

The main feature of difference between the discrete groups in this structure and those of the corresponding hydrated chloride (Penfold & Grigor, 1959) is the equivalence of all water molecules in the fluoride, making individual groups much more closely octahedral. This is likely to be a consequence partly of the greater ionic character of the bonds in the fluoride, and also of the much greater similarity in size of fluoride ion (radius 1.35 Å) and oxygen atom (1.4 Å), as compared with chloride ion (1.8 Å) and oxygen atom.

### 5. The structure of form B

The diffraction symmetry of form B is  $\bar{3}m$ , indicating that, provided there is a center of symmetry as in A, the space group is  $R\bar{3}m$ . The intensity distribution of  $hki0$  and  $hki2$  reflections is similar but not identical to the distribution in  $hki0$  and  $hki1$  reflections of form A. It appears, therefore, that the major difference between the two forms concerns the nature of the P, Q sequence, discussed above for form A. The only quantitative intensity data at present available for form B are from Cu  $K\alpha$  radiation for  $hki0$  and  $hki1$  reflections, and a detailed examination of this slightly less disordered form must await the accumulation of more data.

The final refinement of this structure was completed by one of us (B. R. P.) at the University of Minnesota during an appointment supported by the International Cooperation Administration under the Visiting Re-

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### References

- BAUR, W. H. (1958). *Acta Cryst.* **11**, 488.  
 BERGHUIS, J., HAANAPPEL, IJ. M., POTTERS, M., LOOPSTRA, B. O., MACGILLAVRY, C. H. & VEENENDAAL, A. L. (1955). *Acta Cryst.* **8**, 478.  
 BILLY, C. & HAENDLER, H. M. (1957). *J. Amer. Chem. Soc.* **79**, 1049.  
 BILTZ, W. & RAHLFS, E. (1927). *Z. Anorg. Chem.* **166**, 351.  
 FERRARI, A., CELERI, A. & GIORGIO, F. (1929). *R. C. Accad. Lincei*, **9**, 782.  
 GELLER, S. & BOND, W. L. (1958). *J. Chem. Phys.* **29**, 925.  
 HANAWALT, J. D., RINN, H. W. & FREVEL, L. K. (1938). *Industr. Engng. Chem. (Anal.)* **10**, 457.  
 PAULING, L. (1940). *The Nature of the Chemical Bond*. Ithaca: Cornell University Press.  
 PENFOLD, B. R. & GRIGOR, J. A. (1959). *Acta Cryst.* **12**, 850.  
 PETERSEN, S. W. & LEVY, H. A. (1957). *J. Chem. Phys.* **26**, 220.  
 POULENC, C. (1894). *Ann. Chim. Phys.* (7), **2**, 5.  
 ROSSMANN, M. G., JACOBSON, R. A., HIRSHFELD, F. L. & LIPSCOMB, W. N. (1959). *Acta Cryst.* **12**, 530.  
 THOMAS, L. & UMEDA, K. (1957). *J. Chem. Phys.* **26**, 298.  
 WELLS, A. F. (1947). *J. Chem. Soc.* p. 1670.

## Short Communications

*Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 1000 words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible; and proofs will not generally be submitted to authors. Publication will be quicker if the contributions are without illustrations.*

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### The perovskite-type structures of $\text{DyAlO}_3$ , $\text{DyFeO}_3$ , and some related lanthanon mixed oxides.

By J. A. W. DALZIEL and A. J. E. WELCH, *Inorganic Chemistry Research Laboratories, Imperial College, London, S. W. 7, England*

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#### 1. Introduction

The perovskite-type structures of selected lanthanon mixed oxides ( $\text{LnBO}_3$ ) have been investigated in an attempt to elucidate the factors that influence their distortion. Lanthanum, neodymium, gadolinium and dysprosium, which have a suitable range of ionic radii, were chosen for the tripositive Ln ions. Aluminium, iron and gallium, which have tripositive ions with an inert-gas, half-filled *d*-shell and eighteen-electron configuration, respectively, were chosen as B ions that would demonstrate the influence of partial covalent character of B-O linkages on the distortion. The definitive work of

Geller and his colleagues (Geller, 1956; Geller & Wood, 1956; Geller & Bala, 1956; Gilleo, 1957; Geller, 1957) on crystals of many  $\text{LnBO}_3$  perovskites has already been reported. In this note, therefore, brief reference only is made to the X-ray powder studies by which, as far as possible, these data were confirmed. The orthorhombic structures of  $\text{DyAlO}_3$  and  $\text{DyFeO}_3$ , which have not been reported before, are described in more detail.

#### 2. Experimental

Hundred-milligram quantities of the lanthanon mixed oxides were prepared from 'Specpure' grade materials

Table 1. *Line-splitting produced by trigonal and orthorhombic distortion of the perovskite lattice*

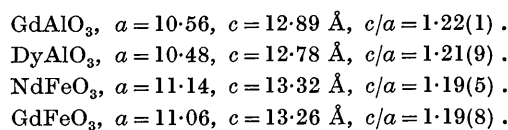
Cubic ( $Z=1$ )	Trigonal ( $Z=3$ ) when $c/a \leq 3/2$		Orthorhombic ( $Z=4$ ) when $c^2/ab \leq 2$	
100 becomes	101	singlet	110 002	two lines, outer line weaker
110 becomes	110 102 111	three lines, outer line probably weak	020 112 200	three lines, two of equal intensity
111 becomes	201 003 112	three lines of unequal intensity	022 202	two lines of equal intensity
200 becomes	202 210	two lines of un- equal intensity	220 004	two lines, outer line weaker
210 becomes	211 113	two lines of equal intensity	310/130 222/114	two pairs of equi- intensity lines
211 becomes	300 212 104	three lines of nearly equal intensity	312/132 204/024	two pairs of equi- intensity lines

(Johnson, Matthey and Co., Ltd.). The starting materials were made into standardised nitrate solutions, and calculated volumes delivered into platinum dishes. The mixed nitrate solutions were evaporated to dryness and then decomposed to the oxides by ignition for one hour at 1100 °C. Powder photographs showed that the perovskite phases were already predominant at this stage. To complete the solid-state reactions the pelleted samples were heated for twenty hours at 1450 °C. in air. X-ray powder photographs were taken in calibrated 19-cm. cameras (Unicam Instruments Ltd.) using cobalt radiation filtered through iron foil. Later, in order to study low-angle line splitting in more detail, powder photographs were taken in a Nonius Guinier-type camera (De Wolff, 1948).

### 3. Results

Complete reactions to perovskite-type oxides were obtained in all cases except  $Gd_2O_3 + Ga_2O_3$  and  $Dy_2O_3 + Ga_2O_3$ . In these two cases no perovskite phases could be detected but many lines of the complex powder patterns were indexed on the basis of cubic, probably garnet-type, phases, in agreement with the findings of Keith & Roy (1954).

In the cases where perovskite-type oxides were obtained it was evident that distortion increased with the lanthanide contraction in each of the series  $LnAlO_3$ ,  $LnFeO_3$  and  $LnGaO_3$ . These patterns were indexed with the aid of line-splitting data (Megaw, 1946) extended to include trigonal and orthorhombic distortion of the perovskite lattice (Table 1). The structures of cubic  $LaAlO_3$  (3.792 Å) and rhombohedral  $NdAlO_3$  (3.751 Å,  $\alpha = 90.31^\circ$ ) and  $LaGaO_3$  (3.895 Å,  $\alpha = 90.28^\circ$ ) were found from 19-cm. photographs in this way. The extra lines from which Geller has deduced that the rhombohedral lattices contain two formula weights per unit cell ( $Z=2$ ) were observed as very weak lines only in the case of  $LaGaO_3$ . The 19-cm. patterns of  $LaFeO_3$  were indexed on the basis of a large cubic pseudo-cell (7.855 Å). It was more difficult, from 19-cm. data alone, to decide with certainty between hexagonal and orthorhombic distortion for the other structures. At first apparently satisfactory results were obtained by using hexagonal parameters, thus:

Table 2. *Orthorhombic indices of  $DyAlO_3$  and  $DyFeO_3$* 

$I/I_{10}$	$DyAlO_3$ $\sin^2 \theta \times 10^4$		$hkl$	$DyFeO_3$ $\sin^2 \theta \times 10^4$		$I/I_{10}$
	(obs.)	(calc.)		(calc.)	(obs.)	
4	0582	0579	110	0540	0541	3
		0584	002	0551		
1	0726	0725	111	0678	0676	2
$\frac{1}{2}$	0864	0868	012	0835	0843	$\frac{1}{2}$
		0879	102			
$\frac{1}{2}$	0934	—	—			
			020	1023	1022	2
10	1167	1163	112	1091	1090	10
			200	1138	1137	2
1	1283	1282	021	1161	1157	2
$\frac{1}{2}$	1612	1608	211	1532	1528	1
		1609	103	1524		
2	1722	1720	022	1574	1574	1
2	1769	1762	202	1689	1687	2
$\frac{1}{2}$	1898	1893	113	1780	1777	2
			122	1858	1858	$\frac{1}{2}$
			212	1945	1946	$\frac{1}{2}$
5	2329	2314	220	2161	2158	4
		2337	004	2204	2202	4
			023	2263	2264	2
3	2463	2460	221	2299	2296	4
			213	2634	2638	$\frac{1}{2}$
2	2920	2916	114			
2	2997	2997	131	2724	2725	7
			310	2816	2815	1
$\frac{1}{2}$	3088	3081	311	2954	2954	2
1	3443	3435	132	3137	3138	4
			024	3227	3225	4
6	3529	3519	312	3367	3365	7
$\frac{1}{2}$	3631	3628	223			

Table 2 (cont.)

$I/I_{10}$	DyAlO <sub>3</sub>		$hkl$	DyFeO <sub>3</sub>		$I/I_{10}$
	(obs.)	(calc.)		(calc.)	(obs.)	
1	4168	4165	133	3826	3825	4
			115	3983	3981	$\frac{1}{2}$
			041	4230	4229	2
2	4657	4651	224	4365	4365	4
			025	4466	4465	$\frac{1}{2}$
			400	4551	4552	1
1	5285	5272	314	5020		
1	5362	5253	331	5000	5011	4
3	5867	5869	241	5368	5362	3
			116	5498	5500	4
			225	5604	5603	2
1	5987	5995	421	5712	5711	1
			324	5787		
			403	5791	5794	$\frac{1}{2}$
			135	6029	6030	
$\frac{1}{2}$	6438	6433	422			
		6436	206			
1	6525	6521	333	6102	6108	4
			126	6265	6268	$\frac{1}{2}$
			243	6470	6476	5
			150	6678	6679	$\frac{1}{2}$
$\frac{1}{2}$	6889	6882	044			
2	7050	7050	404	6755	6756	$\frac{1}{2}$
$\frac{1}{2}$	7175	7177	144			
3	7554	7542	151	6816	6822	4
		7572	226	7119	7128	$\frac{1}{2}$
$\frac{1}{2}$	7664	7648	510			
		7685	052			
6	8016	8019	136	7544	7546	3
$\frac{1}{2}$	8053	8060	244			
6	8198	8193	316			
		8196	045			
			424	7778		
			145	7819	7791	8
$\frac{1}{2}$	8235	8232	512	7918		
3	8707	8710	153	7918	7926	8
1	8875	8863	252			
			335	8305	8313	3
5	9364	9374	245	8673	8678	3
			154	8882	8881	3
			227	8910	8917	3
			425	9017	9029	2
5	9403	9404	441			
2	9887	9898	351	9092	9095	2
			137	9335		
			061	9345	9341	6
			443	9883	9890	3

Eventually the true orthorhombic structures reported by Geller for these compounds, and NdGaO<sub>3</sub>, were confirmed with the aid of Guinier powder photographs. These showed sufficient resolution for the low-angle line splitting, particularly of the 100 lines, to be seen. The patterns of LaAlO<sub>3</sub> and LaGaO<sub>3</sub> were those of cubic and rhombohedral perovskite-type lattices, respectively, and therefore, according to Geller, were the metastable high-temperature modifications of the compounds. No evidence of phase changes was obtained from the patterns of specimens of LaAlO<sub>3</sub> and LaFeO<sub>3</sub> which had been annealed for several hours below the transition temperatures reported by Geller.

The Guinier photographs of DyAlO<sub>3</sub> and DyFeO<sub>3</sub> showed that they were nearly isomorphous with other orthorhombic perovskites. The parameters were calculated to be:

$$\text{DyAlO}_3, a = 5.21(5), b = 5.31(1), c = 7.40(7) \text{ \AA}.$$

$$\text{DyFeO}_3, a = 5.30(4), b = 5.60(0), c = 7.62(1) \text{ \AA}.$$

The estimated error was less than  $\pm 0.01 \text{ \AA}$ . In Table 2 the observed values of  $\sin^2 \theta$ , from duplicate 19-cm. powder photographs, are compared with those calculated from these parameters. The approximate intensities, estimated visually with respect to the strongest line, are also given. Each pattern contained a weak line which must be either a 102 or an 012 reflection. These reflections are forbidden for the space group *Pbnm*,  $Z=4$ . In the pattern of DyAlO<sub>3</sub>, a weak line appeared at  $\sin^2 \theta = 0.0934$  which could not be indexed, and a similar line at  $\sin^2 \theta = 0.0923$  appeared in the pattern of GdAlO<sub>3</sub>.

The physical significance of the distortion of *LnBO*<sub>3</sub> perovskite-type lattices has been discussed elsewhere (Dalziel, 1959).

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#### References

- DALZIEL, J. A. W. (1959). *J. Chem. Soc.* p. 1993.  
 GELLER, S. (1956). *J. Chem. Phys.* **24**, 1236.  
 GELLER, S. (1957). *Acta Cryst.* **10**, 243.  
 GELLER, S. & BALA, V. B. (1956). *Acta Cryst.* **9**, 1019.  
 GELLER, S. & WOOD, E. A. (1956). *Acta Cryst.* **9**, 563.  
 GILLES, M. A. (1957). *Acta Cryst.* **10**, 161.  
 KEITH, M. L. & ROY, R. (1954). *Amer. Min.* **39**, 1.  
 MEGAW, H. D. (1946). *Proc. Phys. Soc.* **58**, 133.  
 WOLFF, P. M. DE (1948). *Acta Cryst.* **1**, 207.