is the internal energy content of a solid at any temperature T and is tabulated (*American Institute of Physics Handbook*, 1963) as a function of temperature, knowing the characteristic temperature of the solid. The internal energy content of Er is obtained by treating it as a Debye solid. The values of the parameters V_0, ϱ, θ_D and B_{00} for Er are given in Table 3. The values of V_0, ϱ and θ_D correspond to those at room temperature. The agreement between the calculated B_s values and those obtained from the measured elastic constants (Fisher & Dever, 1967), at various temperatures up to 298 K, is good to within 2%.

Table 3. *Values of the constants of erbium used in the present calculations*

Debye temperature θ_D (K)	V_0	ϱ	B_{00} $(10^{11}$ dynes cm$^{-2})$
191	18·45	9·064	4·63

5. Discussion

The close agreement between the calculated $\bar{\gamma}_H$ and the thermal $\bar{\gamma}_H$, the calculated and experimental A–G parameters and the calculated and experimental B_s values of Er amply justifies the use of the C.F. model to explain the thermal and mechanical properties of this rare-earth metal. The calculated pressure derivative $\partial C_{44}/\partial p$ is positive for Er, from which it may be inferred that the pressure-induced phase transformation from h.c.p. to b.c.c. structure is not possible in this metal. The G.P.'s in Er (both γ' and γ'') have small values, which is a characteristic feature of the h.c.p. rare-earth metals. The agreement of the frequencies of Er calculated on the C.F. model in the symmetry directions with the extrapolated frequencies is better than that obtained by Ramji Rao & Menon (1973) using Keating's (1966) approach.

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The Structure of NaTaO₃ by X-ray Powder Diffraction

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The structure of NaTaO₃ has been determined from X-ray powder diffraction spectra by measuring the intensities of the difference reflexions caused by the deviations from the ideal cubic perovskite structure. The structure is compared with that determined on the basis of single-crystal measurements.

1. Introduction

In general, it is much easier to obtain a powder specimen than a truly untwinned single crystal. On the other hand, the powder method suits only the simplest structures because of the overlap of adjacent Bragg peaks in more complex structures. Rietveld (1969) has, however, developed a refinement method for neutron powder diffraction patterns. In this method the detailed shape of the powder pattern is used to decide between various structural models. This method is a structure refinement technique, *i.e.* the structure has already been solved approximately by X-ray or other techniques.

In this work, the structure of NaTaO₃ is determined by the X-ray diffraction powder method by making

use of the knowledge available about certain types of perovskites. This knowledge has been collected over many years (e.g. Megaw, 1966, 1969, 1972, 1973; Glazer, 1972, 1975). Megaw has shown that the perovskite structures can be split into various components: (i) tilting of the anion octahedra, (ii) displacements of the cations, (iii) distortions of the octahedra. Glazer has considered in detail the effect of the octahedral tilts and has shown how, when present, they establish the overall space group symmetry of the particular perovskite. Furthermore, the tilting of the octahedra causes doubling of the unit-cell axes and gives rise to difference reflexions. There are two types of tilt, in-phase (+) and antiphase (−), producing two types of difference reflexion which allow the tilt system to be identified. In addition, the antiparallel displacements of the cations cause difference reflexions which can differ from those due to octahedral tilts.

We therefore concentrate on the information given by difference reflexions and try to fit this to a suitable model which can then be checked against all measured reflexions. The X-ray powder intensity measurements are based on the experience acquired in this laboratory (e.g. Suortti & Jennings, 1977). Ahtee & Glazer (1976) have recently made qualitative use of the same type of approach in proposing structural models for the various phases of Na/K niobate solid solutions both at room temperature and above.

X-ray diffraction studies of NaTaO₃ have been carried out by Voudsen (1951) and by Kay & Miles (1957, hereinafter K & M) with single crystals. The accuracy obtained by K & M was limited by the small number of observed difference reflexions. R in this case was 0·22.

2. Experimental work

The NaTaO₃ powder was high-purity material supplied by Johnson Matthey Chemicals Ltd., England, with an average particle size of about 3–5 μm. The samples were prepared in a polished steel mould with different moulding pressures. The preferred orienta-

tion was checked by measuring the 200, 220, 222 and 400* reflexions (Järvinen, Merisalo, Pesonen & Inkinen, 1970). On the basis of these experiments a 1000 kp cm⁻² sample was chosen for the final measurements.

After correction for texture effects there may still exist reduction of the diffracted intensity due to porosity and surface roughness of the sample. No attempt was made to correct for these errors.

The absolute intensity measurements were made on a Siemens diffractometer with Cu $K\alpha$ radiation monochromatized by a bent quartz crystal. Scattering by air was avoided by measuring the sample in vacuum and the possible extra reflexions caused by the measuring system were eliminated with beam tunnels both behind the monochromator and in front of the scintillation counter.

The diffraction pattern was measured in steps of 0·05° in 2θ from 8 to 75° (Fig. 1). When 2θ was larger than 75° the peaks overlapped so much that only qualitative information could be obtained. To obtain the integrated intensities the slit sizes were chosen to be large enough to measure the whole peak at once. Background was measured as the average of both sides

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* Unless explicitly stated otherwise, our axes of reference are those of the pseudocubic doubled cell.
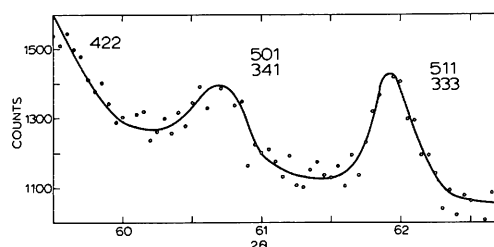

Fig. 2. Difference reflexions (501; 341) and (511; 333) corresponding to in-phase and antiphase tilts of the oxygen octahedra respectively.
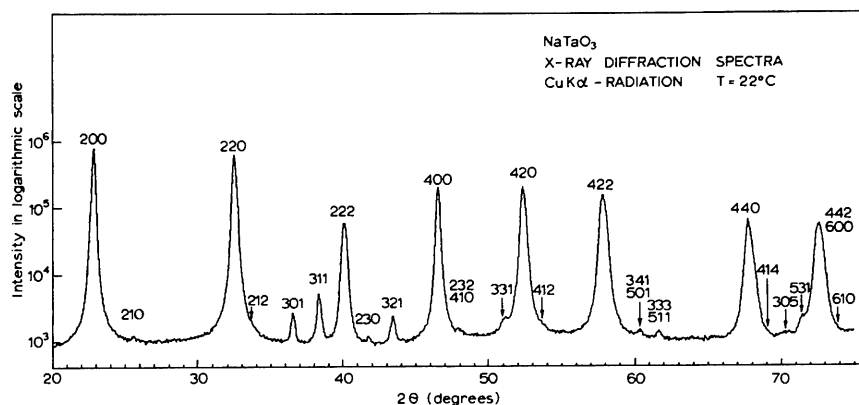

Fig. 1. X-ray diffraction patterns of polycrystalline NaTaO₃ on a logarithmic scale of intensities.

of the peaks. Some of the difference reflexions were so close to the main peaks that they had to be separated by hand calculation, in which case the intensities are only approximate. The observed intensities are given in Table 3. The errors can be estimated to be within 10% except for those cases where the peaks had to be separated by hand (30% error) (Fig. 2).

Table 1. *The lattice parameters of* NaTaO₃ *measured by Kay & Miles* (1957) *from single crystals*

Orthorhombic	Pseudocubic
$a_o = 5\cdot5130$ Å	$a_p = 7\cdot7832$ Å
$b_o = 7\cdot7508$	$b_p = 7\cdot7508$
$c_o = 5\cdot4941$	$c_p = 7\cdot7832$
	$\beta = 90\cdot20°$

3. The structure model based on difference reflexions

K & M measured the lattice parameters of NaTaO₃ from a single crystal (Table 1). The relations $a_p = c_p > b_p$ and $\beta \neq 90°$ for the pseudocubic-subcell parameters are consistent with tilt system $a^-b^+a^-$ or $a^-b^0a^-$ (Glazer, 1972, 1975). In the diffraction spectra (Fig. 1) there are difference reflexions with two odd indices and one even index (*e.g.* 301, 321, 341; 501, 503), probably produced by in-phase (+) tilts, and also difference reflexions with all indices odd (*e.g.* 311, 331, 333; 511, 531), probably produced by antiphase (−) tilts. This implies that the overall tilt system is $a^-b^+a^-$. The existence of the two (−) tilts is also supported by the fact that the intensity of the 311 group (3900) is considerably higher than that of the 301 reflexions (1100) (see Table 3).

The magnitudes of the tilt angles about [100], [010] and [001], denoted α, β and γ respectively, were estimated from the intensities of the difference reflexions relative to the main ones. Thus, the 301 reflexion gave a measure of β and the 311 reflexion gave α and γ. These latter two are equal in magnitude as a consequence of the equality of a_p and c_p.

The tilting of the octahedra suggests the possible displacement directions for the Na cations (Fig. 3).

O(1), O(2) and O(3) are the nearest neighbours of Na(1) and by repulsion suggest a movement along [101]. On the next layer Na(2) should move along [10̄1]. This antiparallel arrangement of Na atoms is further supported by the existence of the difference reflexions having two even indices and one odd index (*e.g.* 230, 232; 410). In Table 2 the intensities of these reflexions have been calculated in different ways. The measured values have been obtained by separating these reflexions by hand from the main peaks (Fig. 4). In the calculations we assumed that the components of Na displacement along the a_p and c_p axes were equal although this is not required by symmetry. The Ta displacements are zero because the space group requires the Ta atoms to be on centres of symmetry. Furthermore, the intensities of difference reflexions fell off very rapidly at higher angles.

Table 2. *The intensities of the difference reflexions* (230 *and* 232; 410)

The intensities were calculated by taking into account the displacements of I_O oxygens only, I_{Na} sodiums only, I_{O+Na} both oxygens and sodiums. I_{obs} is the observed intensity.

Reflexions	I_O	I_{Na}	I_{O+Na}	I_{obs}
230	40	70	220	250
232; 410	50	260	520	480

The total diffracted energy E^{hkl} from an ideal powder specimen depends on the measuring geometry $G(\theta)$, the multiplicity p_{hkl}, and the structure factor F_{hkl} of the reflexion:

$$E^{hkl} \propto G(\theta)p_{hkl}|F_{hkl}|^2 .$$

The structure factor, F_{hkl}, on the other hand, depends on the geometrical structure factor and the atomic scattering factor f which has to be corrected for dispersion and thermal scattering with the aid of the expression

$$f = (f_0 + \Delta f' + i\Delta f'') \exp\left[-B(\sin\theta/\lambda) \right]^2 ,$$

where f_0 is the scattering factor independent of the X-ray wavelength and $\Delta f'$ and $\Delta f''$ are the anomalous dispersion corrections; B is the isotropic temperature factor. The theoretical intensities were fitted by iterating the atomic coordinates in the geometrical structure
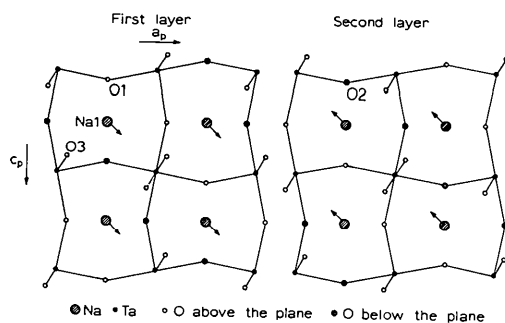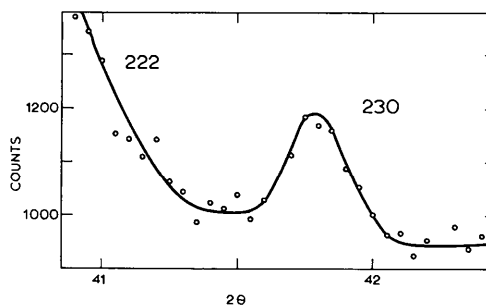

Fig. 3. Plan of the structure of NaTaO₃ showing the tilts of the oxygen octahedra ($a^-b^+a^-$). The direction of the Na displacements is indicated by arrows.

Fig. 4. The even-odd-even reflexion, 230, corresponding to Na displacements.

Table 3. *The observed integrated intensities* I_{obs}
for $NaTaO_3$ *compared to the theoretical intensities
calculated on the basis of our structure,* I_{ns}, *and that
of Kay & Miles* (1957), $I_{K \& M}$

Reflexions	I_{obs}	I_{ns}	$I_{K \& M}$
200	676000	679000	667000
220	677000	681000	669000
301	1100	1100	2700
311	3900	4000	4600
222 } 230 }	83000 250	84000 220	95000 330
321	970	1000	1800
400 } 232; 410 }	213000 480	209000 510	195000 1700
420 } 412 } 331 }	282000	269000	277000
422 } 430 }	280000	264000	259000
341; 501	400	270	270
333; 511	480	410	530
440 } 252; 414 }	110000	105000	96000
442; 600 } 503 } 531 } 610 }	127000	116000	116000

factor and the temperature factor *B*. The calculated
intensities are given in Table 3 with the observed
intensities and the intensities calculated on the basis
of the structure given by K & M.

4. Discussion

In our model we assumed that (i) the octahedra are
regular, (ii) the off-centre displacements of the Na ions
are towards the midpoints of the octahedron edge (the
so called two-corner displacement) and (iii) the tilt
angles α and γ are equal. The atomic coordinates ob-
tained by us are compared with those given by K & M
in Table 4, and the bond lengths calculated from both
sets of parameters in Table 5.

K & M give the space group as $Pc2_1n$ which is
polar whereas our coordinates fit the non-polar space
group $Pcmn$ with the Ta ions at symmetry centres and
the Na ions on mirror planes. Space group $Pc2_1n$
allows the Na ions to have a shift along [010] also and
it is this component which is responsible for the large
displacement (0·26 Å) of Na in the model of K & M.
According to our calculations the effect of this kind

Table 4. *Comparison of the atomic parameters of* $NaTaO_3$ *obtained by Kay & Miles* (1957) (*space group* $Pc2_1n$)
with single crystals and those in this work (*space group* $Pcmn$) *with a powder specimen*

The atomic parameters are based on the orthorhombic cell.

		This work			Kay & Miles (1957)		
		x	y	z	x	y	z
Ta	4(b)	0	0	0·5	0	0	0·5
Na	4(c)	0	0·25	−0·02 (1)	0·01	0·28	−0·02
O(1)	4(c)	0·054 (1)	0·25	0·5	0·02	0·26	0·48
O(2)	8(d)	0·275 (1)	−0·027 (1)	0·275	0·29	−0·03	0·29
O(3)					0·79	0·06	0·21

Table 5. *Bond lengths* (Å) *in* $NaTaO_3$ *calculated on the basis of the atomic parameters given in Table* 4

The number enclosed in square brackets indicates the number of symmetry-equivalent Na–O bonds.

	Kay & Miles (1957)	This work		Kay & Miles (1957)	This work
Ta–O1(a)	2·02	1·96	O1(a)–O2(a)	3·01	2·79
–O1(b)	1·87	1·96	–O2(b)	2·89	2·76
–O2(a)	1·99	1·97	–O3(a)	2·63	2·79
–O2(b)	1·98	1·97	–O3(b)	2·49	2·76
–O3(a)	2·02	1·97	O1(b)–O2(a)	2·98	2·76
–O3(b)	2·03	1·97	–O2(b)	3·09	2·79
Mean	1·98	1·96	–O3(b)	3·07	2·79
			O2(a)–O2(b)	2·78	2·76
Na–O(1) [2]	2·76	2·65	–O3(a)	2·88	2·80
–O(1) [2]	2·59	2·46	O3(b)–O2(b)	2·88	2·80
–O2(a)	2·84	2·72	–O3(a)	2·78	2·76
–O2(b)	3·33	3·09	Mean	2·87	2·78
–O2(c)	2·67	2·69			
–O2(d)	2·29	2·52			
–O3(a)	2·80	2·69			
–O3(b)	2·45	2·52			
–O3(c)	2·65	2·72			
–O3(d)	3·16	3·09			
Mean	2·74	2·69			

of shift is too small to be observed in the powder spectra, and, on the other hand, the reflexions with one odd index and two even indices (*e.g.* 230, 232) are consistent with having cations within any layer perpendicular to [010] displaced parallel to one another, but with the displacements in successive layers antiparallel. This arrangement is very common with the tilt system $a^-b^+a^-$ [*e.g.* CaTiO₃: Kay & Bailey (1957); Na$_{1-x}$K$_x$NbO₃ ($x<0.15$): Ahtee & Hewat (1975); SrZrO₃: Ahtee, Ahtee, Glazer & Hewat (1976)]. In accordance with the second assumption we therefore suggest that the Na atoms are displaced almost along c_0, the total displacement being 0.11 Å.

We also found that the tilt angles $\alpha = \gamma = 6.1$ (2) and $\beta = 5.8$ (2)° are clearly smaller than those calculated from the data of K & M, 10 and 9° respectively. The effect of the smaller tilt angles is most readily seen in Table 3 in the reduction of the theoretical intensities of 301, 321 and 232; 410 difference reflexions as compared with those calculated on the basis of the structure suggested by K & M. Darlington & Megaw (1973) suggested certain empirical generalizations applicable to most distorted perovskites, *e.g.* that the tilts are such as to provide an environment in which the A cation has nearly equidistant O neighbours holding it in position. In the model of K & M the Na–O distances vary from 2.29 to 3.33 Å, the average being 2.74 Å (Table 5). In our model the variation of Na–O distances is somewhat smaller, from 2.46 to 3.09 Å (average 2.69 Å). This is a consequence partly of smaller tilts, partly of a smaller Na displacement.

The regularity of the O octahedra has been frequently reported in these types of perovskites [*e.g.* CaTiO₃: Kay & Bailey (1957); NaNbO₃, phase *P*: Sakowski-Cowley, Łukaszewicz & Megaw (1969); NaNbO₃, phase *N*: Darlington & Megaw (1973); Na$_{1-x}$K$_x$NbO₃, phase *Q*: Ahtee & Hewat (1975)]. For example, in the room-temperature phase *P* of NaNbO₃ the octahedra are very regular even though the Nb atoms are displaced inside the octahedra; the mean of all twelve edges is 2.80 Å, with extreme values 2.76 and 2.83 Å. Therefore the irregularity of the octahedra in NaTaO₃ in the model of K & M seems rather conspicuous (average 2.83 Å with extreme values of 2.49 and 3.09 Å).

It can be concluded that information about a perovskite structure can be obtained by measuring the intensities of the difference reflexions caused by the deviations from the ideal cubic form from X-ray powder diffraction patterns. But to overcome the problem of overlapping reflexions we have made use of a number of simplifying assumptions. In order to obtain truly reliable results more accurate methods, *e.g.* neutron powder diffraction or single-crystal diffraction experiments, are needed.

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