 (6)	151 (8)	176 (7)	$2U_{13}$	-10 (3)	$\frac{1}{2}U_{22}$
Al(6)	12(k)	195 (12)	104 (13)	92 (11)	$2U_{13}$	-2 (5)	$\frac{1}{2}U_{22}$
Al(7)	24(l)	102 (5)	96 (5)	137 (4)	19 (4)	3 (4)	50 (4)
Al(8)	24(l)	114 (5)	107 (5)	115 (4)	-9 (4)	4 (4)	41 (4)
Al(9)	12(k)	187 (6)	114 (8)	111 (6)	$2U_{13}$	2 (3)	$\frac{1}{2}U_{22}$
Al(10)	12(k)	198 (7)	133 (8)	123 (7)	$2U_{13}$	0 (3)	$\frac{1}{2}U_{22}$
Al(11)	12(k)	111 (5)	108 (8)	161 (7)	$2U_{13}$	-11 (3)	$\frac{1}{2}U_{22}$
Al(12)	12(k)	314 (9)	440 (15)	553 (15)	$2U_{13}$	123 (6)	$\frac{1}{2}U_{22}$
Al(13)	12(k)	294 (9)	383 (13)	443 (13)	$2U_{13}$	103 (5)	$\frac{1}{2}U_{22}$
Mg(1)	4(e)	138 (9)	U_{11}	151 (15)	0	0	$\frac{1}{2}U_{11}$
Mg(2)	6(h)	258 (12)	290 (17)	199 (14)	0	0	$\frac{1}{2}U_{22}$
Mg(3)	12(k)	217 (8)	136 (9)	199 (9)	$2U_{13}$	-3 (4)	$\frac{1}{2}U_{22}$
Li(9)	24(l)	188 (16)	183 (17)	222 (15)	5 (12)	-1 (12)	82 (14)

in the b.c.c. structure and (d) a large rhombic triacontahedron of Li. Such an atomic cluster of 160 atoms adopts a nearly perfect icosahedral symmetry. Another description, more useful for a comparison with the Z structure, requires a consideration of

Table 4. *Selected interatomic distances* (Å) *(limited to $d = 4$ Å) in Z phase* Al$_{0.59}$Cu$_{0.05}$Li$_{0.26}$Mg$_{0.10}$

Al(1) polyhedron
1 × Al(5) 2·583 (1)
1 × Al(4) 2·609 (1)
2 × Al(3) 2·621 (1)
2 × Al(8) 2·694 (1)
2 × Li(9) 2·986 (3)
1 × Li(7) 3·012 (2)
2 × Li(8) 3·052 (4)
Mean = 2·810

Al(2) polyhedron
4 × Al(3)   2·573 (1)
3 × Al(11) 2·841 (2)
3 × Mg(2)   2·977 (2)
3 × Li(5)   3·083 (7)
Mean = 2·869

Al(3) polyhedron
1 × Al(3) 2·512 (2)
1 × Al(3) 2·604 (1)
2 × Al(1) 2·621 (1)
2 × Al(8) 2·661 (1)
1 × Li(1) 3·010 (5)
2 × Li(8) 3·012 (7)
2 × Li(7) 3·033 (5)
Mean = 2·798

Al(4) polyhedron
1 × Al(2)   2·573 (1)
1 × Al(11) 2·584 (1)
1 × Al(1)   2·609 (1)
2 × Al(8)   2·647 (1)
2 × Li(5)   2·915 (5)
2 × Li(9)   3·120 (3)
2 × Mg(2)   3·194 (1)
Mean = 2·865

Al(5) polyhedron
1 × Al(1) 2·583 (1)
2 × Al(9) 2·662 (1)
2 × Al(5) 2·736 (1)
1 × Mg(3) 2·852 (2)
2 × Li(9) 3·018 (4)
1 × Li(3) 3·112 (14)
1 × Li(7) 3·119 (9)
2 × Li(8) 3·157 (5)
Mean = 2·901

Al(6) polyhedron
2 × Al(6)   1·526 (1)
1 × Al(13) 2·501 (3)
1 × Al(12) 2·517 (3)
2 × Al(6)   2·642 (2)
2 × Li(6)   2·979 (8)
1 × Al(6)   3·051 (2)
1 × Li(2)   3·096 (16)
1 × Li(2)   3·129 (16)
2 × Al(13) 3·254 (2)
2 × Al(12) 3·318 (2)
Mean = 2·782

Al(7) polyhedron
1 × Al(8)   2·620 (1)
1 × Al(7)   2·655 (2)
1 × Al(7)   2·658 (1)
1 × Al(12) 2·721 (2)
1 × Al(13) 2·754 (2)
1 × Mg(1)   2·960 (1)
1 × Li(4)   3·070 (3)
1 × Li(8)   3·087 (3)
1 × Li(1)   3·129 (3)
1 × Li(2)   3·130 (10)
1 × Li(5)   3·165 (7)
1 × Li(9)   3·179 (3)
Mean = 2·927

Al(8) polyhedron
1 × Al(7)   2·619 (1)
1 × Al(4)   2·647 (1)
1 × Al(3)   2·661 (1)
1 × Al(8)   2·664 (1)
1 × Al(1)   2·694 (1)
1 × Li(5)   2·871 (8)
1 × Li(4)   2·947 (6)
1 × Li(9)   3·059 (2)
1 × Li(8)   3·114 (6)
1 × Li(1)   3·115 (7)
1 × Mg(2)   3·156 (2)
Mean = 2·868

Al(9) polyhedron
1 × Al(12) 2·626 (2)
1 × Al(10) 2·628 (1)
2 × Al(5)   2·662 (1)
1 × Li(3)   2·975 (7)
2 × Mg(3)   2·983 (1)
1 × Li(8)   3·066 (8)
2 × Li(9)   3·114 (3)
2 × Li(6)   3·143 (7)
Mean = 2·925

Al(10) polyhedron
1 × Al(9)   2·628 (1)
2 × Al(11) 2·657 (1)
1 × Al(13) 2·663 (2)
1 × Li(5)   2·892 (10)
1 × Li(3)   2·964 (7)
2 × Mg(3)   3·026 (1)
2 × Li(6)   3·043 (7)
2 × Li(9)   3·178 (3)
Mean = 2·913

Al(11) polyhedron
1 × Al(4)   2·584 (1)
2 × Al(10) 2·657 (1)
2 × Al(11) 2·761 (1)
1 × Al(2)   2·841 (2)
1 × Mg(3)   2·863 (2)
2 × Li(9)   2·998 (4)
1 × Li(3)   3·005 (14)
2 × Li(5)   3·046 (6)
Mean = 2·852

Al(12) polyhedron
1 × Al(6)   2·517 (3)
1 × Al(9)   2·626 (2)
2 × Al(7)   2·721 (2)
1 × Al(13) 2·953 (1)
1 × Li(2)   3·028 (4)
2 × Li(6)   3·036 (2)
1 × Li(8)   3·180 (7)
1 × Li(9)   3·243 (3)
1 × Al(6)   3·318 (2)
Mean = 2·944

Al(13) polyhedron
1 × Al(6)   2·501 (3)
1 × Al(10) 2·663 (2)
1 × Al(7)   2·754 (2)
1 × Al(12) 2·953 (1)
2 × Li(6)   3·010 (2)
1 × Li(2)   3·018 (4)
1 × Li(5)   3·018 (9)
2 × Li(9)   3·253 (3)
1 × Al(6)   3·254 (2)
Mean = 2·972

Mg(1) polyhedron
1 × Mg(1) 2·771 (4)
6 × Al(7) 2·960 (1)
1 × Li(2) 2·960 (19)
3 × Li(4) 3·254 (6)
3 × Li(1) 3·474 (6)
Mean = 3·120

Mg(2) polyhedron
2 × Al(2)   2·977 (2)
2 × Li(5)   3·134 (10)
4 × Al(4)   3·156 (1)
4 × Al(4)   3·194 (1)
1 × Li(4)   3·219 (10)
2 × Mg(2)   3·441 (2)
Mean = 3·181

Mg(3) polyhedron
1 × Mg(3)   2·684 (1)
1 × Li(3)   2·741 (1)
1 × Al(5)   2·852 (2)
1 × Al(11) 2·863 (2)
2 × Al(9)   2·983 (1)
2 × Al(10) 3·026 (1)
2 × Li(6)   3·157 (6)
2 × Li(9)   3·364 (3)
2 × Li(9)   3·568 (3)
Mean = 3·095

Li(1) polyhedron
2 × Al(3) 3·010 (9)
2 × Li(4) 3·072 (10)
4 × Al(8) 3·115 (5)
4 × Al(7) 3·129 (3)
2 × Li(8) 3·227 (9)
2 × Mg(1) 3·474 (9)
Mean = 3·159

Li(2) polyhedron
1 × Mg(1)   2·960 (19)
3 × Al(13) 3·018 (4)
3 × Al(12) 3·028 (4)
3 × Al(6)   3·096 (16)
3 × Al(6)   3·129 (16)
6 × Al(7)   3·130 (10)
Mean = 3·082

Li(3) polyhedron
3 × Mg(3)   2·741 (1)
3 × Al(10) 2·964 (7)
3 × Al(9)   2·975 (7)
3 × Al(11) 3·005 (14)
3 × Al(5)   3·112 (14)
Mean = 2·959

Li(4) polyhedron
4 × Al(8)   2·947 (6)
4 × Al(7)   3·070 (3)
2 × Li(1)   3·072 (9)
1 × Mg(2)   3·219 (10)
2 × Mg(1)   3·254 (9)
2 × Li(5)   3·704 (11)
Mean = 3·156

Li(5) polyhedron
2 × Al(8)   2·871 (7)
1 × Al(10) 2·892 (10)
2 × Al(4)   2·915 (6)
1 × Al(13) 3·018 (9)
2 × Al(11) 3·046 (8)
2 × Li(9)   3·051 (6)
1 × Al(2)   3·083 (7)
1 × Mg(2)   3·134 (10)
2 × Al(7)   3·165 (7)
1 × Li(4)   3·704 (11)
Mean = 3·062

Table 4 *(cont.)*

Li(6) polyhedron
2 × Al(9)   2·961 (4)
2 × Al(6)   2·979 (8)
2 × Al(13) 3·010 (5)
2 × Al(12) 3·036 (5)
2 × Al(10) 3·043 (1)
2 × Al(9)   3·143 (1)
2 × Mg(3)   3·157 (7)
Mean = 3·047

Li(7) polyhedron
3 × Al(1)   3·012 (1)
6 × Al(3)   3·033 (5)
3 × Al(5)   3·119 (9)
3 × Li(8)   3·215 (6)
1 × Li(7)   3·259 (15)
Mean = 3·093

Li(8) polyhedron
2 × Al(3)   3·012 (7)
2 × Al(1)   3·052 (4)
1 × Al(9)   3·066 (8)
2 × Al(7)   3·087 (5)
1 × Al(8)   3·114 (4)
2 × Al(5)   3·157 (6)
1 × Al(12) 3·180 (7)
1 × Li(7)   3·215 (6)
1 × Li(1)   3·227 (9)
1 × Li(9)   3·235 (5)
Mean = 3·118

Li(9) polyhedron
1 × Li(6)   2·961 (4)
1 × Al(6)   2·986 (3)
1 × Al(11) 2·998 (2)
1 × Al(5)   3·018 (4)
1 × Li(5)   3·051 (8)
1 × Al(8)   3·059 (3)

Li(9) polyhedron
1 × Al(9)   3·114 (3)
1 × Al(4)   3·120 (2)
1 × Al(10) 3·178 (3)
1 × Al(7)   3·179 (3)
1 × Li(8)   3·235 (5)
1 × Al(12) 3·243 (3)

Li(9) polyhedron
1 × Al(13) 3·253 (4)
1 × Mg(3)   3·364 (4)
1 × Li(9)   3·366 (5)
1 × Mg(3)   3·568 (3)
Mean = 3·168

Friauf polyhedra (Friauf, 1927*a,b*). The Friauf polyhedron is a truncated tetrahedron bounded by four hexagons and four triangles, where atoms are located at its 12 vertices and in its central cavity. In complex intermetallics, the Friauf polyhedra are more or less distorted as a result of the necessity of the atoms at the vertices to enforce their own coordination requirements. Samson (1968) noted that with relatively slight distortions, 20 such Friauf polyhedra can arrange themselves at the vertices of a pentagonal dodecahedron to form what is now called the Samson polyhedron (Figs. 2*a* and 2*b*). As shown by this author, this corresponds to the structural motif of the well known compound Mg$_{32}$(Zn,Al)$_{49}$ (Bergman, Waugh & Pauling, 1957), but also to that of the nearly isostructural R-Al$_5$CuLi$_3$ phase. From Fig. 2(*a*), it can be deduced that vertices of the Samson polyhedron are occupied by all Al, Cu atoms of the R phase, *i.e.* the three shells (*a*), (*b*) and (*c*) shown in Fig. 1, and that 20 Li atoms occupy the central cavities of the 20 Friauf polyhedra (Li atoms shown in Fig. 1*b*). The last shells of Li atoms are in front of hexagonal faces.
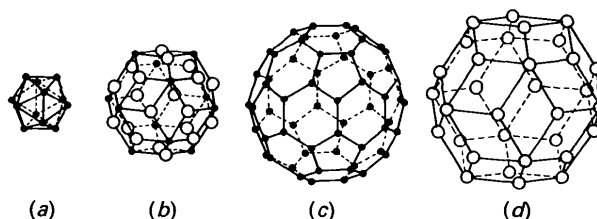

(*a*)   (*b*)   (*c*)   (*d*)

Fig. 1. Atomic cluster of nearly perfect icosahedral symmetry exhibited by the b.c.c. R-Al$_5$CuLi$_3$ phase, from Audier *et al.* (1988). Black dots represent Al, Cu atoms and circles represent Li atoms. The different shells are (*a*) an icosahedron, (*b*) an Li dodecahedron which, assembled with an Al, Cu icosahedron, forms a triacontahedron, (*c*) a truncated icosahedron and (*d*) a larger triacontahedron.

In the following description of the hexagonal Z phase, it is demonstrated that an arrangement of half-Samson polyhedra (Fig. 2c), *i.e.* constituted of ten Friauf polyhedra, can be considered. The structure is shown in Figs. 3(a), 3(b), 3(c) and 3(d), in puckered layers perpendicular to the z axis and centered successively at $z = 0.037 \pm 0.039$, $z = 0.093 \pm 0.005$, $z = 0.16 \pm 0.02$ and $z = 0.22 \pm 0.03$. The other layers, not represented, can be generated by the symmetry operation deduced from the space group: a mirror plane at $z = \frac{1}{4}$ and the twofold axis at $z = \frac{1}{2}$ in the [110] direction. Lines between atomic positions define the edges of a half-Samson polyhedron, seen along a threefold axis. The resulting stacking of these half-Samson polyhedra along the z axis is shown in Fig. 3(e). Vertices of the Friauf polyhedra are either occupied by (Al, Cu) or Mg atoms and their central cavity is always occupied preferentially by an Li atom, namely Li(9), Li(8) and Li(7). These last atoms define half of the vertices of a dodecahedron as it is found in the R phase (Fig. 1b). One Li atom [Li(3)] may be considered at the center of this half-icosahedral cluster and, as in the R phase structure, other Li atoms [Li(6), Li(5), Li(1)] are situated in front of hexagonal faces, outside Friauf polyhedra.

Between two half-Samson polyhedra, disposed symmetrically on both sides of the plane $z = \frac{1}{4}$, one can define three additional Friauf polyhedra,
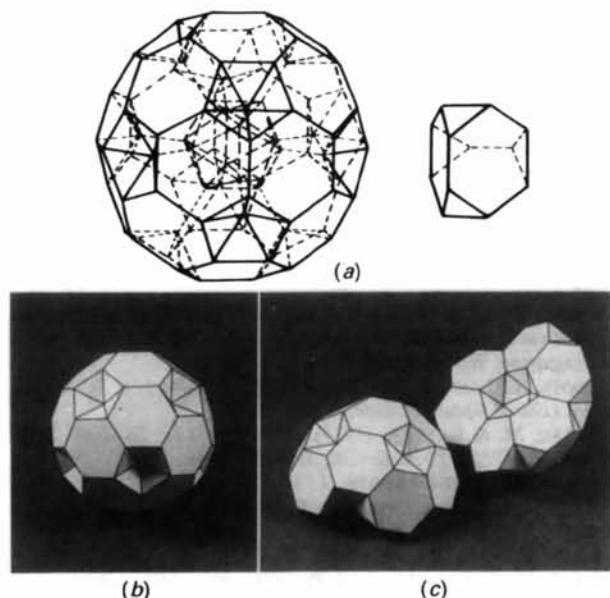
centered on this plane. Only one is drawn in Fig. 3(e), but the construction of a model showing the arrangement of all these Friauf polyhedra is presented on the photographs of Figs. 4(a) and 4(b), where the puckering of the layer at $z = 0$ can be seen and where it can be noticed that part of the small icosahedra not only exist inside half-Samson polyhedra but also occur in between. The model here is composed of four half-hexagonal cells (from $z \simeq 0$ to $\frac{1}{2}$) and shows the relative position of a half-Samson polyhedron belonging to an upper slice (Fig. 4a).
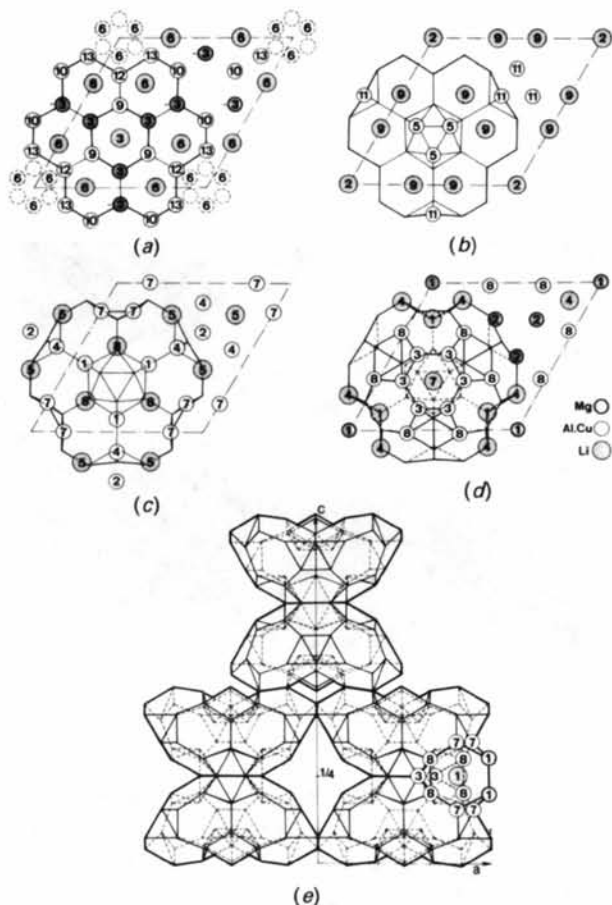

(a)

(b)

(c)

(d)

Mg ○
Al,Cu ○
Li ○

(e)

Fig. 3. (a)–(d) Atomic puckered layers in the Z-$Al_{0.59}Cu_{0.05}Li_{0.26}Mg_{0.10}$ crystal structure perpendicular to the z axis. Other layers are generated by the operation of the mirror plane at $z = \frac{1}{4}$ and the twofold axis at $z = \frac{1}{2}$ in the [110] direction [dotted line circles in (a) signify that atomic sites Al(6) are half occupied]. The successive layers are centered successively at $z = 0.04 \pm 0.04$, $z = 0.093 \pm 0.005$, $z = 0.16 \pm 0.02$ and $z = 0.22 \pm 0.03$; the lines between the atomic sites correspond to the edges of a half-Samson polyhedron the same as those shown in Fig. 2(c). The drawing (e) indicates (i) how these half-Samson polyhedra are stacked along the z axis and (ii) that other Friauf polyhedra are defined between symmetrical half-Samson polyhedra (the vertices of one of these additional Friauf polyhedra are decorated by atoms). The numbers in the circles are related to the labeling of the atomic sites in Table 2.

(a)

(b)   (c)

Fig. 2. Alternative description of the atomic cluster of the R-Al_5CuLi_3 phase. (a) All Al, Cu atomic sites, shown in Fig. 1, also define the vertices of a Samson polyhedron. (Samson, 1968); it is constituted of 20 Friauf polyhedra, one of which is shown next to the Samson polyhedron. (b) and (c) are photographs of models of a Samson polyhedron and half-Samson polyhedra. This last type of polyhedron is exhibited by the hexagonal Z structure.

Discussion

According to the preceding description, the structure of the hexagonal Z phase exhibits a direct relationship with that of b.c.c. R-Al$_5$CuLi$_3$. Diameters of half- and complete-Samson polyhedra in both phases are the same and this is the reason why the cell parameters $a(R)$ and $a(Z)$ are nearly equal. If the Samson polyhedron can be assimilated to a sphere, the second cell parameter c of the Z phase, which is nearly equal to $2a$, thus results in a stacking of four half spheres. Such an arrangement was, *a priori,* unpredictable. In a previous paper, we had assumed that the icosahedral cluster defined in the b.c.c. R phase (Fig. 1) could be energetically stable with respect to other non-icosahedral atomic configurations. Although complete Samson polyhedra have been found in the structure of the τ phase (Leblanc *et al.,* 1991), the present results seem to indicate that such an idea is not valid for all structures. The only common structural unit between both phases R and Z appears to be the Friauf polyhedron, *i.e.* a basic structural unit considered a long time ago by Samson (1968) in the interpretation of many complex intermetallic structures.

The Z structure therefore exhibits only a type of fragment of an icosahedral atomic cluster. This conclusion is similar to that of a recent study, carried out with the same aim, of the structure of the μ-Al$_4$Mn phase (Shoemaker, Keszler & Shoemaker, 1989). In that case, the μ-Al$_4$Mn phase is related both to the icosahedral Al–Mn phase (Shechtman, Blech, Gratias & Cahn, 1984) and to the cubic Al–Mn–Si phase (Cooper & Robinson, 1966). Results have shown that complete Mackay icosahedra (Mackay, 1962), characteristic of the cubic Al–Mn–Si phase, are not encountered in μ-Al$_4$Mn, but that fragments of Mackay icosahedra only are present.
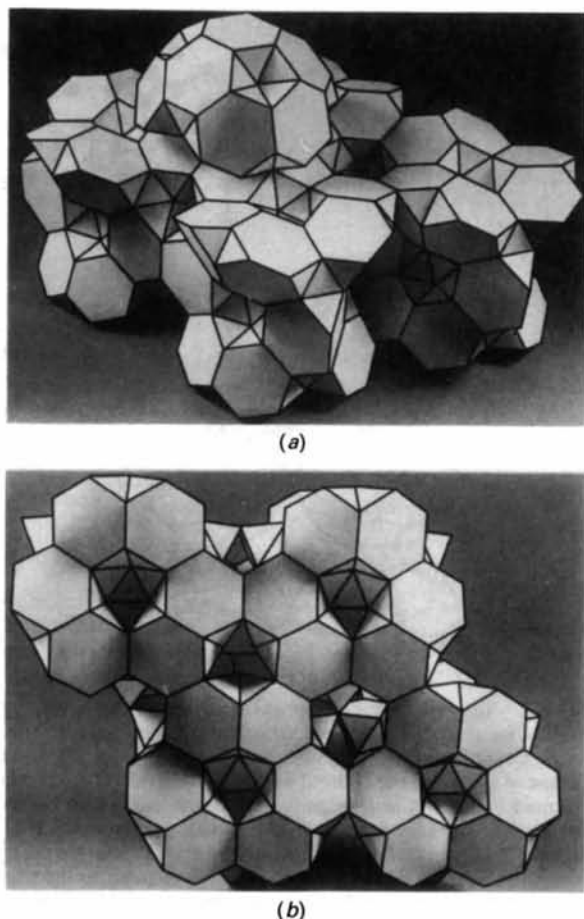
(a)

(b)

Fig. 4. A model showing the arrangement of Friauf polyhedra in the hexagonal Z structure: (a) general view of the configuration of four half-hexagonal cells (from $z \simeq 0$ to $\frac{1}{2}$) where the relative position of a half-Samson polyhedron at $z \geq \frac{1}{2}$ is also shown and (b) the aspect of the puckered layer at $z \simeq 0$.

References

AUDIER, M. & GUYOT, P. (1988a). *Quasicrystalline Materials,* edited by C. JANOT & J. M. DUBOIS, pp. 181–194. Singapore: World Scientific.

AUDIER, M. & GUYOT, P. (1988b). *Philos. Mag. Lett.* **58,** 17–23.

AUDIER, M., JANOT, C., DE BOISSIEU, M. & DUBOST, B. (1989). *Philos. Mag.* B**60,** 437–466.

AUDIER, M., PANNETIER, J., LEBLANC, M., JANOT, C., LANG, J. M. & DUBOST, B. (1988). *Physica,* B**153,** 136–142.

AUDIER, M., SAINFORT, P. & DUBOST, B. (1986). *Philos. Mag.* B**54,** L105–L111.

BERGMAN, G., WAUGH, J. L. T. & PAULING, L. (1957). *Acta Cryst.* **10,** 254–259.

BOISSIEU, M. DE, JANOT, C., DUBOIS, J. M., PANNETIER, J., AUDIER, M. & DUBOST, B. (1991). *J. Phys. Condens. Matter,* **3,** 1–25.

CASSADA, W. A., SHIFLET, G. J. & POON, S. J. (1986). *Phys. Rev. Lett.* **56,** 2276–2279.

CHERKASHIN, E. E., KRIPYAKEVICH, P. I. & OLEKSIV, G. I. (1964). *Sov. Phys. Crystallogr.* **8,** 681–685.

CLEGG, W. (1981). *Acta Cryst.* A**37,** 22–28.

COOPER, M. & ROBINSON, K. (1966). *Acta Cryst.* **20,** 614–617.

DUBOST, B., BOMPARD, P. & ANSARA, I. (1987). *J. Phys. (Paris),* **48,** C3473–C3479.

DUBOST, B., COLINET, C. & ANSARA, I. (1988). *Quasicrystalline Materials,* edited by C. JANOT & J. M. DUBOIS, pp. 39–52. Singapore: World Scientific.

DUBOST, B., LANG, J. M., TANAKA, M., SAINFORT, P. & AUDIER, M. (1986). *Nature (London),* **324,** 48–50.

DUNEAU, M. & KATZ, A. (1985). *Phys. Rev. Lett.* **54,** 2688–2691.

ELSER, V. (1985). *Phys. Rev. B,* **32,** 4892–4898.

ELSWIJK, H. B., DE HOSSON, J. T. M., VAN SMAALEN, S. & DE BOER, J. L. (1988). *Phys. Rev. B,* **38,** 1681–1685.

FRIAUF, J. B. (1927a). *J. Am. Chem. Soc.* **49,** 3107–3114.

FRIAUF, J. B. (1927b). *Phys. Rev.* **29,** 34–40.

GUYOT, P., AUDIER, M. & DE BOISSIEU, M. (1989). *Quasicrystals and Incommensurated Structures in Condensed Matter,* edited by J. YACAMAN, D. ROMEU, V. CASTANO & A. GOMEZ, pp. 251–259. Singapore: World Scientific.

HENLEY, C. L. & ELSER, V. (1986). *Philos. Mag.* B**53,** L59–L66.

JANOT, C., PANNETIER, J., SAINFORT, P., DUBOST, B., AUDIER, M. & BOUVAIST, J. (1987). ILL Experiment Report 6-07-100. Institute Laue–Langevin, Grenoble, France.

KATZ, A. (1988). *Quasicrystalline Materials,* edited by C. JANOT & J. M. DUBOIS, pp. 195–204. Singapore: World Scientific.

LANG, J. M., AUDIER, M., DUBOST, B. & SAINFORT, P. (1987). *J. Cryst. Growth*, **83**, 456–465.

LEBLANC, M., LE BAIL, A. & AUDIER, M. (1991). *Physica*. In the press.

LOISEAU, A. & LAPASSET, G. (1986). *J. Phys. (Paris)*, **47**, C3331–C3340.

LOISEAU, A. & LAPASSET, G. (1987). *Philos. Mag. Lett.* **56**, 165–171.

MACKAY, A. L. (1962). *Acta Cryst.* **15**, 916–918.

ROBINSON, W. T. & SHELDRICK, G. M. (1988). *Crystallographic Computing 4: Techniques and New Technologies*, edited by N. W. ISAACS & M. R. TAYLOR, pp. 366–377. Oxford Univ. Press.

SAMSON, S. (1968). *Structural Chemistry and Molecular Biology*, edited by A. RICH & N. DAVIDSON, pp. 687–717. San Francisco: Freeman.

SHECHTMAN, D., BLECH, I., GRATIAS, D. & CAHN, J. W. (1984). *Phys. Rev. Lett.* **53**, 1951–1954.

SHELDRICK, G. M. (1976). *SHELX76. Program for crystal structure determination*. Univ. of Cambridge, England.

SHELDRICK, G. M. (1985). *Crystallographic Computing 3*, edited by G. M. SHELDRICK, C. KRÜGER & R. GODDARD, pp. 175–189. Oxford Univ. Press.

SHELDRICK, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

SHOEMAKER, C. B., KESZLER, D. A. & SHOEMAKER, D. P. (1989). *Acta Cryst.* B**45**, 13–20.

Structures of Orthorhombic and Monoclinic Ni3(AsO4)2

BY J. BARBIER AND C. FRAMPTON

Department of Chemistry, McMaster University, 1280 *Main Street West, Hamilton, Ontario L8S* 4*M*1, *Canada*

Abstract

The crystal structures of two hydrothermally grown polymorphs of nickel orthoarsenate o- and m-$Ni_3(AsO_4)_2$ have been determined by single-crystal X-ray diffraction. Crystal data: o-$Ni_3(AsO_4)_2$, $M_r = 454 \cdot 01$, orthorhombic, $Cmca$, $Z = 4$, $F(000) = 859 \cdot 95$, $\lambda(Mo\ K\alpha) = 0 \cdot 71069$ Å, $T = 295\,(1)$ K, $a = 5 \cdot 943\,(2)$, $b = 11 \cdot 263\,(4)$, $c = 8 \cdot 164\,(3)$ Å, $V = 546 \cdot 5\,(3)$ Å^3, $D_x = 5 \cdot 517$ g cm^{-3}, $\mu(Mo\ K\alpha) = 228 \cdot 69$ cm^{-1}, $R = 0 \cdot 035$, $wR = 0 \cdot 030$ for 439 independent reflections; m-$Ni_3(AsO_4)_2$, monoclinic, $P2_1/c$, $Z = 4$, $F(000) = 859 \cdot 95$, $\lambda(Mo\ K\alpha) = 0 \cdot 71069$ Å, $T = 295\,(1)$ K, $a = 5 \cdot 764\,(1)$, $b = 9 \cdot 559\,(2)$, $c = 10 \cdot 194\,(2)$ Å, $\beta = 92 \cdot 95°$, $V = 560 \cdot 9\,(1)$ Å^3, $D_x = 5 \cdot 374$ g cm^{-3}, $\mu(Mo\ K\alpha) = 222 \cdot 76$ cm^{-1}, $R = 0 \cdot 040$, $wR = 0 \cdot 031$ for 1640 independent reflections. The crystal chemistry of nickel orthoarsenate is intermediate between those of the corresponding phosphate and vanadate, and its dimorphism is closely related to the olivine–spinel phase relations.

1. Introduction

Following the earlier work of Calvo and co-workers on the crystal chemistry of cobalt arsenates (Krishnamachari & Calvo, 1970*a*,*b*, 1974; Ozog, Krishnamachari & Calvo, 1970), a similar study of the NiO–As$_2$O$_5$ system has recently been undertaken. Interest in this system also stems from the recognition of structural relationships between some of the nickel arsenate phases and a newly identified series of germanate compounds (Barbier, 1987; Fleet & Barbier, 1988, 1989).

Initial crystal-growth experiments using a nickel arsenate hydrate melt led to the synthesis and structure determination of the Ni-rich phase Ni$_{8 \cdot 5}$As$_3$O$_{16}$ (Fleet & Barbier, 1989), the synthetic analog of the mineral aerugite (Davis, Hey & Kingsbury, 1965) and isostructural with the corresponding magnesium and cobalt arsenates (Bless & Kostiner, 1973; Krishnamachari & Calvo, 1970*a*). Attempts to grow single crystals of the Ni$_3$(AsO$_4$)$_2$ phase [*i.e.* xanthiosite, the other mineral identified by Davis *et al.* (1965)] were unsuccessful using the same technique. Further experiments were therefore based on hydrothermal crystal growth using a powder of composition Ni$_3$(AsO$_4$)$_2$.8H$_2$O as starting material. These experiments yielded several anhydrous and hydrated nickel arsenates including the two Ni$_3$(AsO$_4$)$_2$ polymorphs which are the subject of the present paper: monoclinic m-Ni$_3$(AsO$_4$)$_2$, or synthetic xanthiosite, isostructural with Co$_3$(AsO$_4$)$_2$ (Krishnamachari & Calvo, 1970*b*), and orthorhombic o-Ni$_3$(AsO$_4$)$_2$ with no cobalt analog known at present but isostructural with the vanadates Ni$_3$(VO$_4$)$_2$ and Co$_3$(VO$_4$)$_2$ (Sauerbrei, Faggiani & Calvo, 1973).

2. Hydrothermal crystal growth

The starting material for the hydrothermal growth experiments consisted of a commercial powder of nominal composition Ni$_3$(AsO$_4$)$_2$.8H$_2$O (synthetic