The authors are indebted to Dr B.T.M.Willis for pointing out the simplified derivation which can be used for one-phonon X-ray scattering and for his interest and encouragement.

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The use of Neutron Resonance Scattering in the Structure Determination of $Sm(BrO_3)_3.9H_2O$

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The structure of $Sm(BrO_3)_3.9H_2O$ has been solved by the neutron anomalous-dispersion method, with the use of data collected at two wavelengths. Five out of eight atoms in the asymmetric unit were located from the 'anomalous difference Patterson' synthesis, and the remaining three from a Fourier synthesis. The structure is centrosymmetric, and the signs of 78% of the reflexions were determined correctly from the differences in the F_{obs} values at the two wavelengths.

1. Introduction

It has been known for some time that certain isotopes (especially ^{113}Cd and ^{149}Sm) when present in crystals, give rise to resonance scattering of thermal neutrons and this can be used to solve the phase problem in a structure analysis from neutron diffraction intensity data (Peterson & Smith, 1962; Ramaseshan, 1966; Dale & Willis, 1966). In the first reported application of this technique (Macdonald & Sikka, 1969), anomalous scattering from the Cd atom was utilized to solve the structure of $Cd(NO_3)_2.4D_2O$. Macdonald & Sikka showed that the 'direct phase' method of Ramachandran & Raman (1956) and the sine Patterson approach of Okaya, Saito & Pepinsky (1955) can be directly applied in neutron diffraction. These methods were devised originally for X-ray diffraction, where the intensities are measured at one wavelength. This paper is concerned with the third approach, that of the use of data at two wavelengths. Peterson & Smith (1962) pointed out that the real and imaginary parts of the scattering amplitude for ^{113}Cd and ^{149}Sm vary with the wavelength of the neutrons; the measurement of data at two different wavelengths would then correspond to the replacement of one atom of the crystal by an atom of different scattering amplitude. In this way the isomorphous replacement method can be used in neutron diffraction.

The substance chosen to test the suitability of the two wavelength method was $Sm(BrO_3)_3.9H_2O$. This choice was dictated largely by the need to obtain a large single crystal, suitable for a neutron study and containing Sm as the anomalous scatterer. From an experimental point of view, Sm is preferable to Cd as the anomalous scatterer since the range of wavelength, over which the real (b'_{Sm}) and imaginary (b''_{Sm}) parts of the scattering amplitude for the Sm atom vary, lies well within the experimentally useful region of the thermal neutron spectrum from a reactor. (For Sm, resonance occurs at 0·92 Å; for Cd it occurs at 0·67 Å and on the lower wavelength side of the Cd resonance the neutron flux is extremely low.) At the start of this study, it was thought that this crystal would be isomorphous with $Nd(BrO_3)_3.9H_2O$, whose X-ray structure is non-centrosymmetric (Helmholz, 1939). Later, as no Bijvoet differences could be observed from $Sm(BrO_3)_3.9H_2O$, it was realized that the crystal structure was centrosymmetric and belonged to a different space group, $P6_3/mmc$, in the hexagonal system.

2. Experimental

Single crystals of $Sm(BrO_3)_3.9H_2O$ were grown by slow evaporation of an aqueous solution of samarium bromate. The crystals were pink hexagonal prisms, bounded by {100} and {101} faces.

Three-dimensional neutron intensity measurements were made at two wavelengths with the Mark I auto-

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matic neutron diffractometer at the Harwell *PLUTO* reactor (Arndt & Willis, 1963). The choice of the first wavelength 1·27 Å was arbitrary; this wavelength was obtained by reflecting a neutron beam from the (200) face of a lead monochromator. The sample examined at 1·27 Å weighed 6 mg and was 2·5 mm long. It was mounted with the *c* axis along the axis of the goniometer head.

Initial values of the setting angles were calculated assuming the same cell constants as for $Nd(BrO_3)_3 . 9H_2O$ (Helmholz, 1939). The correct cell constants were later refined by the method of least-squares from observed 2θ angles: $a = 11\cdot86 \pm 0\cdot03$ and $c = 6\cdot76 \pm p\cdot02$ Å. Systematic absences were *hhl* with *l* odd, indicating one of the three space groups: $P6_3mc$, $P\bar{6}2c$ and $P6_3/mmc$. To determine which of these three was the correct space group we proceeded as follows.

Dale & Willis (1966) have shown that in a non-centrosymmetric crystal, when some atoms scatter the neutrons anomalously, the average value of the Bijvoet ratio $\Delta I/I$ is given by

$$\left\langle \frac{\Delta I}{I} \right\rangle \simeq \frac{8}{\pi} \frac{F_A''}{\sqrt{N}b_0} .$$

Here F_A'' is the structure factor resulting from the imaginary part of the scattering length of the anomalously scattering atom, N is the number of atoms in the unit cell and b_0 is the average scattering length of the atoms in the unit cell. Assuming that the Sm atom is at $\frac{1}{3},\frac{2}{3},\frac{1}{4}$ or $\frac{2}{3},\frac{1}{3},\frac{3}{4}$ (the position occupied by the Nd atom in $Nd(BrO_3)_3 . 9H_2O$) and that $b_{Sm}' = 0\cdot40 \times 10^{-12}$ cm [calculated from the Breit Wigner formula with parameters given by Brockhouse (1953)] we obtain $\langle \Delta I/I \rangle = 23\%$. Thus, if the space group is non-centrosymmetric, about half the reflexions should have $\Delta I/I > 23\%$. Table 1 lists the F_o^2 values for some pairs hkl and $\bar{h}\bar{k}\bar{l}$, together with the standard deviation $\sigma(F_o^2)$, derived from counting statistics. It can be seen that the F_o^2 values for hkl and $\bar{h}\bar{k}\bar{l}$ are in agreement with each other to within the expected statistical limits, which are much smaller than 23%. This rules out the space groups $P6_3mc$, $P\bar{6}2c$ and fixes the space group as $P6_3/mmc$.

Table 1. F_o^2 *values for some hkl and* $\bar{h}\bar{k}\bar{l}$ *pairs*

h	k	l	$F_o^2(hkl)$	$F_o^2(\bar{h}\bar{k}\bar{l})$	$\sigma(F_o^2)$
0	0	2	26·7	26·6	0·8
0	0	4	124·6	126·7	1·4
0	0	8	38·1	42·1	2·3
0	2	1	31·2	31·4	0·6
0	6	0	38·5	39·0	1·0
0	8	0	77·1	73·7	1·6
1	4	0	24·7	25·0	0·8
2	3	1	19·5	19·9	0·9
4	4	0	41·1	35·7	1·0
4	4	2	53·8	47·8	1·8
5	5	2	40·2	39·0	1·4

By use of the θ–2θ scan technique, neutron intensities for 320 independent reflexions up to $\theta = 50°$ were meas-

ured at $\lambda = 1\cdot27$ Å. For some reflexions, many different symmetry-related values were recorded. The intensities of 178 independent reflexions were greater than one standard deviation; the remainder were treated as unobservables.

From the curves given by Dale & Willis (1966) for the wavelength dependence of the real, b_{Sm}', and imaginary, b_{Sm}'', parts of the scattering factor, it was clear that the second wavelength at which the data was to be recorded must be on the other side of resonance (0·92 Å), preferably in the region of 0·75 Å. The actual choice (0·88 Å), was somewhat higher than this because
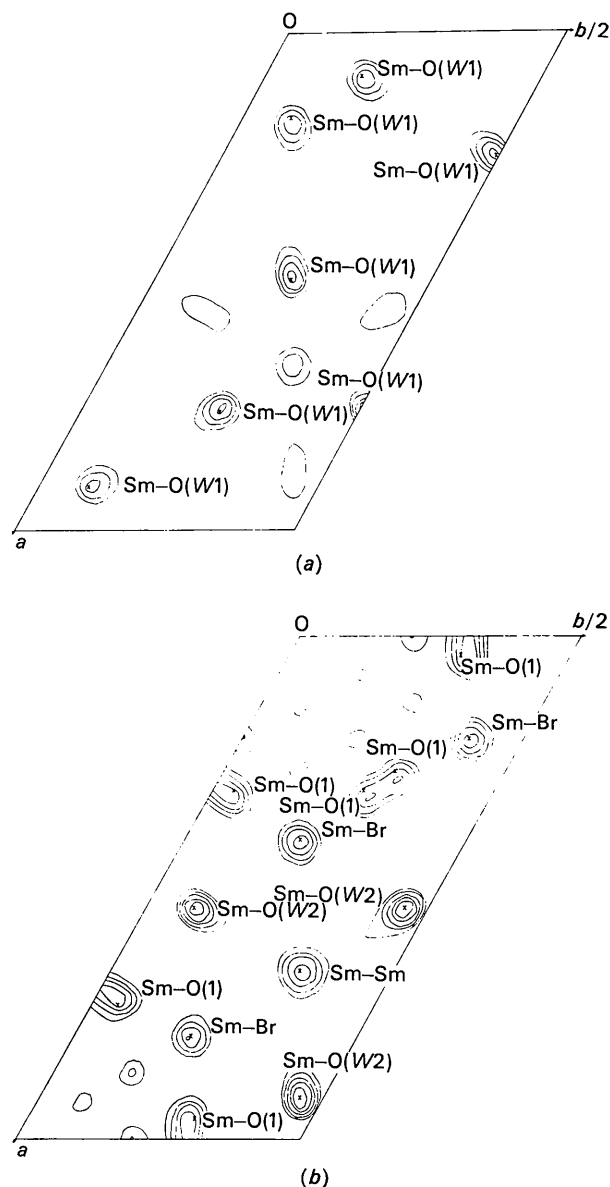

Fig. 1. Anomalous difference Patterson map (*a*) section $z = \frac{1}{4}$ and (*b*) section $z = \frac{1}{2}$. The contours are at equal arbitrary intervals. The negative, zero and first positive contours are omitted.

(a) the reactor flux falls off very sharply as the wavelength decreases below 1 Å,

(b) the reflectivity of both the monochromator and the sample decreases at lower wavelengths.

For the 220 reflexion of a standard KCl crystal, the number of counts per second at the peak position were 320, 80 and 6 at 1·27, 0·88 and 0·76 Å respectively (these wavelengths could be obtained by rotating the Pb monochromator about its [110] zone axis). Attempts to observe Bragg reflexions from the $Sm(BrO_3)_3.9H_2O$ crystal at 0·76 Å (absorption about the same as at 1·27 Å) by counting for much longer times did not yield positive results.

Unfortunately, the crystal examined at 1·27 Å was accidentally damaged before measurements could be continued at 0·88 Å. A new sample weighing 10 mg was mounted on the diffractometer, and the reflexions could be picked up at 0·88 Å, but were very weak. For this second crystal, the number of counts at the peak position of the 330 reflexion were 39 and 3 counts per second at 1·27 and 0·88 Å respectively. The intensities of 73 reflexions with $F_o^2/\sin 2\theta \geq 10$, were remeasured at 0·88 Å, with the use of the θ–2θ step scan method. The counting time at each 2θ step was ten times greater than the counting time at 1·27 Å.

The integrated intensities were corrected for absorption. The absorption coefficients both at 1·27 and 0·88 Å were experimentally determined by measuring the transmission of a monochromatic neutron beam (after reflexion by a UO_2 crystal) through a thin plate of $Sm(BrO_3)_3.9H_2O$. The measured values were 19·9 and 37·7 cm^{-1}. The dimensions of both specimens were measured and the absorption factors calculated with the program *ORABS* (Wehe, Busing & Levy, 1962). The range of absorption factors was 0·159 to 0·209 at 1·27 Å and 0·029 to 0·064 at 0·88 Å. The F_o^2 values were then derived in the usual manner. The relative accuracy of the two sets of data may be judged from the values of $\Sigma \sigma(F^2)/\Sigma F^2$, which were 0·107 and 0·055 for the 73 reflexions measured at 0·88 and 1·27 Å respectively.

3. Solution of the structure

The structure was solved by the anomalous difference Patterson technique (A.D.P.), described by Ramaseshan, Venkatesan & Mani (1957). In this technique a Patterson synthesis with coefficients $(|F(\lambda_1)|^2 - |F(\lambda_2)|^2)$ is calculated. This map then contains the vectors from the anomalous atom to the other atoms. The structure can be derived if the position of the anomalous atom is known. The various steps used are described below.

(a) Derivation of the common scale factor

This was done by comparing the F_o^2's of those reflexions for which the Sm contribution to F_o was zero and hence which should have the same F_o^2 values at the two wavelengths. Since there are two Sm atoms in the unit cell, these must occupy one of the twofold sets $2(a)$, $2(b)$, $2(c)$ and $2(d)$ of the space group $P6_3/mmc$. For the $2(a)$ and $2(b)$ positions the Sm contribution is zero for hkl when $l=2n+1$; and for $2(c)$ and $2(d)$ the contribution is zero when $h-k=3n$ and $l=2n+1$. The F_o^2 values of reflexions which satisfied both these conditions (033, 063, 065, 173, 251, 255, 281) were used to place the data at 1·27 and 0·88 Å on the same relative scale.

(b) Location of the Sm atom

If the Sm atoms lie at $2(a)$ or $2(b)$ positions, the vector peak $Sm_I - Sm_{II}$ should be at $0,0,\frac{1}{2}$ in the A.D.P.; if they are at $2(c)$ or $2(d)$, the vector peaks should be at $\frac{2}{3},\frac{1}{3},\frac{1}{2}$ and $\frac{1}{3},\frac{2}{3},\frac{1}{2}$. A section at $z=\frac{1}{2}$ of the A.D.P. computed from $(|F(0·88)|^2 - |F(1·27)|^2|$ is shown in Fig. 1(*b*). The peak height at $\frac{2}{3},\frac{1}{3},\frac{1}{2}$ was about 3 times that at $0,0,\frac{1}{2}$, thus fixing the position of the Sm atom as $2(c)$ or $2(d)$. The position $2(c)$ could now be chosen arbitrarily.

(c) Deconvolution of the A.D.P.

Knowing the position of the Sm atom, all the high vector peaks in the A.D.P. could be successfully assigned to various atomic vectors. Fig. 1(*a*) and (*b*)

Table 2. *Final positional and thermal parameters**

The least-squares standard deviations are given in parentheses. All parameters are multiplied by 10^4.

	$P6_3/mmc$ position	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Sm	2 (c)	3333	6666	2500	62 (30)	62 (30)	145 (43)	31 (30)	0	0
Br	6 (h)	1313 (5)	2626 (5)	7500	50 (9)	28 (11)	357 (42)	14 (11)	0	0
O(1)	12 (j)	680 (11)	3610 (11)	7500	59 (10)	75 (12)	210 (25)	35 (10)	0	0
O(2)	12 (k)†	943 (18)	1886 (18)	5515 (66)	90 (17)	212 (51)	812 (200)	106 (51)	−160 (84)	−320 (84)
O(W1)	12 (k)	4212 (5)	8424 (5)	4977 (19)	87 (13)	64 (10)	170 (23)	32 (10)	−15 (17)	−29 (17)
O(W2)	12 (h)	2092 (8)	4184 (8)	2500	38 (10)	44 (13)	292 (50)	22 (13)	0	0
H(1)	24 (l)	3744 (14)	5036 (13)	5636 (21)	57 (11)	56 (14)	228 (33)	−16 (12)	−18 (15)	14 (16)
H(2)	12 (j)	2498 (22)	−1188 (24)	2500	76 (21)	109 (29)	415 (71)	47 (20)	0	0

b'_{Sm} $(\lambda=1·27$ Å$)= -0·12$ (4)
b'_{Sm} $(\lambda=0·88$ Å$)= \ \ 0·59$ (8)

* The expression for the temperature factor is $T=\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$.
† Half atom at each position.

Table 3. Observed and calculated structure factors for $Sm(BrO_3)_3 . 9H_2O$

The neutron scattering factors used were: $b_{Sm} = -0.12 + 0.40i$ for F_1; $b_{Sm} = 0.59 + 90i$ for F_2; $b_{Br} = 0.67$; $b_O = 0.577$ and $b_H = -0.374$ ($\times 10^{-12}$ cm). The five columns in each set contain respectively k, l, $10F_1^2$, $10F_c^2$, $10F_2^2$, a and b, where $F_1 =$ observed structure factor at 1.27 Å, $F_c =$ calculated structure factor at 1.27 Å, $F_2 =$ observed structure factor at 0.88 Å, $a =$ final sign, $b =$ sign determined from differences in F_1 and F_2. The * indicates reflexions used for placing F_1 and F_2 on the same relative scale.

			h = 0			
0	2	300	386	476	–	–
0	4	1,418	1,587	1,915	+	+
0	6	67	48		+	
0	8	437	454	589	+	+
1	3	218	238	141	+	+
1	4	20	20		–	
1	5	27	21		+	
1	6	87	87		–	
2	0	102	111		–	
2	1	366	402	632	–	–
2	2	26	22		+	
2	3	171	160	314	+	+
2	4	20	6		–	
2	5	97	87	140	–	–
2	6	61	60		+	
3	1	71	81		–	
3	2	45	41	108	–	–
3	3*	216	273	217	+	
3	4	35	28		–	
3	6	93	92		–	
4	0	53	63		–	
4	1	166	210	67	–	–
4	2	29	24		+	
4	3	18	17		+	
4	4	88	83	174	–	–
4	5	65	89		–	
4	6	36	40		–	
5	0	129	121	123	+	+
5	1	166	166	224	–	–
5	2	240	226	323	+	–
5	3	17	20		+	
5	5	106	102	135	–	–
6	0	444	467	323	–	–
6	2	55	73	192	–	–
6	3*	408	379	418	–	
6	4	52	40		–	
6	5*	188	141	187	+	
7	0	318	355	289	+	+
7	1	17	7		+	
7	2	198	237	299	+	
7	4	79	86		+	
7	6	57	35		+	
8	0	850	977	1,067	–	–
8	1	120	115	245	–	–
8	2	124	110	70	–	–
8	3	141	151	271	+	+
8	4	57	61		–	
9	0	29	24		+	
9	1	78	107		+	
10	1	53	52		–	
12	2	170	185	106	+	+

			h = 1			
1	2	180	212		–	
1	4	11	11		–	
1	6	52	73		+	
2	1	115	133		–	
2	2	37	45	43	–	+
2	3	62	50	151	–	–
2	5	114	104	103	–	–
2	6	30	13		–	
3	1	102	117	75	+	+
3	2	82	61	118	+	+
3	3	155	147	92	–	–
3	4	132	125	180	+	–
3	5	42	34		+	
3	6	138	139	152	+	
4	0	280	295	253	–	–
4	2	52	47		–	
4	3	11	19		–	
4	4	40	39		–	
5	1	48	14		+	
5	2	23	6		+	
5	3	73	68	86	+	–
5	4	31	8		+	
6	1	34	30		+	
6	2	119	113	138	–	+
6	5	28	23		+	
7	1	33	26		–	
7	2	166	173	244	–	–
7	3*	244	245	208	+	
7	6	76	56		+	
8	0	196	209	146	+	+
8	1	31	17		+	
8	2	54	72		+	
8	3	133	105		+	
8	4	78	65	40	+	+
10	0	31	32		+	
10	1	129	168		–	
10	2	109	108		+	
10	3	38	43		+	

			h = 2			
2	4	47	40		–	
2	6	51	35		+	
3	1	221	254	400	+	+
3	2	65	58	115	–	–
3	3	209	225	333	–	–
3	5	103	80	198	–	
4	0	216	236	164	+	+
4	2	17	15		–	
4	4	27	34		–	
5	0	21	12		–	
5	1*	253	301	279	–	
5	2	183	218	154	+	+
5	4	22	2		–	
5	5*	112	135	115	–	
5	6	25	37		–	
6	0	8	3		–	
6	1	71	70	131	–	+
6	2	24	32		+	
6	3	84	87	105	+	–
7	1	55	47		+	
7	2	53	50		+	
7	4	38	20		+	
8	1*	140	138	146	+	–
8	2	43	46		–	
8	3	53	65		–	
9	0	104	93	128	–	–
9	1	26	25		+	
9	4	30	43		+	
10	0	84	53		+	
10	3	25	1		+	
11	0	142	166	229	+	+

			h = 3			
3	0	1,240	1,224	1,825	+	+
3	2	19	24		+	
3	4	468	396	709	+	+
4	0	133	142	207	–	–
4	1	40	41		+	
4	2	19	14		+	
4	3	43	41		+	
4	4	57	53		+	
5	0	126	103	165	–	–
5	2	165	166	261	+	+
5	3	102	113	213	+	+
5	4	194	220	270	–	–
5	5	45	11		+	
5	6	41	1		+	
6	0	108	123		–	
6	1	23	11		–	
6	2	121	135	71	+	+
6	3	49	66		+	
6	4	71	77		+	
7	0	288	261	360	–	–
7	1	43	40		+	
7	4	98	67		+	
8	0	196	200	152	+	+
8	2	57	60		+	
8	4	86	64		+	
9	0	97	97	84	–	–
9	3	85	48		+	
10	1	72	53		+	
10	2	43	26		–	

			h = 4			
4	0	444	569	766	+	+
4	2	573	584	391	+	+
4	4	54	60		+	
4	6	31	39		+	
5	2	483	504	488	+	
5	4	19	27		+	
5	6	42	46		+	
6	2	92	102	171	+	+
7	0	252	187	110	–	–
7	2	58	55		–	
7	3	36	7		–	
7	4	41	31		–	
8	1	21	24		–	
8	2	66	58		–	
8	4	9	1		+	

			h = 5			
5	0	455	620	668	+	+
5	2	447	319	643	–	–
5	4	189	151	332	+	+
7	0	48	32		–	
8	1	48	70		–	
8	2	48	18		–	
8	3	92	98		+	
9	1	93	60		+	

			h = 6			
7	2	36	10		+	
7	3	26	9		–	
8	0	38	42		–	
8	1	38	13		–	

			h = 7			
7	0	30	29		+	

shows two sections at $z = \frac{1}{4}$ and $z = \frac{1}{2}$ where all these peaks were situated. These maps are almost free of spurious peaks. This analysis yielded the position of 5 out of 8 atoms in the asymmetric unit. These were identified as Sm, the water oxygen atoms $O(W1)$, $O(W2)$, Br and $O(1)$ atoms.

An F_o Fourier synthesis with data at 1.27 Å and signs calculated from the above 5 atoms showed the two hydrogen atom positions. In addition, in the asymmetric unit, two peaks with height roughly equal to $\frac{1}{4}$ that of $O(1)$ and related by a mirror plane at $z = \frac{1}{4}$ were found at a distance of 1.6 Å from the Br atom. These were assigned to the atom $O(2)$ in position $12(j)$ with an occupancy of one half. This meant that the BrO_3 group in the structure was disordered.

4. Refinement

The structural parameters obtained in § 3 were refined by the method of least-squares with the use of the program $XFLS$ (Busing, Martin & Levy, 1962). The refinement was carried out with F_o^2's measured at 1.27 Å and with a weighting scheme

$$\omega^{-1/2} = \sigma(F_o^2) + 0.02F_o^2,$$

where the standard deviations $\sigma(F_o^2)$ were derived from counting statistics alone. For the Sm atom, in the isotropic refinement only the real term of the scattering factor was included and refined. This converged at an R value $(= \Sigma ||F_o| - |F_c|| / \Sigma ||F_o||)$ of 0.147. On anisotropic refinement, in which the imaginary part of the scattering factor for the Sm atom was also included but kept fixed, the R value dropped to 0.069. However, the β_{11} value for the Sm atom was negative. At this stage 32 strong reflexions with $F_o^2/\sin 2\theta \geq 25$ were omitted from the refinement, as they were considered to be affected by extinction. Even then, the β_{11} of the Sm atom remained negative, indicating that there were still some systematic errors in the data. Consequently in the final refinement, the temperature parameters of the Sm atom were constrained to the isotropic value. This gave an R value of 0.098.

A satisfactory anisotropic refinement of the structural parameters with the F_o^2 data at 0.88 Å could not be completed as the ratio m/n ($m =$ number of reflexions and $n =$ number of variable parameters) was low and the data were affected by extinction. The R value after the isotropic refinement was 0.099.

The final positional and thermal parameters from the 1.27 Å data are presented in Table 2. A comparison of the final F_o^2 and F_c^2 is included in Table 3.

Discussion

Determination of signs from the anomalous data

Ramaseshan *et al.* (1957) have shown that the signs of the structure factors of centrosymmetric crystals can be found satisfactorily by the anomalous dispersion technique in the X-ray case. To test this technique for

neutron diffraction, the signs were derived directly from the observed differences in the values of F_o. If we denote by F_1 and F_2 the structure factors at 1·27 and 0·88 Å, then it can be easily shown that

$$F_2 - F_1 = (\varDelta b' + i\varDelta b'') \sum_A \cos 2\pi(hx_A + ky_A + lz_A) \quad . (1)$$

Here $\varDelta b'$ and $\varDelta b''$ are the changes in the real and imaginary parts of the scattering factor for the anomalous atom, A, located at (x_A, y_A, z_A). If we consider structure factors of large magnitude only, we can see that the change in intensity produced by $\varDelta b'$ will be much larger than that of $\varDelta b''$ and, further, the departure of the phase from 0 or π for large structure factors, as caused by $\varDelta b''$, will be small. Under these assumptions, (1) can be approximated to

$$F_2 - F_1 = \varDelta b' \sum_A \cos 2\pi(hx_A + by_A + lz_A) \quad . (2)$$

Since the coordinates of the Sm atoms are known, the geometric part of (2) could be computed and the signs of F_1 and F_2 fixed by inspection. These signs are also listed in Table 3. Comparison with the final signs (signs of the real part of F_c) shows that for 78% of the reflexions recorded at 0·88 Å, the signs were correct.

The above analysis shows that if the intensities are recorded at two wavelengths, the structure can be determined in a straightforward manner by the two-wavelength method used in X-rays.

Description of the structure

A projection of the structure on the (001) plane is shown in Fig.2 and some important bond distances and angles are given in Table 4. The structure consists of columns of $Sm(OH_2)_9^{3+}$ and BrO_3^-. The $Sm(OH_2)_9^{3+}$ columns pass through the positions $\frac{1}{3},\frac{2}{3},0$ and $\frac{2}{3},\frac{1}{3},0$ and the BrO_3^- groups are packed about the origin of the unit cell, leading to infinite columns about the 6_3 axis. The two groups, $Sm(OH_2)_9^{3+}$ and BrO_3^-, are linked together by hydrogen bonds from the water molecules to the O(1) atom of the bromate group. This coordination is similar to that found by Helmholz (1939) in $Nd(BrO_3)_3.9H_2O$. The difference between the two structures lies in the point symmetry at the rare-earth ion, which is D_{3h} in $Sm(BrO_3)_3.9H_2O$ and C_{3v} in $Nd(BrO_3)_3.9H_2O$.

The six water-oxygen atoms O(W1), are arranged above and below the Sm^{3+} ion at the six corners of a triangular prism. The water-oxygen atoms O(W2), are on lines passing through the centre of the vertical faces of the O(W1) prism, in the same plane as the Sm^{3+} ion, but at a greater distance (Sm–O(W1)=2·46±0·01 and Sm–O(W2)=2·55±0·01 Å).

The shape of the bromate group is pyramidal with the Br atom at the apex. The atoms Br and O(1) lie in the mirror planes $z= \pm\frac{1}{4}$ and the atom O(2) can then position itself either above or below these planes, thus giving rise to disorder. The present analysis is of moderate accuracy and so does not rule out other models of the disordered bromate groups in the structure. The dimensions of the BrO_3^- group are in close agreement with those found in $HgBrO_3$ (Dorm, 1967).

Both water molecules donate their hydrogen atoms to the O(1) atom of the bromate group. Each O(1) acts as an acceptor of three hydrogen bonds. The lengths of the hydrogen bonds are 2·82±0·02 and 2·85±0·02 Å. The O–H distances are 0·90 and 0·93 Å and HOH angles are 107·3 and 113·9° (uncorrected for thermal motion), which appear to be normal. All the hydrogen bonds in the structure are bent. The lone pair coordi-

Table 4. *Interatomic distances* (Å) *and bond angles* (°), *uncorrected for thermal motion**

Sm—O(W1)	2·46 (1)		
Sm—O(W2)	2·55 (1)		
Br —O(1)	1·67 (2)	O(1) –Br —O(1)^I	105·7 (0·7)
Br —O(2)	1·54 (4)	O(1) –Br —O(2)	107·3 (1·3)
O(1)–O(1)^I	2·67 (2)	O(1)^I–O(1)–O(2)	59·0 (0·9)
O(1)–O(2)	2·59 (3)	O(1) –O(2)–O(1)^I	62·0 (0·9)

Water molecules and hydrogen bonds

O(W1)–H(1)^{II}	0·90 (2)	H(1)^{II} –O(W1)–H(1)^{IV}	107·3 (1·8)
H(1)^{II} –O(1)^{III}	1·94 (2)	O(1)^{III}–O(W1)–O(1)^{VIII}	93·3 (0·5)
O(W1)–O(1)^{III}	2·82 (2)	O(W1)–H(1)^{III}–O(1)^{III}	168·8 (1·7)
H(1)^{II} –H(1)^{IV}	1·45 (3)	Sm——O(1)——H(1)^{II}	125·1 (1·2)
O(W2)–H(2)^V	0·93 (3)	H(2)^V –O(W2)–H(2)^{VII}	113·4 (3·0)
H(2)^V –O(1)^{VI}	1·93 (4)	O(1)^{VI}–O(W2)–O(1)^{IX}	126·3 (0·5)
O(W2)–O(1)^{VI}	2·85 (2)	O(W2)–H(2)——O(1)^{IX}	170·4 (3·3)
H(2)^V –H(2)^{VII}	1·55 (4)	Sm——O(W2)–H(2)^V	123·3 (2·2)

* The errors given in parentheses have been calculated from the standard deviations of the coordinates given in Table 2 and do not include standard deviations of the unit-cell constants.
† Code for symmetry related atoms:

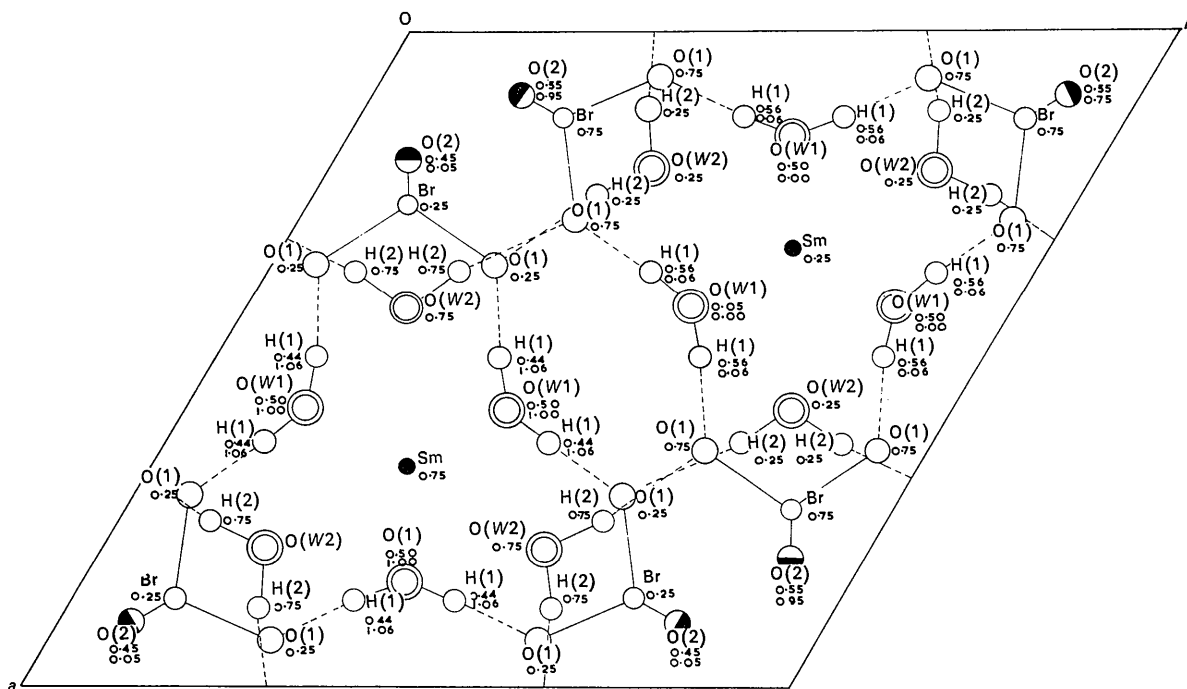|	x	y	z			x	$x-y$	z
–	x	y	z	V		x	$x-y$	z
I	$y-x$	y	z	VI		y	$y-x$	$z-\frac{1}{2}$
II	x	$1+x-y$	z	VII		$-y$	$x-y$	z
III	$y-x$	$1-x$	z	VIII	$1-y$	$1-x$	z
IV	$1-y$	$1+x-y$	z	IX		$-x$	$y-x$	$z-\frac{1}{2}$

Fig. 2. Projection of the structure of $Sm(BrO_3)_3.9H_2O$ along the c axis. The decimal fractions indicate fractional z coordinate of each atom.

nation of both the water molecules with the Sm^{3+} ion is planar trigonal and falls under type D of the classification given by Chidambaram, Sequeira & Sikka (1964).

The author expresses his thanks to Dr B. T. M. Willis for his support and interest in this work. Thanks are due to Dr A. C. Macdonald for many discussions, and also to Mr T. M. Valentine and Mr J. Hitchcock for some experimental assistance.

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