exclusively with only one of the compounds without mention of the other (Miller, 1936; Frevel, 1940; Dasgupta, 1953, 1954; Niggli, 1954). Although Fischmeister asserted, possibly quite correctly, that the two compounds are isomorphous, he did not present supporting evidence, and his claim that Frevel (1940) has shown this isomorphism is not strictly accurate. Frevel proposed a structure for Na_2SO_4 (III) which, as it happens, was isomorphous with the Miller (1936) proposal for Na_2CrO_4 (II) which was rejected by Niggli (1954) and by Fischmeister (1954) himself. Following Fischmeister it appears to have been generally accepted that Na_2SO_4 (III) and Na_2CrO_4 (II) are isomorphous (Wyckoff, 1964; Pistorius, 1965; Eysel, 1973), but evidence for this has not been published.

It would be useful to make a rigorous structure determination of Na_2SO_4 (III) and to check for isomorphism with Na_2CrO_4 (II). However, it may not be possible to obtain Na_2SO_4 (III) single-crystal data. Attempts to heat Na_2SO_4 (V) crystals for neutron diffraction through to phase III have resulted in destruction of the crystal. Probably it will be necessary to use a powder specimen.

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New Study of the Structure of $MnAl_6$

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Abstract. $MnAl_6$, orthorhombic, *Cmcm*, a = 7·5551 (4), b = 6·4994 (3), c = 8·8724 (17) Å, $Z = 4$, V = 435·67 Å^3, D_c = 3·31 Mg m^{-3}, $R(F)$ = 0·0209 for 530 reflections refined. The structural parameters agree within experimental error with those of Nicol [*Acta Cryst.* (1953). **6**, 285–293] except for the Al(2)—Al(3) bond length which was erroneously reported previously. The structure consists of approximately planar layers of Mn and Al atoms with a spacing of about 2·6 Å. Short Mn—Al and Al—Al bond lengths are comparable to those observed in Mn_4Al_{11}.

Introduction. The structure of $MnAl_6$ has been determined by Nicol (1953) using two-dimensional Fourier methods, and investigated again by Forsyth (1959), measuring only a limited number of reflections in the [001] zone. In preparation for a possible electron density study the structure was redetermined from three-dimensional counter data.

Small single crystals were supplied by Dr J. B. Forsyth and Dr A. Harding. A nearly cubic crystal of approximate dimensions 0·09 × 0·10 × 0·10 mm was chosen for data collection at room temperature, using monochromatized Mo $K\bar{\alpha}$ radiation (λ = 0·71069 Å). Cell dimensions were calculated by a least-squares refinement of the setting angles of 25 reflections with $\theta > 22°$. A quadrant of reflections ($\sin\theta/\lambda$ < 0·8 Å^{-1}) was measured with a θ–2θ scan. Each reflection was measured at three different values of the azimuthal angle ψ (0, 1·5, 3·0°). No large discrepancies were found between measurements at different ψ values.

3705 reflections were averaged after Lorentz–polarization and absorption corrections (μ = 3·913

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Table 1. *Positional and equivalent isotropic thermal parameters*

The isotropic extinction parameter is 0·090 (8) × 10^{-4}.

	x	y	z	U_{eq} ($\times 10^{-5}$ Å^2)
Mn	0	0·45686 (4)	$\frac{1}{4}$	525 (17)
Al(1)	0·32602 (6)	0	0	965 (24)
Al(2)	0	0·13917 (8)	0·10039 (6)	1110 (25)
Al(3)	0·31768 (6)	0·28622 (7)	$\frac{1}{4}$	1001 (24)

Table 2. *Bond lengths* (Å)

	Nicol (1953)	Present study
Mn–Al(2)	2·435 (25)	2·4547 (6)
Al(3)	2·54 (3)	2·5455 (5)
Al(1)	2·600 (25)	2·5935 (5)
Al(3)	2·64 (3)	2·6440 (5)
Al(1)–Al(1)	2·640 (35)	2·6289 (9)
Al(2)	2·76 (4)	2·7710 (5)
Al(2)	2·84 (4)	2·8321 (6)
Al(3)	2·84 (3)	2·8336 (6)
Al(3)	2·88 (3)	2·8956 (5)
Al(2)–Al(2)	2·57 (3)	2·5389 (10)
Al(2)	2·62 (3)	2·6549 (12)
Al(3)	2·890 (45)	2·9045 (6)
Al(3)	2·999 (45)*	2·9869 (7)
Al(3)–Al(3)	2·77 (4)	2·7549 (10)

* This value was erroneously reported by Nicol to be 2·770 (45) Å.

mm^{-1}), yielding 533 unique reflections. The internal agreement factor between symmetry-related reflections was $R(F^2) = 0{\cdot}034$. Reflections with $F < 0$ were excluded, giving 530 reflections for a full-matrix least-squares refinement. Nicol's (1953) atomic positions, with the a and b axes interchanged to convert to the conventions used in *International Tables for X-ray Crystallography* (1969), were used as starting values for refining the positional, anisotropic thermal and isotropic extinction parameters.

The final R factors for the centrosymmetric space group *Cmcm* were $R(F) = 0{\cdot}0209$ and $R_w(F) = 0{\cdot}0288$ $\{R(F) = \sum|F_o - |F_c||/\sum F_o$; $R_w(F) = (\sum w|\Delta F|^2/\sum wF_o^2)^{1/2}$, $w = \sigma^{-2}$, $\sigma(F) = [\sigma(F^2)^2 + (0{\cdot}03F^2)^2]^{1/2}/2F\}$. Final parameters are in Table 1,† and bond lengths are listed in Table 2. The U_{eq}'s listed in Table 1 are calculated from the formula $U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$, which for an orthogonal system becomes $U_{eq} = \frac{1}{3}\sum_i U_{ii}$. The Mn atom was found to be almost isotropic, but the Al atoms showed anisotropy, especially Al(1) where the value of U_{22} was about twice as large as U_{11} or U_{33}. The difference between U_{33} and U_{11} or U_{22} for Al(3) was not as pronounced.

Since no chemical analysis of the crystals was made, the data set was also refined varying the Mn occupancy. This resulted in a lowering of occupancy less than 2σ, so it was concluded that there were no significant impurities present in the crystal.

Discussion. The present study is in fair agreement with the earlier studies. The bond lengths compare well except in one case, Al(2)–Al(3), where there is a calculational error in Nicol's (1953) values. The best value for an atomic diameter in aluminum metal is 2·71 Å (Nicol, 1953), so the Al(2)–Al(2) bond (2·54 Å) is exceptionally short. The two Al(2) atoms also are the ones closest to the Mn atom, the bond length being 2·45 Å, compared to the 'normal' value of 2·68 Å (Nicol, 1953). This bond length is comparable to the Mn(1)–Al(0) and Mn(2)–Al(5) distances in Mn_4Al_{11}, 2·40 and 2·41 Å respectively (Kontio *et al.*, 1980). Also the coordination polyhedron of the Mn atom (Fig. 1) is very similar to the coordinations of Mn(1) and Mn(2) in Mn_4Al_{11}. The number of neighbors for Mn is 10, all of which are Al atoms, and that for the Al atoms is 11, two neighbors being Mn, except for Al(2) which only has one Mn neighbor. The structure shows rather prominent layering with sheets of Al atoms with a spacing of about 2·6 Å in the [011] direction. The Mn atoms lie slightly above and below these planes.

The possible noncentrosymmetry of the structure, suggested for $MnAl_6$ by Forsyth (1959) and detected for the isostructural α (Al–Cu–Fe) (Black, Edwards & Forsyth, 1961), was investigated by refining the parameters also in the noncentrosymmetric space group *Cmc*2_1. The R factors became slightly lower at $R(F) = 0{\cdot}0205$ and $R_w(F) = 0{\cdot}0269$. These refinements with the shifts in different directions all converged after a few cycles with the positions within two or three standard deviations of the centrosymmetric values, the largest difference being ~0·003 Å.

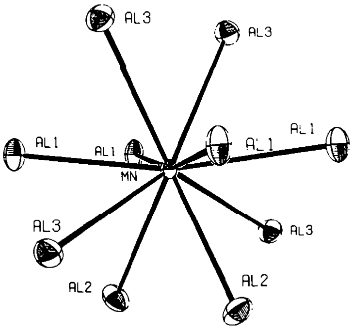

Fig. 1. The ten Al atoms surrounding the Mn atom. The b axis is vertical. The ellipsoids correspond to 75% probability.

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† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35701 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Therefore, we conclude that, within the accuracy of this experiment, the structure is centrosymmetric.

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Structure of Bromapatite and the Radius of the Bromide Ion

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Abstract. $Ca_5(PO_4)_3Br$, hexagonal, $P6_3/m$, a = 9·761 (1), c = 6·739 (1) Å, V = 556·06 Å^3, Z = 2, μ(Mo $K\alpha$) = 6·609 mm^{-1}, D_c = 3·374 Mg m^{-3}. The structure was refined to wR on F^2 of 3·08%. Bromapatite has a typical hexagonal apatite structure with most of the Br^- ions at (0,0,0) and about 2% at (0,0,0·103) (plus equivalent positions). There was no evidence of a Br^- distribution as has been described in non-stoichiometric cadmium bromapatite. The packing of the Br^- ions requires an apparent radius of the Br^- ion of 1·68 Å which is appreciably smaller than the traditional value of 1·95 Å.

Introduction. Calcium bromapatite is of interest because if it is stoichiometric it must contain two Br^- ions along the z axis per unit cell, which is apparently inconsistent with the usual value given for the crystal radius of Br^- of 1·95 Å (Pauling, 1960), so that four times the crystal radius (7·80 Å) is appreciably greater than the c-axis dimension of 6·739 Å (Fig. 1*a*). The same situation occurs in other apatites, $Cd_5(VO_4)_3I$, $Cd_5(PO_4)_3Br$, $Cd_5(AsO_4)_3Br$ and $Cd_5(VO_4)_3Br$, which contain large halide ions. These compounds have been found to have a halide non-stoichiometry of between 8 and 27% which has been associated with a distribution of the halide ions along the z axis (Fig. 1*b*) (Sudarsanan, Young & Wilson, 1977; Wilson, Sudarsanan & Young, 1977). Another point of interest is that in some stoichiometric apatites an ordered arrangement of Cl^- or hydroxyl ions occurs which results in a doubling of the b axis and the lowering of the symmetry to the monoclinic space group $P2_1/b$ (Mackie, Elliott & Young, 1972; Elliott, Mackie & Young, 1973).

Crystals of bromapatite were grown by slowly cooling a mixture of powdered bromapatite and $CaBr_2$ in a HBr atmosphere from 1073 to 1013 K at a rate of 0·67 K h^{-1} (Dykes, 1974). A spherical crystal 0·309 mm in diameter was used for X-ray data collection with a Picker FACS-1 diffractometer and Mo $K\alpha$ radiation. A 2θ scan with unfiltered radiation was used for reflections for which there was no interference from $K\beta$ peaks in the range of reflection and background scan. The other reflections were collected by either the balanced-filter ω-scan method or by the single-filter 2θ-scan method (Mackie, 1972). Simultaneous diffraction effects were assessed by a second measurement of each reflection after the specimen had been rotated 1° about the diffraction vector. Those reflections which for

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