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A Refinement of the Crystal Structure of Yttria

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The crystal structure of yttria, Y_2O_3, has been refined using single-crystal X-ray diffraction data. The results confirm the general features of earlier analyses using powder diffraction data, but a considerable improvement in accuracy has been achieved.

Introduction

Yttria, Y_2O_3, is one of a series of metal oxides which have similar face-centered cubic structures conforming to the space group $Ia3$ (T_h^7)*. Eight metal ions are in the special positions $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$; the remaining twenty-four occupy the sites $u, 0, \frac{1}{4}$. The forty-eight oxygen ions are in general positions x, y, z, and are arranged in distorted octahedra around the metal ions, the metal–oxygen bonding distances being unequal. This structure is generally referred to as the *C*-type metal oxide structure. All the sesquioxides of the rare earths belong to this system, as do Ga_2O_3, In_2O_3, Tl_2O_3 and the mineral bixbyite, $(Fe,Mn)_2O_3$.

The first basically correct determination of the structure of a *C*-type metal oxide was carried out by Pauling & Shappel (1932), using a trial-and-error method to analyse the powder-diffraction pattern of bixbyite. The accuracy of the analysis was low, for there are relatively few non-overlapping lines in the powder pattern. Moreover, the atomic scattering factor curves were quoted as having a possible error of twenty per cent. The oxygen positions were not determined directly, but from packing and bonding considerations they were deduced to be at sites equidistant from the metal ions. This structure was redetermined by Dachs (1956), who made a least-squares analysis of the powder-diffraction pattern. The parameters obtained were quite different from those found by Pauling & Shappel.

The first experimental determination of the structure of yttria itself was reported by Villian (1957) who examined the neutron-diffraction powder pattern. A similar study was made by Fert (1962) who used a least-squares method on sixteen reflexions to find the parameters x, y, z, u as well as the neutron scattering length of yttrium.

Table 1 shows the results of these independent determinations, and it can be seen that there is a large range in the atomic coordinates quoted. Standard deviations on neither the atomic coordinates nor thermal parameters have been reported.

Table 1. *Structure parameters from previous investigations*

	u	x	y	z
Pauling & Shappel	0·030	0·385	0·145	0·380
Dachs	0·034	0·375	0·162	0·400
Villian	0·034	0·396	0·155	0·383
Fert	0·034	0·389	0·150	0·377

In view of the importance of the *C*-type metal oxide structure in oxide chemistry an analysis has been carried out with three-dimensional X-ray diffraction data collected from a single crystal. Since there is no overlapping of non-equivalent reflexions the number of independent observations is much greater than can be

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* The space groups of several *C*-type crystals are reported incorrectly in the ASTM Card File as T_5. The systematic absences of the reflexions for this space group are similar to those of T_h^7 except that the condition $hk0$ $h(k) = 2n + 1$ is allowed.

obtained from the powder pattern. The accuracy of the atomic coordinates has been correspondingly improved, and thermal parameters have been calculated.

Experimental

Single crystals of yttrium oxide were kindly supplied by Dr D. J. M. Bevan and Mr W. Barker, of the Department of Chemistry, University of Western Australia. The starting material was a powdered sample of 99·99% purity. An oxy-acetylene flame was directed at a quantity of the powdered material until partial fusion occurred. The sample was then cooled slowly, and several single crystals suitable for X-ray photography were obtained. In order to verify that the material was unchanged by the growing process some of the crystals were crushed, and the powder pattern from this material was compared with that from the original sample. The patterns were identical.

Many of the specimens were multiple or only partly fused. The best were clear and very small. Although they were by no means regular in shape there was a tendency for growth to be restricted in the [111] direction, and several crystals had the form of truncated tetrahedra. That chosen for X-ray data collection was elongated in the $[1\bar{1}0]$ direction and had a roughly rectangular cross section. Its approximate dimensions were $0{\cdot}03 \times 0{\cdot}06 \times 0{\cdot}22$ mm.

The systematic absences on preliminary photographs confirmed that the space group was $Ia3$. Weak reflexions apparently corresponding to the condition $hk0$ $h(k)=2n+1$ were observed on both single-crystal and powder patterns, but on closer investigation it was found that these were due to double Bragg scattering and $K\beta$ contribution respectively. The cell dimension was measured from a powder photograph to be $10{\cdot}604 \pm 0{\cdot}002$ Å.

The X-ray diffraction data were collected on Weissenberg photographs using the multiple film, multiple exposure technique with Cu $K\alpha$ radiation. Intensity data recorded for appropriate ranges on the layers zero to eight included all non-equivalent reflexions. Of the 223 independent reflexions within the Cu $K\alpha$ sphere 220 were actually observed. The intensities were estimated visually, but the film factors were determined by comparing the peak densities of several reflexions on adjacent films using a microdensitometer. The intensity data were corrected for Lorentz and polarization factors and placed on a common scale by a comparison of the relative intensities of the equivalent reflexions occurring on different layers. The linear absorption coefficient for yttria is high (524 cm^{-1}), but because of the very small crystal size, errors due to absorption were small, though not entirely negligible. It was not possible to calculate correction factors because of the irregular crystal shape, but in the few instances where the intensities of equivalent reflexions were significantly different the larger value was chosen as the more reliable. The Renninger reflexions were very weak and of low order, however, so it could reasonably be assumed that the errors caused by double Bragg scattering were small. In order to verify this the intensities from the single-crystal photographs were checked for consistency with values obtained from a powder-diffraction photograph. The sample was of 99·99% purity, the tube voltage was kept low to eliminate fluorescence excited by the white radiation, and fine-grained film was used for recording the diffraction pattern. This resulted in a photograph with a very low background, and the line intensities were measured with a microdensitometer, 77 lines being recorded. The data were corrected for Lorentz, polarization and absorption factors and were then compared with the corresponding single-crystal intensities, or sums of intensities in the case of overlapping lines. The results agreed within the limits of error of the measurements on all but the seven strongest reflexions, where the single-crystal intensities were weaker than the powder values. This was interpreted as resulting from extinction in the reflexions from the single crystal.

Structure refinement

Structure factors were evaluated using the positional parameters derived by Fert, and an overall temperature factor coefficient estimated from a Wilson plot. This gave an R index of 0·14, confirming that the structure was basically correct. In this and subsequent structure-factor calculations the scattering factor curve for O^{2-} was that evaluated by Suzuki (1960) by the self consistent field method for the negative ion in a +2 well, and is accurate to about 0·5%. No scattering-factor curve for triply ionized yttrium is available, so an approximate curve was derived as follows. Yttrium has an atomic number of 39, which is halfway between those of scandium and cerium, so the difference between the scattering curve of Y and Y^{3+} should be approximately equal to the mean difference between the scattering factor curves of Ce and Ce^{3+} and Sc and Sc^{3+}. Values calculated by the self-consistent field method are available for Sc^{3+} and Ce^{3+} (Watson & Freeman, 1961; Blume, Freeman & Watson, 1962) and for the neutral atoms scattering-factor curves have been calculated from the Thomas–Fermi–Dirac model (*International Tables for X-ray Crystallography*, 1962). The mean differences between the scattering factors of the neutral and ionized atoms were evaluated as a function of the scattering angle, and applied to the scattering-factor curve for neutral yttrium calculated from the Thomas Fermi-Dirac model, to give the values listed in Table 2.

The yttrium scattering factors must be further corrected for the effect of anomalous dispersion. The real and imaginary components of the correction factors are those from *International Tables for X-ray Crystallography* (1962).

The real part of the anomalous-dispersion correction was added to the interpolated Y^{3+} curve. The imagin-

Table 2. *Scattering factors for* Y^{3+}

$\sin\theta/\lambda$	e
0·00	36·00
0·10	34·13
0·20	29·87
0·30	25·43
0·40	21·82
0·50	19·06
0·60	16·87
0·70	15·06
0·80	13·57

ary part cannot be treated in such a simple manner, but it has only a small effect on most of the intensities, and can generally be ignored. The imaginary contribution is appreciable only when the real contributions of the yttrium and oxygen ions are fairly large, nearly equal in magnitude, and opposite in sign. Thus occurs infrequently, and in the early stages of the refinement it was possible to ignore the effect completely.

Three-dimensional Fourier and difference syntheses were calculated and these indicated small changes in some of the atomic parameters. A second set of structure factors was evaluated, giving an R value of 0·12. The difference synthesis indicated that the ions were vibrating anisotropically, and it was decided to continue the refinement using least-squares methods. For the seven strongest reflexions the observed structure factors were less than the corresponding calculated values. These differences were consistent with extinction errors, so the structure factors were assigned zero weight in the least-squares calculations. The remaining reflexions were given a weight inversely proportional to $|F|^2$, which was chosen on the basis of an analysis of the agreement between the observed and calculated structure factors. The structure-factor least-squares calculations were carried out using a block-diagonal approximation to the least-squares matrix which refined atomic coordinates, scaling factor and thermal parameters. Because of the symmetry the thermal vibrations of the yttrium ions in the special positions related to $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$ must be isotropic, and the principal axis of the ellipsoids of vibration of the yttrium ions related to $u, 0, \frac{1}{4}$ necessarily coincide with the cell edges. The vibrations of the oxygen atoms are not restricted by symmetry. The total number of independent parameters is fifteen.

Five least-squares rounds were completed. Each time full shifts were applied to all parameters. In the later rounds the structure factors were corrected for the imaginary contribution of the yttrium. At the end of the fifth round the shifts indicated were considerably less than the standard deviations and the refinement was terminated. When the F_o values for the seven strongest intensities, which were affected by extinction, were substituted with the corresponding values from the powder data, the R value was 0·082. The final parameters are listed in Tables 3 and 4, and the structure factors in Table 5.

Table 3. *Fractional atomic coordinates*

Atom	x	y	z
Y(1)	0·2500	0·2500	0·2500
Y(2)	−0·0328	0·0000	0·2500
O	0·389	0·154	0·378

Discussion of the structure

The standard deviations of the parameters evaluated in the usual manner from the inverse to the normal equations matrix are as follows:

Yttrium $\sigma(u)=0·0002$

Oxygen $\sigma(x)=\sigma(y)=\sigma(z)=0·001$

The accuracies of the results obtained by previous workers from the powder patterns are not quoted, but since the single-crystal analysis is based on more than three times the number of independent observations it may reasonably be assumed that the results of the present investigation are more reliable. The values obtained actually lie between those proposed by Villian and Fert from neutron diffraction analyses. It is not possible to make a precise comparison with the values obtained by Pauling & Shappel and by Dachs, since the effect of the cation size on the structure is not known.

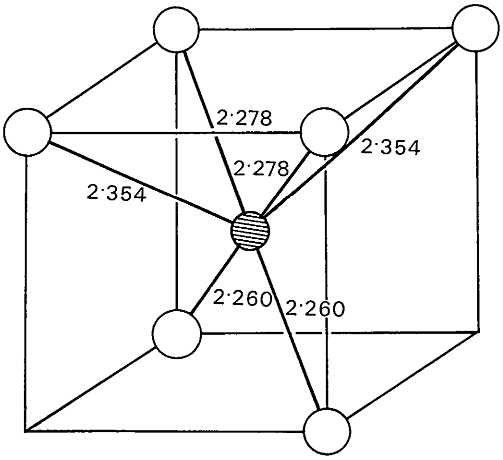

Fig. 1. Oxygen ions at the corners of a slightly distorted cube surrounding the yttrium ion in the general positions. Y–O distances in Å are shown.

Table 4. *Thermal parameters*

Atom	B	B_{11}	B_{22}	B_{33}	B_{23}	B_{13}	B_{12}
Y(1)	0·98Å^2						
Y(2)		0·0019	0·0028	0·0018	0·0000	0·0000	0·0000
O		0·0031	0·0027	0·0035	−0·0001	−0·0006	0·0017

The anisotropic temperature factors have the form $\text{T.F.}=\exp\{-(B_{11}L^2+B_{22}k^2+B_{33}l^2+B_{23}kl+B_{13}hl+B_{12}hk)\}$

Table 5. *Observed and calculated structure factors*

h k l	$F_{obs.}$	$F_{calc.}$	h k l	$F_{obs.}$	$F_{calc.}$	h k l	$F_{obs.}$	$F_{calc.}$	h k l	$F_{obs.}$	$F_{calc.}$	h k l	$F_{obs.}$	$F_{calc.}$
2 0 0	150	107	8 5 1	291	281	8 6 2	175	180	13 1 4	125	176	11 6 5	170	178
4 0 0	1570	1540	10 5 1	289	307	10 6 2	428	448	6 2 4	139	135	8 7 5	281	275
6 0 0	426	308	12 5 1	174	173	12 6 2	270	277	8 2 4	297	268	10 7 5	237	193
8 0 0	1334	1324	7 6 1	247	252	7 7 2	229	217	10 2 4	281	296	9 8 5	247	246
10 0 0	534	508	9 6 1	314	306	9 7 2	177	138	12 2 4	389	354	8 0 6	193	185
12 0 0	644	520	11 6 1	293	317	11 7 2	50	65	5 3 4	266	255	10 0 6	270	245
4 2 0	197	192	8 7 1	322	290	10 8 2	640	563	7 3 4	278	274	12 0 6	241	220
6 2 0	264	244	10 7 1	277	231	4 1 3	418	445	9 3 4	305	268	7 1 6	299	268
8 2 0	392	434	9 8 1	283	253	6 1 3	470	487	11 3 4	202	166	9 1 6	364	334
10 2 0	401	458	11 8 1	202	225	8 1 3	326	344	4 4 4	1078	1073	11 1 6	254	247
12 2 0	445	440	10 9 1	127	134	10 1 3	299	282	6 4 4	264	226	8 2 6	507	548
4 4 0	1563	2067	4 0 2	177	170	12 1 3	183	161	8 4 4	836	831	10 2 6	451	452
6 4 0	195	209	6 0 2	277	291	5 2 3	235	240	10 4 4	428	435	12 2 6	472	543
8 4 0	704	789	8 0 2	324	353	7 2 3	27	7	12 4 4	387	331	7 3 6	380	367
10 4 0	357	357	10 0 2	343	389	9 2 3	141	124	5 5 4	287	261	9 3 6	220	226
12 4 0	447	470	12 0 2	455	461	11 2 3	226	220	7 5 4	247	236	11 3 6	237	186
6 6 0	54	58	3 1 2	83	76	13 2 3	94	105	9 5 4	245	229	8 4 6	48	19
8 6 0	553	532	5 1 2	301	277	4 3 3	349	347	11 5 4	131	169	10 4 6	210	239
10 6 0	187	168	7 1 2	314	265	6 3 3	316	308	6 6 4	158	155	7 5 6	299	317
12 6 0	515	539	9 1 2	87	59	8 3 3	345	362	8 6 4	389	440	9 5 6	177	169
8 8 0	615	555	11 1 2	65	59	10 3 3	274	275	10 6 4	154	158	11 5 6	202	174
10 8 0	164	132	13 1 2	156	128	12 3 3	156	160	7 7 4	225	212	6 6 6	405	589
2 1 1	289	325	2 2 2	2542	2314	5 4 3	332	331	9 7 4	162	146	10 6 6	295	277
4 1 1	357	378	4 2 2	208	197	7 4 3	297	289	11 7 4	177	165	7 7 6	185	202
6 1 1	418	469	6 2 2	1302	1424	9 4 3	237	221	8 8 4	361	349	9 7 6	233	211
8 1 1	382	421	8 2 2	399	421	11 4 3	202	195	10 8 4	150	130	8 8 6	162	131
10 1 1	233	248	10 2 2	646	718	6 5 3	384	363	9 9 4	158	163	8 1 7	322	327
12 1 1	137	154	12 2 2	432	493	8 5 3	382	377	6 1 5	361	348	10 1 7	277	251
3 2 1	73	39	3 3 2	426	458	10 5 3	218	208	8 1 5	378	338	9 2 7	121	134
5 2 1	258	243	5 3 2	262	230	12 5 3	148	116	10 1 5	305	290	8 3 7	262	292
7 2 1	364	346	7 3 2	54	40	7 6 3	399	411	12 1 5	185	148	10 3 7	181	197
9 2 1	117	126	9 3 2	139	141	9 6 3	274	285	7 2 5	66	56	9 4 7	177	203
13 2 1	110	100	11 3 2	139	140	11 6 3	168	172	9 2 5	202	170	11 4 7	154	172
4 3 1	399	402	13 3 2	79	68	8 7 3	308	278	11 2 5	191	181	8 5 7	229	231
6 3 1	496	475	4 4 2	91	64	10 7 3	245	198	6 3 5	366	349	10 5 7	200	207
8 3 1	391	370	6 4 2	380	345	9 8 3	310	282	8 3 5	295	316	9 6 7	220	211
10 3 1	293	275	8 4 2	264	259	6 0 4	428	464	10 3 5	214	236	8 7 7	235	247
12 3 1	141	146	10 4 2	536	492	8 0 4	719	790	7 4 5	297	290	9 1 8	322	300
5 4 1	372	355	12 4 2	316	313	10 0 4	505	559	9 4 5	197	214	11 1 8	208	201
7 4 1	260	267	5 5 2	83	77	12 0 4	505	479	6 5 5	382	400	10 2 8	106	99
9 4 1	262	261	7 5 2	112	87	5 1 4	420	397	8 5 5	343	326	9 3 8	189	183
11 4 1	241	222	9 5 2	214	200	7 1 4	293	277	10 5 5	181	172	10 4 8	445	499
13 4 1	123	159	11 5 2	172	131	9 1 4	206	180	7 6 5	326	334	9 5 8	181	196
6 5 1	335	305	6 6 2	891	941	11 1 4	202	186	9 6 5	222	220			

The oxygen ions can be considered as being placed at six of the corners of a slightly distorted cube around each yttrium ion (Fig. 1). For the yttrium ions in the more general positions the oxygens are missing from opposite corners of one face. Three Y–O contacts not equivalent by symmetry are unequal, with lengths:

$$2{\cdot}260 \pm 0{\cdot}012\ \text{Å}$$
$$2{\cdot}278 \pm 0{\cdot}012$$
$$2{\cdot}354 \pm 0{\cdot}012$$

The yttrium ion is thus significantly closer to the less densely packed faces of the cube. The assumption made by Pauling & Shappel in deriving the oxygen positions in bixbyite is therefore not substantiated.

For the yttrium ion at $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$, the oxygen ions are missing from diagonally opposite corners, and the Y–O contacts are all equal to $2{\cdot}250 \pm 0{\cdot}012$ Å.

The mean thermal displacement of the yttrium ion at the special position $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$, is 0·12 Å. The axes of the ellipsoid of vibration of the yttrium ion at u, 0, $\frac{1}{4}$ have lengths 0·11, 0·13, and 0·10 Å, maximum vibration occurring the y direction. The vibration of the oxygen ion at 0·389, 0·154, 0·378 can be represented by an ellipsoid whose axes have lengths 0·124, 0·177 and 0·066 Å in the directions [100], [00·67 0·75] and [0 0·75 0·67] respectively. There is no obvious relation between the modes of thermal vibration and packing forces.

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