Table 2 shows that the harmonic amplitude of thermal displacement u_{11} increases significantly for Te as the Mn content increases, whereas the corresponding u_{11}(Cd, Mn) amplitude remains rather constant with composition. The absolute magnitude of u_{11}(Cd, Mn) however significantly exceeds u_{11}(Te). The anharmonic displacement coefficient u_{123} for both atomic sites increases with increasing Mn content, with the absolute magnitude of u_{123} for the composite Cd, Mn atom exceeding that for Te at all three compositions. In view of the results of Balzarotti *et al.* (1985), it is likely that the anharmonicity present originates in static, rather than thermal, atomic displacements. In this case, the Mn atom is not located exactly at $\frac{1}{4}\frac{1}{4}\frac{1}{4}$, in accordance with Balzarotti *et al.* (1985), but is distributed several hundredths of an ångström distant along each body diagonal from the Cd site. The smaller u_{123}(Te) magnitudes suggest that Te is similarly distributed but over smaller displacements about the unit-cell origin. The electron-density distribution in the (110) plane through the Te atom site, shown in Fig. 1(*a*), exhibits small maxima along the body diagonals with somewhat reduced maxima also observable in the corresponding section through the Cd, Mn atom site, shown in Fig. 1(*b*). An experimental test of the static displacements proposed may be made by undertaking a thermal dependence study. As pointed out by a referee, analysis of any diffuse scattering that may subsequently be found near reciprocal-lattice points, in terms of possible short-range order at the atomic sites, would also be informative.

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Structure of $NaMnF_3$ at Room Temperature

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Abstract. Manganese sodium fluoride, $NaMnF_3$, $M_r = 134{\cdot}92$, orthorhombic, *Pnma*, $a = 5{\cdot}751\ (4)$, $b = 8{\cdot}008\ (6)$, $c = 5{\cdot}548\ (4)$ Å, $V = 255{\cdot}5\ (5)$ Å^3, $Z = 4$, $D_x = 3{\cdot}51$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 5{\cdot}41$ mm^{-1}, $F(000) = 252$, $T = 298\ (1)$ K, final $R = 0{\cdot}043$ for 347 observed reflexions. The Mn^{2+} ions are surrounded by six F^- ions forming a distorted octahedron with Mn—F distances between 2·105 (2) and 2·123 (2) Å. The model obtained has been analysed from the point of view of distortion from the ideal cubic perovskite-type arrangement.

Introduction. The structure of $NaMnF_3$ is closely related to the ideal cubic perovskite structure, characteristic of the crystal of general formula AMX_3. For $NaMnF_3$ at room temperature a distortion from the ideal cubic symmetry is observed. This distortion can be caused by various components such as: (i) tilting of the anion octahedra, (ii) distortion of the octahedra and (iii) displacements of the cations (Glazer, 1972).

In earlier studies on the crystal structure of $NaMnF_3$, lattice parameters were obtained by the X-ray powder method (Simanov, Batsanova & Kovba, 1957)

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Table 1. *Final atomic parameters for* $NaMnF_3$

	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mn	4(*a*)	0·5	0·5	0·5	0·0059 (4)	0·0052 (4)	0·0063 (4)	−0·0007 (2)	−0·0005 (2)	0·0006 (2)
Na	4(*c*)	0·0543 (6)	0·75	0·5127 (4)	0·0130 (10)	0·0229 (11)	0·0175 (10)	0	0·0038 (8)	0
F(1)	8(*d*)	0·3053 (4)	0·5603 (3)	0·8093 (4)	0·0111 (8)	0·0202 (11)	0·0123 (8)	−0·0052 (8)	0·0067 (8)	−0·0058 (9)
F(2)	4(*c*)	0·4469 (6)	0·75	0·3854 (5)	0·0179 (13)	0·0044 (10)	0·0129 (11)	0	0·0004 (11)	0

for the orthorhombic unit cell and monoclinic subcell. The atom coordinates have been previously reported (Pompa & Siciliano, 1969*a,b*). Relationships between the orthorhombic unit cell, monoclinic subcell and atom coordinates were determined by the X-ray powder profile refinement method (Ratuszna, Majewska & Rodek, 1985).

The aim of the present work is to determine exactly the coordinates of the atoms and to show which components are taking part in lattice distortion, by using a single crystal X-ray diffraction method.

Experimental. Single crystals of $NaMnF_3$ were prepared by modified horizontal Bridgman method from a stoichiometric mixture ($NaF + MnF_2$). The components, after careful mixing, were melted at 1233 K in a furnace filled with pure argon. The melted mixture moved into the graphite crucible at a speed of 1 mm h^{-1} from the melting-temperature area. The procedure lasted about 40 hours. Blocks of about 1 mm^3 volume, transparent-pink in colour, were obtained. The crystals are strongly elastic and easily twin. It was very difficult to prepare mono-domain samples suitable for single crystal X-ray work. Using a very careful procedure, a small specimen was obtained by cutting it from the larger bulk and polishing it using concentrated HCl, to size 0·1 × 0·15 × 0·07 mm.

Table 2. *Distances* (Å) *and angles* (°) *for the sodium and manganese coordination spheres*

Mn—F(1)	2·105 (2)	Mn—F(1^{i})	2·106 (2)
Mn—F(2)	2·123 (2)	Na—F(1^{ii})	2·309 (3)
Na—F(2)	2·366 (4)	Na—F(2^{iii})	2·294 (3)
Na—F(1)	2·664 (3)	Na—F(1^{i})	2·846 (3)
F(1)—Mn—F(2)	87·2 (1)	F(1^{i})—Mn—F(2)	86·9 (1)
F(1)—Mn—F(1^{i})	91·1 (1)	F(1^{iv})—Na—F(2)	136·0 (2)
F(1^{iv})—Na—F(2^{iii})	104·2 (2)	F(1^{iv})—Na—F(1^{ii})	82·3 (2)
F(2^{iii})—Na—F(2)	88·3 (2)		

Symmetry operations: (i) $0{\cdot}5-x$, $1-y$, $-0{\cdot}5+z$; (ii) $-0{\cdot}5+x$, y, $1{\cdot}5-z$; (iii) $-0{\cdot}5+x$, $1{\cdot}5-y$, $0{\cdot}5-z$; (iv) $-0{\cdot}5+x$, $1{\cdot}5-y$, $1{\cdot}5-z$.

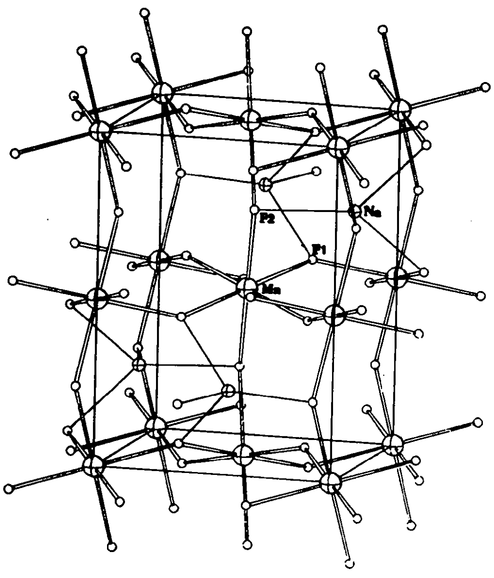

Fig. 1. Perspective drawing of orthorhombic $NaMnF_3$ (*ORTEP*II, Johnson, 1976).

Systematic absences on Weissenberg photographs indicate two possible space groups: *Pnma* or *Pn*2_1*a*. Syntex *P*2_1 diffractometer and Mo *K*α radiation, 15 reflexions for lattice parameters ($17 < 2\theta < 26°$) and intensity measurements; ω–2θ scan; 1239 reflexions measured below $2\theta = 70°$ (h −9→9, k 0→12, l 0→8); two standard reflexions measured after every 50 reflexions, variation 5%. Most calculations performed on a NOVA 1200 computer with locally modified *XTL/XTLE* (Syntex, 1976) programs. Scattering factors for Mn^{2+}, Na^{+} and F^{-} were from *International Tables for X-ray Crystallography* (1974); f' and f'' for all atoms. The Mn atom was found from a Patterson map. All other atoms were found from difference syntheses. An absorption correction following the *DIFABS* procedure (Walker & Stuart, 1983) was applied on isotropically refined data; min. and max. absorption corrections: 0·879 and 1·746. The symmetry-related reflexions were averaged after *DIFABS* to give 347 independent data with $I > 2\sigma(I)$; $R_{\rm int}(wF^2) = 0{\cdot}026$. Final refinement was performed (on F) with *SHELX*76 (Sheldrick, 1976), using anisotropic thermal parameters for all atoms and an isotropic extinction correction of the form: $1 - xF_c^2/\sin\theta$; refinement of x gave the value $3{\cdot}9\,(3) \times 10^{-6}$. Weighting scheme $w^{-1} = \sigma^2(F) + gF^2$ was applied; the g parameter refined to 0·0048. Final $R = 0{\cdot}043$ and $wR = 0{\cdot}043$; max. $\Delta/\sigma = 0{\cdot}01$. Residual electron density in final difference-Fourier map within $-1{\cdot}81$ and $0{\cdot}99$ e $Å^{-3}$. The final atomic parameters are given in Table 1.* The crystal structure and atom-numbering scheme are

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51539 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Restrictions on atom displacements corresponding to the space group Pnma*

	Position	*x*	*y*	*z*	*u*	*v*	*w*
Mn	4(*a*)	0·5	0·5	0·5	0	0	0
Na	4(*c*)	0·5+*u*(Na)	0·25	*w*(Na)	−0·0543	0	0·0127
F(1)	8(*d*)	0·25+*u*[F(1)]	0·5+*v*[F(1)]	0·75+*w*[F(1)]	0·0553	0·0603	0·059
F(2)	4(*c*)	*u*[F(2)]	0·25	*w*[F(2)]	0·0531	0	−0·1146

shown in Fig. 1. The principal interatomic distances and bond angles are summarized in Table 2.

Discussion. Now, we try to consider the structure obtained as a deformation of the ideal cubic perovskite type. In the orthorhombic unit, four pseudo-cubic perovskite-type subcells containing MnF_6 octahedra are distinguished. The subcells are slightly distorted towards the monoclinic unit. In Table 3 are listed displacements *u*, *v* and *w* from the cubic perovskite positions in the space group *Pnma*, calculated from Table 1.

Displacements of F^- ions cause the rotation of whole octahedra, which are treated as rigid. For the parameters of displacement, the tilt angle amplitudes have been calculated as: $\alpha = 2{\cdot}3\,(1)$, $\beta = 3{\cdot}4\,(1)$ and $\gamma = 2{\cdot}2\,(1)^\circ$ where α, β and γ are the tilt angles of octahedra around [100], [010] and [001] axes, respectively (Glazer, 1972). In Fig. 2(*a*) and (*b*) schematic projections along [010] are drawn. From these one can see that the distortion is caused by the tilting octahedra according to Glazer's classification $a^-b^+a^-$ ($\alpha = \gamma$).

The Mn atoms are located at the centres of distorted octahedra formed by F atoms. Such octahedra are connected in the $[0\bar{1}0]$ direction by F(2) atoms, and in the [101] and $[10\bar{1}]$ directions by F′(1) and F″(1) atoms. The Mn—F distances do not differ significantly, 2·105 (3)–2·123 (3) Å, but these octahedra are distorted from the regular shape which exists in the cubic symmetry.

Finally, we can notice the movement of the Na^+ cations from their ideal position along the [101] direction. Every Na^+ cation is surrounded by four F atoms which are placed at the vertices of distorted tetrahedra, at 2·294 (3)–2·366 (3) Å. Two further F atoms are placed at 2·664 (3) Å and two at 2·846 (3) Å.

In conclusion, we can state: at room temperature $NaMnF_3$ is orthorhombic (with space group *Pnma*), but the structure is a result of a distortion from ideal perovskite symmetry. This deformation is caused by tilting of MnF_6 octahedra according to the sequence of tilts $a^-b^+a^-$, by deformation of octahedra, and by displacement of Na^+ cations. The data obtained from single crystal X-ray measurements fully confirm the mechanism of the structure deformation described earlier by Glazer (Glazer, 1972, 1975).

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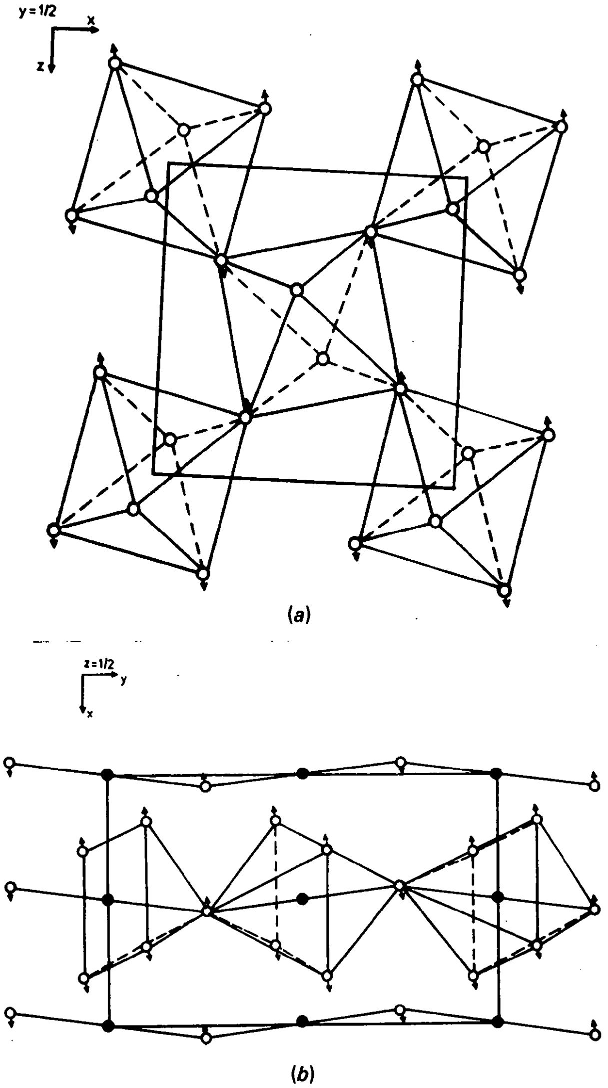

Fig. 2. Schematic diagram of the structure. (*a*) Projection on (010) plane at height $y = \frac{1}{2}$. The arrows drawn up indicate the atoms lying above the plane, and down, indicate the atoms lying below the plane. The type of tilting octahedra is a^- and c^- along [101] and $[10\bar{1}]$ directions (pseudo-cubic axis). (*b*) Projection on (001) plane at height $z = \frac{1}{2}$. Along the [010] direction the octahedra are tilting b^+ (black circles are Mn^{2+}).

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Structure of Calcium Metaphosphate $Ca(PO_3)_2$

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Abstract. $Ca(PO_3)_2$, $M_r = 198{\cdot}024$, monoclinic, $P2_1/a$, $a_0 = 16{\cdot}960\ (9)$, $b_0 = 7{\cdot}7144\ (2)$, $c_0 = 6{\cdot}9963\ (2)$ Å, $\beta = 90{\cdot}394\ (5)°$, $V = 915{\cdot}40$ Å^3, $Z = 8$, $D_x = 2{\cdot}874$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}70926$ Å, $\mu = 19{\cdot}720$ cm^{-1}, $F(000) = 784$, room temperature; final $R = 0{\cdot}0395$ for F^2 and 2113 reflections. The crystal structure consists of meandering chains of PO_4 tetrahedra along the [001] direction, connected by Ca atoms. P—O distances

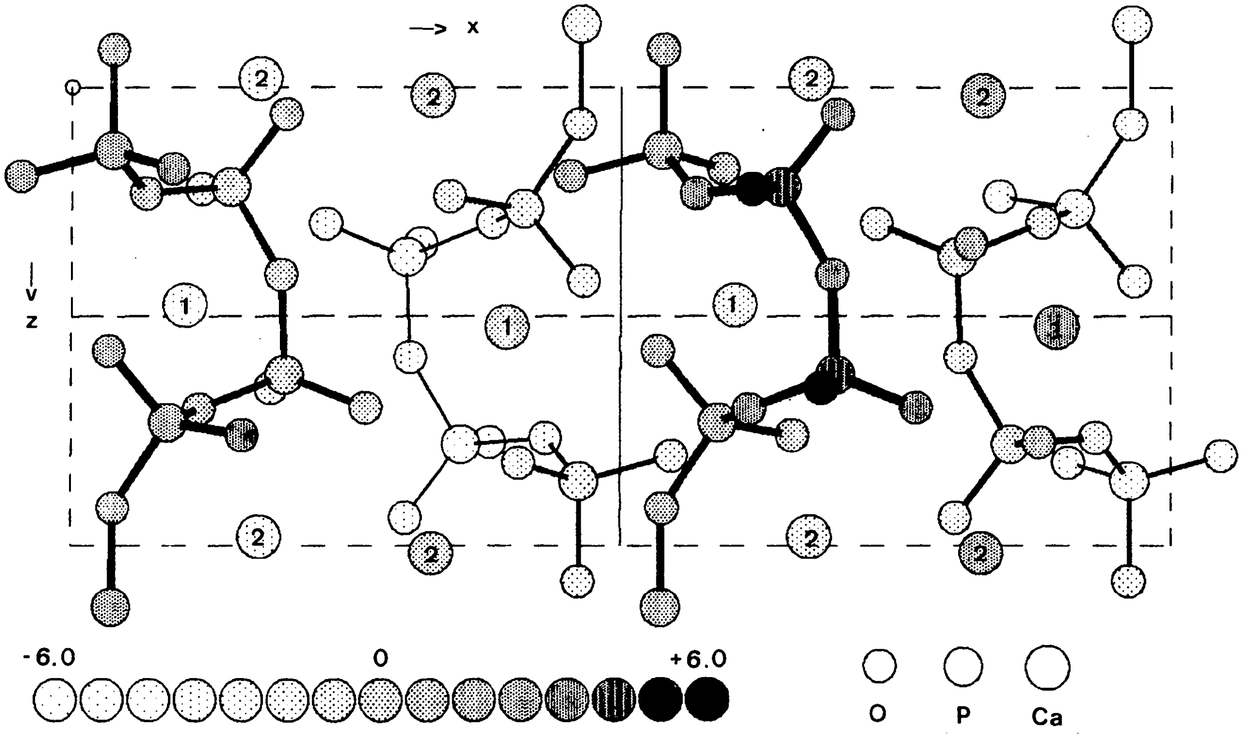

Fig. 1. Projection of a unit cell along **b**. The numbering scheme refers to the labels of atoms in Table 1. The grade of shading indicates different heights of the atoms measured in Å with respect to the drawing plane.