pseudosymmetry in the electron density distribution, was also solved without any human intervention after four cycles, taking 9·3 hr.

The seven organic compounds which were solved by this program contain up to 60 atoms in one asymmetric unit. The use of this program will become more convenient by the advent of machines (CDC 6600) with computing times in the nanosecond range. A more detailed description of the method will be published elsewhere.

We thank Professors Y. Okaya, Y. Iitaka and T. Ashida, and Dr T. Sakurai for their computer programs.

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Cell dimensions of rare earth orthorhodites. By R. D. SHANNON, *Central Research Department, E.I. du Pont de Nemours & Company, Experimental Station, Wilmington, Delaware* 19898, *U.S.A.*

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The cell dimensions of the perovskites, $MRhO_3$ (M = Lu, Tm, Er, Ho, Dy, Tb, Gd, Eu, Sm, Nd and Pr), have been determined from X-ray data.

Marezio, Remeika & Dernier (1968) and Eibschütz (1965) have recently shown for the rare earth orthogallates and orthoferrites, respectively, the variation in cell dimensions as a function of atomic number of the rare earth ion. The *a* and *c* parameters decrease smoothly with atomic number whereas the *b* parameter goes through a maximum at Gd.

Table 1. *Cell dimensions of the perovskites* $MRhO_3$

Compound	*a*	*b*	*c*	*V*
$LuRhO_3$	5·1861 ± 2 Å	5·6700 ± 2 Å	7·5125 ± 3 Å	220·9 Å^3
$TmRhO_3$	5·2028 ± 5	5·6974 ± 5	7·5428 ± 8	223·6
$ErRhO_3$	5·2160 ± 2	5·7117 ± 2	7·5610 ± 4	225·3
$HoRhO_3$	5·2299 ± 4	5·7257 ± 5	7·5823 ± 7	227·0
$DyRhO_3$	5·2449 ± 4	5·7314 ± 5	7·6002 ± 7	228·5
$TbRhO_3$	5·2541 ± 4	5·7492 ± 4	7·6226 ± 6	230·3
$GdRhO_3$	5·2774 ± 4	5·7605 ± 4	7·6584 ± 5	232·8
$EuRhO_3$	5·2985 ± 6	5·7607 ± 6	7·6802 ± 8	234·4
$SmRhO_3$	5·3211 ± 3	5·7613 ± 3	7·7083 ± 4	236·3
$NdRhO_3$	5·3778 ± 6	5·7551 ± 6	7·7745 ± 9	240·6
$PrRhO_3$	5·4143 ± 2	5·7473 ± 2	7·8026 ± 3	242·8

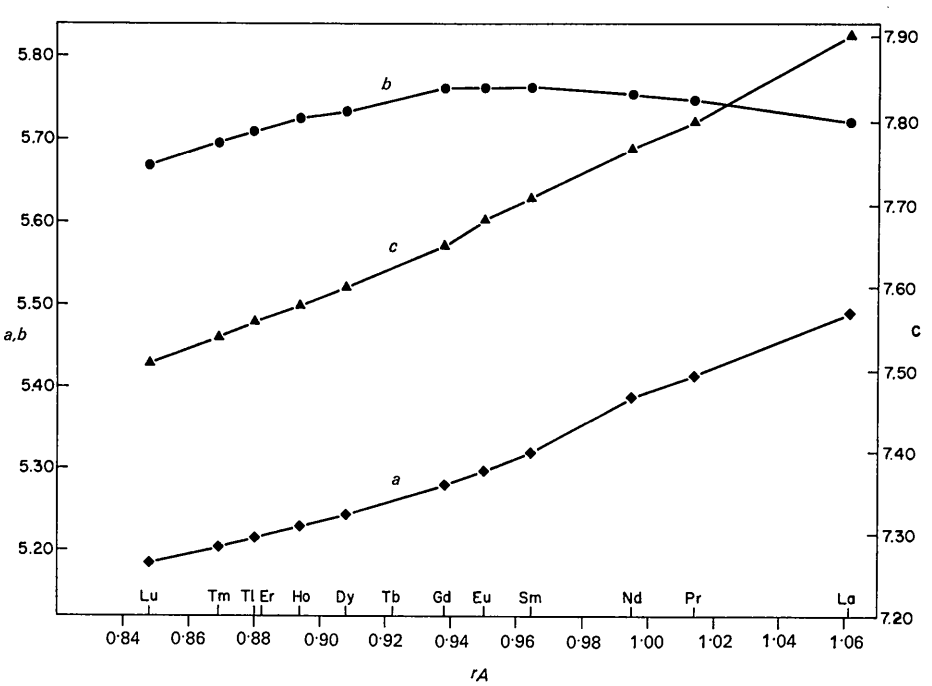

Fig. 1. Cell dimension of $MRhO_3$ perovskites *vs.* the effective ionic radius of M^{3+}.

Chazalon, Bertaut & Duc (1964) reported unrefined cell dimensions for six rare earth orthorhodites, but because the estimated error limits were ±0·01 Å, they were not able to determine the variation in *b* parameter with atomic number of the rare earth ion. In this study we have accurately measured the cell dimensions of the perovskites $MRhO_3$ where M = Lu, Tm, Er, Ho, Dy, Tb, Gd, Eu, Sm, Nd, and Pr, and find behavior similar to that of the

Table 2. *Crystallographic data for the perovskites $MRhO_3$*

	$LuRhO_3$			$TmRhO_3$			$ErRhO_3$			$HoRhO_3$			$DyRhO_3$			$TbRhO_3$		
hkl	d_{obs}	d_{calc}	I_{obs}	d_{obs}	d_{calc}	I_{obs}	d_{obs}	d_{calc}	I_{obs}	d_{obs}	d_{calc}	I_{obs}	d_{obs}	d_{calc}	I_{obs}	d_{obs}	d_{calc}	I_{obs}
101	4.268	4.268	10	4.282	4.283	15	4.293	4.293	20	4.301	4.305	15	4.316	4.317	15	4.327	4.326	15
110	3.826	3.827	5	3.840	3.842	2				3.858	3.861	5	3.872	3.869	5	3.881	3.878	2
002	3.756	3.756	10	3.771	3.771	8	3.779	3.780	10				3.803	3.800	5	3.812	3.811	5
111	3.411	3.410	70	3.423	3.423	50	3.432	3.432	60	3.439	3.441	85	3.448	3.448	80	3.457	3.457	85
020	2.835	2.835	65	2.848	2.849	50	2.855	2.856	60	2.861	2.863	90	2.866	2.866	85	2.874	2.875	85
112	2.681	2.681	100	2.692	2.691	100	2.698	2.698	100	2.705	2.705	100	2.712	2.711	100	2.720	2.718	100
021	2.652	2.652	60	2.664	2.665	45	2.671	2.672	65	2.677	2.678	70	2.682	2.681	70	2.690	2.690	70
200	2.593	2.593	80	2.602	2.601	35	2.608	2.608	70	2.614	2.615	90	2.623	2.622	90	2.627	2.627	95
211	2.250	2.250	30	2.258	2.258	30	2.263	2.264	47	2.269	2.270	50	2.275	2.275	40	2.280	2.280	35
202	2.134	2.134	5	2.142	2.141	5	2.146	2.147	10	2.155	2.153	2	2.158	2.158	5	2.163	2.163	10
113	2.095	2.095	40	2.104	2.104	40	2.109	2.109	50	2.114	2.115	60	2.119	2.119	55	2.126	2.125	50
122	2.074	2.074	10	2.083	2.083	15	2.088	2.088	25	2.093	2.094	20	2.097	2.097	20	2.103	2.103	15
212	1.997	1.997	5	2.004	2.004	10	2.009	2.009	15	2.014	2.015	15	2.020	2.020	10	2.025	2.024	10
220	1.913	1.913	60	1.921	1.921	50	1.926	1.926	60	1.930	1.931	85	1.935	1.935	80	1.939	1.939	80
004	1.878	1.878	70	1.886	1.886	55				1.895	1.896	90	1.899	1.900	85	1.906	1.906	85
023							1.890	1.890	60									
221	1.854	1.854	55	1.862	1.862	50	1.866	1.866	60	1.871	1.871	75	1.875	1.875	65	1.879	1.879	70
130	1.776	1.776	20	1.784	1.784	30	1.788	1.788	45	1.793	1.793	55	1.795	1.795	40	1.800	1.800	40
123	1.765	1.765	1	1.774	1.772	2	1.777	1.777	5	1.781	1.781	2	1.784	1.785	5	1.790	1.790	5
131	1.728	1.728	60	1.736	1.736	50	1.740	1.740	60	1.745	1.745	80	1.747	1.747	80	1.752	1.752	70
213	1.717	1.717	5	1.723	1.723	10	1.727	1.727	15	1.732	1.732	15	1.736	1.736	15	1.741	1.741	15
222	1.705	1.705	5	1.712	1.712	10	1.716	1.716	15	1.720	1.720	30	1.724	1.724	15	1.728	1.728	15
114																		
301	1.685	1.685	5	1.690	1.690	5	1.694	1.694	10	1.699	1.699	5	1.704	1.704	10	1.707	1.707	10
311	1.615	1.615	10	1.620	1.620	15	1.625	1.624	20	1.629	1.629	20	1.633	1.633	20	1.636	1.636	15
132	1.605	1.605	30	1.613	1.613	30	1.617	1.617	50	1.621	1.621	65	1.623	1.623	55	1.628	1.628	50
024	1.566	1.566	40	1.573	1.573	40	1.576	1.576	45	1.580	1.580	70	1.584	1.584	60	1.589	1.588	60
230	1.527	1.527	5	1.534	1.534	5	1.537	1.538	5	1.542	1.542	5						
204	1.521	1.521	60	1.527	1.527	50	1.530	1.530	60	1.535	1.535	85	1.538	1.539	75	1.542	1.542	70
312	1.513	1.513	70	1.519	1.519	55	1.522	1.522	60	1.527	1.527	95	1.531	1.531	85	1.534	1.534	80
223																		
124	1.499	1.499	1	1.505	1.505	2	1.509	1.509	2									
320	1.476	1.476	5	1.481	1.481	10	1.485	1.485	10	1.489	1.489	5	1.492	1.492	10	1.496	1.496	5
105										1.457	1.456	2	1.461	1.460	10			
214													1.487	1.486	5	1.488	1.490	5
133	1.448	1.448	40	1.455	1.455	40	1.458	1.459	50	1.462	1.462	50	1.465	1.465	50	1.469	1.469	45
303	1.423	1.423	5	1.427	1.428	5	1.431	1.431	10	1.435	1.435	5	1.439	1.439	10	1.443	1.442	2
232	1.415	1.415	1	1.421	1.421	1	1.425	1.424	5	1.428	1.428	2	1.431	1.431	2	1.434	1.434	2
115	1.399	1.399	5	1.404	1.404	10				1.412	1.411	10	1.415	1.415	10	1.419	1.419	10
040										1.431	1.431	5						
322	1.374	1.374	5	1.379	1.379	10	1.382	1.382	15	1.386	1.386	10	1.389	1.389	10	1.392	1.392	10
041	1.393	1.393	10	1.399	1.400	15	1.403	1.403	25				1.408	1.408	30	1.412	1.412	20
313	1.380	1.380	2	1.384	1.385	2	1.388	1.388	3	1.392	1.392	2	1.396	1.396	5	1.399	1.399	5
140	1.367	1.367	1	1.373	1.374	2	1.377	1.377	5	1.381	1.381	5	1.382	1.382	10	1.386	1.386	5
224	1.340	1.340	40	1.346	1.346	35	1.349	1.349	50	1.353	1.353	65	1.355	1.356	60	1.359	1.359	55
025													1.342	1.343	15	1.346	1.347	15
042	1.326	1.326	20	1.333	1.332	25	1.336	1.336	40	1.339	1.339	40	1.341	1.341	30	1.345	1.345	25
400	1.296	1.296	10	1.301	1.301	10	1.304	1.304	20	1.308	1.307	20	1.311	1.311	25	1.313	1.313	15

	$GdRhO_3$			$EuRhO_3$			$SmRhO_3$			$NdRhO_3$			$PrRhO_3$		
hkl	d_{obs}	d_{calc}	I_{obs}	d_{obs}	d_{calc}	I_{obs}	d_{obs}	d_{calc}	I_{obs}	d_{obs}	d_{calc}	I_{obs}	d_{obs}	d_{calc}	I_{obs}
101	4.344	4.346	15	4.361	4.361	10	4.380	4.379	15	4.424	4.423	10	4.448	4.448	5
110	3.890	3.891	10	3.899	3.900	10	3.909	3.909	15	3.930	3.929	5	3.941	3.941	5
002	3.828	3.829	10	3.839	3.840	5	3.853	3.854	10	3.887	3.887	5	3.901	3.901	5
111	3.468	3.469	80	3.477	3.477	70	3.486	3.486	80	3.507	3.507	75	3.517	3.518	60
020	2.880	2.880	85	2.880	2.880	75	2.880	2.881	85	2.878	2.878	85	2.874	2.874	75
112	2.730	2.729	100	2.737	2.736	100	2.745	2.744	100	2.764	2.763	100	2.773	2.773	100
021	2.695	2.696	75	2.696	2.697	55	2.698	2.698	75	2.698	2.699	80	2.697	2.697	50
200	2.638	2.639	90	2.649	2.649	75	2.661	2.660	90	2.689	2.689	90	2.707	2.707	80
211	2.289	2.289	40	2.297	2.297	30	2.305	2.305	40	2.325	2.325	35	2.336	2.337	20
202	2.173	2.173	10	2.180	2.181	5	2.190	2.189	15	2.212	2.211	20			
113	2.134	2.134	55	2.140	2.140	40	2.147	2.147	60	2.163	2.163	50	2.171	2.171	40
122	2.109	2.110	20	2.113	2.113	10	2.117	2.117	15	2.124	2.125	15	2.127	2.128	10
212	2.032	2.033	10	2.039	2.039	5	2.047	2.047	10	2.064	2.064	10	2.074	2.074	5
220	1.946	1.946	80	1.950	1.950	70	1.954	1.954	85	1.965	1.965	85	1.970	1.970	80
004	1.914	1.915	80	1.920	1.920	65	1.927	1.927	80	1.944	1.944	80	1.951	1.951	65
023	1.911	1.910	65	1.914	1.913	40	1.917	1.917	55	1.926	1.926	40	1.928	1.928	35
221	1.886	1.886	70	1.890	1.890	55	1.894	1.894	70	1.905	1.905	60	1.911	1.910	50
130	1.804	1.804	40	1.805	1.805	30	1.806	1.806	35	1.807	1.807	25	1.806	1.806	20
123															
131	1.756	1.756	75	1.757	1.757	65	1.759	1.759	80	1.760	1.760	70	1.760	1.759	60
213	1.748	1.748	15							1.775	1.775	5	1.783	1.783	5
222	1.734	1.735	20	1.739	1.739	10	1.743	1.743	15	1.753	1.753	10			
114							1.728	1.728	10				1.748	1.748	2
301	1.715	1.714	10	1.722	1.721	5									
311	1.643	1.643	20	1.649	1.649	10	1.656	1.656	20	1.671	1.671	20	1.681	1.681	15
132	1.632	1.632	55	1.634	1.634	50	1.636	1.636	60	1.639	1.638	60	1.639	1.639	55
024	1.594	1.594	65	1.598	1.598	60	1.602	1.602	65	1.611	1.611	60	1.614	1.614	55
230				1.555	1.555	60									
204	1.549	1.550	70				1.561	1.561	70	1.575	1.575	60	1.583	1.583	60
312				1.546	1.546	80	1.552	1.552	90	1.566	1.566	90	1.575	1.575	85
223	1.548	1.547	55	1.551	1.551	30	1.556	1.556	50				1.571	1.571	30
124	1.527	1.526	5												
320	1.501	1.501	10	1.505	1.506	10	1.510	1.510	5	1.521	1.521	5	1.528	1.528	5
105	1.471	1.471	20	1.475	1.475	40							1.499	1.499	5
214															
133	1.473	1.473	50				1.478	1.478	50	1.482	1.482	45	1.483	1.483	40
303	1.448	1.448	5	1.454	1.454	5	1.459	1.460	5	1.474	1.474	5			
232	1.439	1.439	5												
115	1.425	1.425	10	1.429	1.429	10	1.434	1.434	10	1.446	1.446	10	1.451	1.451	5
040				1.440	1.440	5	1.441	1.440	5	1.439	1.439	5	1.436	1.437	5
322	1.397	1.398	10	1.401	1.402	10							1.423	1.423	5
041	1.415	1.415	20	1.415	1.415	20	1.416	1.416	25	1.415	1.415	25	1.413	1.413	20
313										1.428	1.428	2			
140	1.390	1.389	5	1.390	1.390	5	1.390	1.390	10	1.390	1.390	2			
224	1.365	1.365	55	1.368	1.368	55	1.372	1.372	60	1.382	1.382	60	1.386	1.386	60
025	1.352	1.352	10	1.355	1.355	10	1.359	1.359	10	1.368	1.368	10	1.371	1.371	5
042				1.348	1.348	25	1.349	1.349	25	1.349	1.349	15	1.348	1.348	15
400	1.319	1.319	15	1.325	1.325	15	1.330	1.330	20	1.344	1.344	20	1.353	1.354	15

orthoferrites, -gallates, and -chromites (Quezel-Ambrunaz & Mareschal, 1963).

The materials used in this study were Tb_4O_7, Pr_4O_7, and the sesquioxides of Lu, Tm, Er, Ho, Dy, Gd, Eu, Sm, and Nd and were of at least 99·9% purity. The Rh_2O_3 was supplied by Engelhard. Spectrographic analysis indicated *ca.* 100 p.p.m. each of Fe, Ni, Cr, Si, Al, and Ru and *ca.* 500 p.p.m. Ir, Re, and Pd. The oxides, thoroughly mixed in stoichiometric quantities, were heated in sealed Pt tubes under a pressure of 3 kbar at 1350° for 24 hr. X-ray patterns were obtained at 25° on a Hägg–Guinier camera using monochromatized Cu $K\alpha$ radiation; d values were calculated using (Cu $K\alpha_1$) = 1·54051 Å with a KCl internal standard (a = 6·2931 Å). Cell dimensions were obtained by least-squares refinement of these data using the space group *Pbnm* as determined for $GdFeO_3$ (Geller, 1956) and $YFeO_3$ (Coppens & Eibschütz, 1965). Table 1 lists the cell dimensions and Table 2 lists the crystallographic data for the 11 rare earth orthorhodites.

In Fig. 1 the cell dimensions are plotted *vs.* the effective ionic radii of the trivalent rare earth ions (Shannon & Prewitt, 1969). Cell dimensions of $LaRhO_3$ were taken from Wold, Post & Banks (1957). Effective ionic radii are plotted because it is felt that the variation with radius is more apt to be regular than with atomic number. The plot clearly shows a regular increase in b up to Gd followed by a decrease for Eu, Sm, Nd, Pr, and La. This anomalous behavior has been correlated by Marezio *et al.* (1968) to a regular increase in the average M–O distance of the eight first-nearest neighbors and a decrease in the average M–O distance of the four second-nearest neighbors as M increases from Lu to La. This behavior is also reflected in the plot of r_M^3 *vs.* unit-cell volume for these compounds (Prewitt & Shannon, 1969). Whereas most r^3 *vs.* V plots are linear, r_M^3 *vs.* V plots for the $MM'O_3$ perovskites where M′ = Al, Cr, Ga, Fe, Rh, Sc and In have a pronounced curvature. Plots of $r_m^{3\prime}$ *vs.* V are linear as expected because the coordination of the M′ cations does not change (Shannon, 1967).

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The refinement of the crystal structure of $Na_2Co_5Mo_4Cl_4O_{16}$.

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The diffraction data of the compound $Na_2Co_5Mo_4Cl_4O_{16}$ have been refined by least-squares methods, using the block-diagonal approximation, to R = 9·6%. The site occupancy factors for the non-oxygen atoms have been investigated and shown to be unity. Although the coordinates of the heavy atoms have changed but little the refined oxygen coordinates have yielded significantly different cation–oxygen distances.

The diffraction data of the compound $Na_2Co_5Mo_4Cl_4O_{16}$, the structural details of which were published in an unrefined form (Smith, 1965) have now been subjected to a full three-dimensional least-squares analysis. For the sake of completeness the crystal data are restated.

Crystal data:

Monoclinic, space group $C2/m$
a = 10·706 ± 0·003 Å
b = 8·852 ± 0·002
c = 10·663 ± 0·003
β = 109° 45′ ± 6′
V = 951 Å^3
Z = 2

Atoms are in positions:

4 Na in 4(i)
8 Co(1) in 8(j)
2 Co(2) in 2(c)
4 Mo(1) in 4(i)
4 Mo(2) in 4(i)
8 Cl in 8(j)
8 O(1) in 8(j)
8 O(2) in 8(j)
4 O(3) in 4(i)
4 O(4) in 4(i)
4 O(5) in 4(i)
4 O(6) in 4(i)

Refinement

Starting from the previous atomic parameters an isotropic refinement using the block-diagonal approximation was carried out on 2132 reflexions. Included in this data list were 288 unobserved structure amplitudes which were allocated an F value equivalent to $\frac{1}{2}F_{min}$. Convergence