Decker, B. F. & Kasper, J. S. (1957). *Acta Cryst.* **10**, 332.
Eick, H. A., Baenziger, N. C. & Eyring, L. (1956). *J. Amer. Chem. Soc.* **78**, 5147.
Glasser, F. P., Glasser, L. S. D. & Schieber, M. (1965). *Amer. Ceram. Soc. Bull.* **44**, 299, Abstract 7-B-65.
Hill, P. M., Peiser, H. S. & Rait, J. R. (1956). *Acta Cryst.* **9**, 981.
Johnson, C. K. (1965). Oak Ridge National Laboratory Report ORNL-3794.
Mueller, M. H., Heaton, L. & Miller, K. T. (1960). *Acta Cryst.* **13**, 828.
Pauling, L. (1960). *The Nature of the Chemical Bond*, Chap. 13. Ithaca: Cornell Univ. Press.
Rau, R. C. (1964). *Rare Earth Research* II (ed. Vorres, K. S.), p. 117. New York: Gordon and Breach.
Rundqvist, S. & Hede, A. (1960). *Acta Chem. Scand.* **14**, 893.
Schieber, M. & Holmes, L. (1964). *Proc. Brit. Ceram. Soc.* **2**, 139.
Stewart, J. M. & High, D. F. (1964). Abstracts A.C.A. Bozeman Meeting, B-13, p. 29.
Suzuki, T. (1960). *Acta Cryst.* **13**, 279.
Wickman, F. E. (1951). *Ark. Min. Geol.* **1**, 219.

Acta Cryst. (1966). **20**, 723

Refinement of the Crystal Structure of In_2O_3 at two Wavelengths

By M. Marezio
Bell Telephone Laboratories, Murray Hill, N.J., U.S.A.

(*Received* 17 *June* 1965 *and in revised form* 1 *October* 1965)

Indium sesquioxide is cubic with 16 molecules per unit cell ($a = 10{\cdot}117 \pm 0{\cdot}001$), space group $Ia3$. The crystal structure has been refined from single-crystal X-ray diffraction data with a precision corresponding to an R index of 0·03. The interatomic distances have been determined to an accuracy of 0·01 Å for the In–O distances and 0·02 Å for the O–O distances. The In–O bond lengths are: (6) In(1)–O 2·18 Å, (2) In(2)–O 2·13 Å, (2) In(2)–O 2·19 Å, (2) In (2)–O 2·23 Å. The large difference in the In(2)–O bond lengths is attributed to an unequal distribution of the repulsive forces among the oxygen atoms that form the polyhedron around In(2).

Since the absorption correction was rather high, the intensity data were taken with two radiations, Mo $K\alpha$ and Cu $K\alpha$, and two independent refinements were made and compared. Contrary to what one would expect, the extinction correction is much larger for the Mo data than for the Cu data.

The possible existence of a high pressure phase of In_2O_3 is discussed.

Introduction

Many of the metallic sesquioxides, M_2O_3, crystallize in the corundum type and the A, B and C rare-earth sesquioxide structures. The corundum type and the A modification are trigonal, space group symmetry $R\bar{3}c$ and $P\bar{3}m1$ respectively, the B modification is monoclinic, $C2/m$, and the C modification is cubic, $Ia3$. This paper reports the refinement of the crystal structure of indium sesquioxide which crystallizes in the cubic C modification (Zachariasen, 1927). Many other sesquioxides crystallize with the same structure, for instance: Sc_2O_3, Y_2O_3, Tl_2O_3, Pu_2O_3, Cm_2O_3, Am_2O_3, R_2O_3 (R = rare earth) *etc.* Some of these oxides can also exist in the A and/or B forms. The atomic arrangement of the C modification was first determined for the mineral bixbyite $(Fe,Mn)_2O_3$ (Pauling & Shappell, 1930). In 1956 Dachs refined this structure and gave a more detailed description of it. Since then neutron diffraction studies using powders have been made on several of the C type rare-earth sesquioxides (Table 5).

Recently Remeika & Spencer (1964) of this laboratory prepared single crystals of In_2O_3 by a flux technique for electrical conductivity measurements. These crystals have the shape of rectangular prisms and are dark green. Since single crystals of In_2O_3 were available, an accurate determination of a C modification structure was undertaken with the use of modern techniques to measure X-ray intensities. This refinement provides accurate values of the In–O distance which are necessary for the theoretical and experimental studies on In_2O_3 being carried out at present in this laboratory.

Crystallographic data

Crystals of In_2O_3 are body-centered cubic with 16 molecular weights (M.W. 277·64) in a cell of dimension $a = 10{\cdot}117 \pm 0{\cdot}001$ Å (Roth, 1957), the calculated density is 7·120 g.cm^{-3}; hkl is present only with $h+k+l = 2n$ and $0kl$ only with $k,l = 2n$; the space group is hence taken as $Ia3$ (T_h^7). The 32 metallic atoms are in the special positions, 24 in (d) and 8 in (b), while the 48 oxygen atoms are in the general position.

Experimental

All intensity measurements were made with a General Electric XRD-5 spectrometer equipped with a single-crystal orienter and a scintillation counter. The integrated intensities were obtained manually with the stationary-crystal stationary-counter technique and single filter. Cu *Kα* radiation filtered with nickel foil was used. The X-ray tube was operated under the same conditions throughout the experiment to avoid the introduction of scale factors due to changes of voltage or current. The specimen was a sphere of radius $R = 0{\cdot}0162 \pm 0{\cdot}0003$ cm, which was mounted without any knowledge of the crystal orientation. Adjustments of the arcs of the goniometer head brought the [110] zone parallel to the φ axis of the single-crystal orienter. All possible reflections belonging to the [100], [110], [111] and [112] zones were measured. The symmetry of the X-ray diffraction effects for In_2O_3 is *m*3; in this case the *hkl* and *khl* reflections are different. The total number of 138 independent reflections were measured; each one represents the average of at least four measurements taken on four different planes of the same crystallographic form.

After the intensities were obtained, the relative $|F_{hkl}|^2$ were calculated by applying the Lorentz-polarization and absorption corrections. It was at this point that we became aware of the magnitude of the latter correction. For Cu *Kα* radiation μ for In_2O_3 is 1448 cm^{-1}, which in our case corresponds to a $\mu R = 23{\cdot}5$. *International Tables for X-ray Crystallography* (1959) reports the values of A^* only up to $\mu R = 10$. The absorption correction was therefore made by direct integration procedure. Since it did not seem possible to obtain the degree of accuracy desired for this structure by using data with such a high absorption correction, we decided to use Mo *Kα* radiation filtered with zirconium foil. For this radiation μ for In_2O_3 is 174 cm^{-1} corresponding to $\mu R = 2{\cdot}82$.

As expected in the front-reflection region the intensities were stronger for Mo *Kα* than for Cu *Kα*, the opposite being true in the back-reflection region. In fact with Mo *Kα* it was possible to observe the 200 and 220 reflections which were not observed with Cu *Kα*; on the other hand the 882 reflection was observed with Cu *Kα* and not with Mo *Kα*. This corroborates the suggestion made by Burbank (1965) that it may be desirable to use both Cu and Mo radiation to obtain complete experimental data, particularly if μR is very large. Comparison of the two sets of data also reveals a variation in intensity for equivalent planes. In the case of Cu *Kα* data, this variation was sometimes as much as twenty per cent, while intensity measurements for a given plane were reproducible to within two per cent. In the case of the Mo *Kα* data the intensity variation for equivalent planes is within two per cent. When the absorption is very high, a small departure from the spherical shape of the specimen can cause large intensity differences for equivalent reflections. As stated above, this effect was minimized by averaging the measured intensities of several planes of the same crystallographic form.

Although at this stage the Mo *Kα* data appeared much more precise than the corresponding Cu *Kα* data, we decided to make two independent refinements to determine the effect of the wavelength on the accuracy of the structure determination. In the following paragraph the notations Cu-refinement and Mo-refinement refer to refinements based on the data taken with Cu *Kα* and Mo *Kα* radiation respectively.

Refinement of the structure

The refinements of the structure were carried out with the refinement program of Busing, Martin & Levy (1962), modified by Hamilton & Ibers. This modification takes into account the real and imaginary anomalous dispersion corrections. The atomic scattering factors (for neutral atoms) used were those of Cromer & Waber (1965) and the real and imaginary anomalous dispersion correction coefficients for indium were taken from the values recently reported by Cromer (1965). Since a secondary extinction correction was expected only the medium and weak reflections were included in the first stage of the Cu- and Mo-refinements. In both cases the positional parameters given by Fert (1962) for Y_2O_3 were used as starting values, isotropic temperature factors were used and all observed structure factors were weighted unity. Convergence was achieved in both cases within three cycles. The strong reflections were calculated with the positional and thermal parameters obtained at this stage. By comparing them with the observed values the approximate magnitudes of the extinction corrections were obtained. All the observed structure factors were then corrected by the Zachariasen formula (1963): $F_{\text{corr}} \simeq F_o[1 + \beta C J_o]$ where F_{corr} is the structure factor corrected for secondary extinction, F_o the observed one, J_o the observed intensity on an arbitrary scale, C is a constant to be determined and β takes into account the angular variation of the extinction correction. A number of C values were tried and that value was chosen which gave the best agreement between observed and calculated structure factors and the lowest standard deviations for the parameters varied. After the C coefficients were obtained, anisotropic thermal parameters were introduced, but, as expected, there was no appreciable anisotropy. At first glance, this procedure of determining a value for C based on an isotropic model and then refining the structure with anisotropic thermal parameters might seem somewhat inconsistent since one should establish the extinction correction coefficient together with the anisotropic model. However, there is no interaction between C and anisotropy, as the former is determined by the intense reflections of the front-reflection region, where anisotropy is irrelevant, while the latter is determined by the reflections of the back-reflection region, where extinction is negligible, unless μR is almost zero. Since only the linear term is considered in the secondary extinction correction formula, the reflections for which the extinction correction was larger than twenty-five per cent were omitted in the final refinements. The degree of agreement between observed and calculated structure factors is shown in

Table 1, where F_c represents the calculated structure factor per unit cell. The R values ($\Sigma\,|F_{\text{obs}}-F_{\text{calc}}|/\Sigma\,|F_{\text{obs}}|$) calculated by the Busing–Martin–Levy program were:

	Mo-refinement	Cu-refinement
R(including the 'zeros')	0·034	0·036
R(excluding the 'zeros')	0·033	0·032

The final positional and thermal parameters with their standard deviations are given in Table 2.

Table 1. *Observed and calculated structure factors*

	CuKα		MoKα			CuKα		MoKα			CuKα		MoKα	
hkℓ	F_o	F_c	F_o	F_c	hkℓ	F_o	F_c	F_o	F_c	hkℓ	F_o	F_c	F_o	F_c
200	nil	-37	86	-46	820	275	-262	260	-266	648	nil	0.	nil	-6
211	168	165	172	163	280	224	213	217	214	10.3.3	157	-160	160	-152
220	nil	-9	68	-9	644	147	-143	145	-138	10.4.2	310	310	311	311
222	1254	-1236	1340	-1233	822	232	233	236	235	4.10.2	177	-179	181	-181
321	43	-50	49	-53	660	14	-25	20	-27	954	147	144	149	143
231	63	75	65	72	743	162	-158	157	-163	594	130	131	131	129
400	877	923	953	923	473	155	-156	156	-163	963	157	159	159	165
411	180	205	213	211	662	573	-543	514	-529	693	145	-152	150	-149
420	111	-122	127	-120	752	68	66	69	62	880	330	332	318	313
240	78	82	95	92	572	40	-38	44	-40	10.4.4	246	-246	248	-251
332	212	-212	222	-215	840	482	470	464	464	882	27	-19	nil	-19
422	94	103	120	105	480	487	470	464	465	972	85	-86	90	-87
431	205	220	220	221	833	206	-204	203	-204	792	73	72	76	76
341	214	-236	236	-239	842	146	147	130	155	776	138	-131	136	-133
521	126	133	136	132	482	167	-169	144	-170	10.6.0	115	-112	115	-113
251	135	136	145	147	761	154	-148	147	-149	6.10.0	155	153	158	149
440	1064	1081	1075	1069	671	176	170	170	170	866	165	163	168	163
433	194	-197	199	-196	655	226	222	223	227	10.6.2	248	-275	272	-265
600	174	-182	169	-176	664	94	87	93	88	6.10.2	250	-275	274	-265
442	35	-29	38	-33	844	480	478	442	459	12.0.0	311	333	326	327
611	247	254	263	260	941	144	140	146	146	884	209	216	214	208
532	131	-132	133	-129	491	119	115	121	117	12.1.1	78	83	87	84
352	117	117	129	126	853	221	-220	216	-218	11.4.3	117	-120	119	-118
620	141	-143	151	-147	583	185	190	177	183	4.11.3	113	-118	120	-113
260	169	169	175	172	10.0.0	276	-270	273	-276	981	160	159	156	151
541	202	201	199	197	860	347	-334	331	-338	891	193	192	190	188
451	216	222	217	221	680	105	94	103	108	12.2.0	305	-298	301	-298
622	807	-792	778	-785	10.1.1	140	149	147	139	2.12.0	291	281	284	289
444	651	631	622	626	772	127	-117	125	-120	10.5.5	109	113	105	105
543	178	179	177	185	10.2.0	282	-271	277	-277	12.2.2	277	283	281	282
453	151	-150	148	-151	2.10.0	264	251	253	253	10.6.4	97	-95	97	-99
640	103	-94	111	-105	862	101	100	101	100	6.10.4	156	158	156	158
460	256	-246	258	-256	682	327	321	309	326	11.6.1	183	-184	188	-183
633	190	-185	188	-188	10.2.2	412	-428	414	-417	6.11.1	159	159	145	159
552	78	58	61	54	666	334	-339	331	-331	10.7.3	131	-125	127	-126
642	211	207	208	211	952	105	108	114	115	7.10.3	120	-119	117	-118
462	78	-75	84	-79	592	94	98	101	98	12.4.0	300	298	295	286
732	47	-44	51	-43	765	190	-196	194	-195	4.12.0	301	299	296	285
372	nil	-17	26	-17	675	180	183	182	185	12.3.3	89	-95	94	-92
651	186	191	181	184	871	174	173	168	164	877	149	-146	147	-147
561	197	197	190	197	781	184	-184	179	-185	10.8.0	72	-69	81	-74
800	746	733	714	720	855	201	198	200	192	8.10.0	364	-386	383	-387
811	236	241	241	234	774	138	-134	136	-129	886	92	-92	94	-85
741	155	-155	154	-153	10.4.0	218	-209	217	-203	992	40	37	40	34
471	165	166	166	165	4.10.0	344	-330	324	-330	10.8.2	349	365	354	367
554	161	148	157	152	864	263	-262	269	-266	8.10.2	47	-54	56	-58

Table 2. *Final parameters*

	In(1)	In(2)	O
	Cu *Kα*-refinement		
X	($\frac{1}{4}$)	0·4668 ± 0·0001	0·3905 ± 0·0013
Y	($\frac{1}{4}$)	(0)	0·1529 ± 0·0011
Z	($\frac{1}{4}$)	($\frac{1}{4}$)	0·3832 ± 0·0013
B(Å^2)	0·40 ± 0·04	0·39 ± 0·03	0·44 ± 0·21
	Mo *Kα*-refinement		
X	($\frac{1}{4}$)	0·4663 ± 0·0001	0·3912 ± 0·0012
Y	($\frac{1}{4}$)	(0)	0·1558 ± 0·0011
Z	($\frac{1}{4}$)	($\frac{1}{4}$)	0·3796 ± 0·0013
B(Å^2)	0·46 ± 0·05	0·41 ± 0·04	0·45 ± 0·22

As can be seen, the two refinements are in good agreement with one another except for the discrepancy between some of the positional parameters, which is somewhat larger than expected. This is probably due to the very high absorption corrections applied. As a result of this discrepancy, the interatomic distances calculated from the two sets of data differ from each other, and since it was not possible to determine which one of the two was the more accurate one, the average was taken.

At this point the data taken with Cu radiation can be considered as reliable as the data taken with Mo radiation. The very high absorption correction applied to the Cu radiation data is compensated in part by the extinction correction which is much larger for the Mo radiation data. This is in agreement with Burbank (1965), who emphasized that for the case of spherical crystals no improvement in accuracy can be attained by reducing the absorption correction, unless one can go below $\mu R = 1{\cdot}0$.

Comparison of the two extinction corrections

In Table 4 the secondary extinction correction factors, $1+C\beta J_o$, are reported. For brevity only the *hhl* reflections are included. Contrary to what might be expected, the extinction correction is larger for the data taken with Mo radiation, the shorter of the two radiations used. This behavior may be explained by the following considerations. In the secondary extinction correction factor, $\sqrt{1+x}$, x is given by:

$$x = g\left(\frac{Ne^2}{mc^2}\right)^2 \lambda^3 \,\frac{1}{\sin 2\theta}\,\frac{1+\cos^4 2\theta}{1+\cos^2 2\theta}\,\bar{T}|F_c|^2$$

where $g=\int W^2 d\Delta$, $W(\Delta)$ being the distribution function for the misalignment Δ of the mosaic blocks in the crystal, λ is the wavelength used, $\bar{T}$ is the mean effective path of the X-rays, $\bar{T}=A\,\dfrac{dA^*}{d\mu}$, and $|F_c|$ is the calculated structure amplitude. The only portion of the right hand side of the above equation that changes appreciably with variations in λ is $(\lambda^3/\sin 2\theta)\bar{T}$, and this may be simplified to $\lambda^2\bar{T}$ for small θ. The behavior of $\lambda^2\bar{T}$ with the variation of λ depends upon the value of μR. As λ increases, if the μR is small, λ^2 changes more quickly than $\bar{T}$ and x therefore increases. On the other hand if μR is large, as in the present case: $\mu R_{\text{Mo}}=2{\cdot}82$ and $\mu R_{\text{Cu}}=23{\cdot}5$, with increasing λ the expression $\lambda^2\bar{T}$ is dominated by the decrease of $\bar{T}$ and x also decreases.

This can be easily checked for $\theta°=0°$. In this case the equation $A=1/V\int\int\int \exp\{-\mu(p+q)\}dxdydz$ is integrable and the expression for the transmission factor is $A=3/2(\mu R)^3\{\frac{1}{2}-\exp(-2\mu R)[\frac{1}{2}+\mu R+(\mu R)^2]\}$ (see *International Tables for X-ray Crystallography*, 1959) which for large μR becomes:

$$A=\frac{3}{4}\,\frac{1}{(\mu R)^3}$$

$$\frac{dA^{-1}}{d\mu}=4R^3\mu^2$$

$$\bar{T}=\frac{3}{\mu}$$

$$x\propto\lambda^2\bar{T}=\frac{3}{\mu}\lambda^2\,.$$

For In_2O_3 $x\propto 0{\cdot}87\,.\,10^{-18}$ for Mo *Kα* and $x\propto 0{\cdot}49\,.\,10^{-18}$ for Cu *Kα*.

Table 3. *Interatomic distances and bond angles*

	Mo *Kα*	Cu *Kα*	Average
Polyhedron around In(1)			
In–O(6)	2·16$_0$ ± 0·01 Å	2·19$_2$ ± 0·01 Å	2·18 Å
O^{i}–O^{v}(6)	2·80 ± 0·02	2·83 ± 0·02	
O^{i}–O^{ii}(6)	3·29 ± 0·02	3·35 ± 0·02	
O^{i}–In–O^{v}(6)	81·0°	80·4°	
O^{i}–In–O^{ii}(6)	99·0	99·6	
Polyhedron around In(2)			
In–O^{iv}(2)	2·24$_8$ ± 0·01 Å	2·21$_0$ ± 0·01 Å	2·23 Å
In–O^{vi}(2)	2·18$_7$ ± 0·01	2·19$_2$ ± 0·01	2·19
In–O^{vii}(2)	2·13$_3$ ± 0·01	2·12$_0$ ± 0·01	2·13
O^{iv}–O^{vii}(2)	2·84 ± 0·02	2·76 ± 0·02	
O^{iv}–O^{viii}(2)	2·84 ± 0·02	2·76 ± 0.02	
O^{iv}–O^{vi}(2)	2·80 ± 0·02	2·83 ± 0·02	
O^{vi}–O^{ix}(2)	3·56 ± 0·02	3·53 ± 0·02	
O^{vi}–O^{vii}(2)	3·28 ± 0·02	3·30 ± 0·02	
O^{vii}–O^{ix}	2·91 ± 0·02	2·96 ± 0·02	
O^{iv}–O^{x}	3·76 ± 0·02	3·70 ± 0·02	
O^{vi}–O^{viii}	4·10 ± 0·02	4·10 ± 0·02	
O^{iv}–In–O^{vi}(2)	78·4°	79·9°	
O^{vi}–In–O^{x}(2)	79·6	77·8	
O^{iv}–In–O^{vii}(2)	80·7	79·3	
O^{vi}–In–O^{vii}(2)	98·6	99·7	
O^{vii}–In–O^{ix}(2)	111·0	109·6	
O^{iv}–In–O^{x}	113·3	113·5	
O^{vi}–In–O^{viii}	139·3	138·8	
O^{vii}–In–O^{ix}	86·1	88·6	
Tetrahedron around the oxygen atom			
In(1)–In(2)(2)	3·34 Å	3·35 Å	
In(1)–In(2)	3·83	3·82	
In(2)–In(2)(2)	3·36	3·36	
In(2)–In(2)	3·84	3·84	
In(1)–O–In(2)	98·7°	99·1°	
In(1)–O–In(2)	126·0	124·8	
In(1)–O–In(2)	100·6	99·6	
In(2)–O–In(2)	98·6	99·7	
In(2)–O–In(2)	125·5	125·7	
In(2)–O–In(2)	100·2	102·0	

Table 4. *Secondary extinction correction factors*

	$1+C\beta J_o$	
hkl	Mo *Kα*	Cu *Kα*
200	1·01	—
211	1·05	1·00
220	1·01	—
222	1·80	1·18
400	1·47	1·10
411	1·04	1·01
332	1·04	1·01
422	1·01	1·00
440	1·42	1·13
433	1·03	1·01
600	1·02	1·00
442	1·00	1·00
611	1·04	1·01
444	1·15	1·05
633	1·02	1·00
552	1·00	1·00
800	1·16	1·06
554	1·01	1·00
644	1·01	1·00
822	1·02	1·00
660	1·00	1·00
662	1·09	1·04
833	1·01	1·00
556	1·02	1·00
664	1·00	1·00
844	1·06	1·02
10,0,0	1·02	1·00
10,1,1	1·01	1·00
772	1·00	1·00
10,2,2	1·05	1·01
666	1·03	1·01
855	1·01	1·00
774	1·01	1·00
10,3,3	1·01	1·00
880	1·03	1·01
10,4,4	1·02	1·00
882	—	1·00
772	1·00	1·00
866	1·00	1·00
12,0,0	1·02	1·00
884	1·01	1·00
12,1,1	1·00	1·00
10,5,5	1·00	1·00
12,2,2	1·02	1·00
12,3,3	1·00	1·00
877	1·00	1·00
886	1·00	1·00
992	1·00	1·00

Interatomic distances and angles

The positional parameters reported in Table 2 were used to calculate the interatomic distances and angles given in Table 3. These values and the standard deviations for the distances were computed by using Busing & Levy's ORFFE program. Individual standard deviations were not calculated for the angles, but an estimate of the standard deviation of an O–In–O angle is 0·7° and of an In–O–In angle is 0·5°.

Description of the structure

The *C* modification structure has been described by Zachariasen (1927) as being closely related to the structure of CaF_2 from which it can be derived by removing one-quarter of the anions and then rearranging the atoms. There are two crystallographically nonequivalent indium atoms and only one type of oxygen atom. The indium atoms are 6-coordinated, while the oxygen is 4-coordinated. The coordination of the metal atoms is shown in Fig. 1. Each In(1) is surrounded by six equidistant oxygen atoms (In–O = 2·18 Å) which lie nearly at the corners of a cube with two body-diagonally opposite corners unoccupied. Also each In(2) is surrounded by six oxygen atoms which lie nearly at the corners of a cube, but in this case two face-diagonally opposite corners are unoccupied. In this polyhedron, there are three different sets of In–O distance, (2) 2·13 Å, (2) 2·19 Å, (2) 2·23 Å. The average of these three distances is 2·18 Å, which seems to be the value of the In–O distance for 6-coordinated indium. Because each of the three sets of oxygen atoms is affected differently by the absence of the repulsive forces that would come from the two unoccupied corners, one should expect the three bond lengths In(2)–O to be different. The atom O^{vii} is separated from both unoccupied corners by an edge of the imaginary cube, atom O^{vi} is separated from one of these corners by an edge and is separated from the other by a body-diagonal of the same cube, while atom O^{iv} is separated from either corner by a face diagonal. In other words the repulsive forces among the three sets of oxygen atoms around In(2) increase in going from O^{iv} to O^{vi} to O^{vii} and accordingly the In(2)–O^{iv} distance should be the largest of the three and the In(2)–O^{vii} the smallest as was found in the present study.

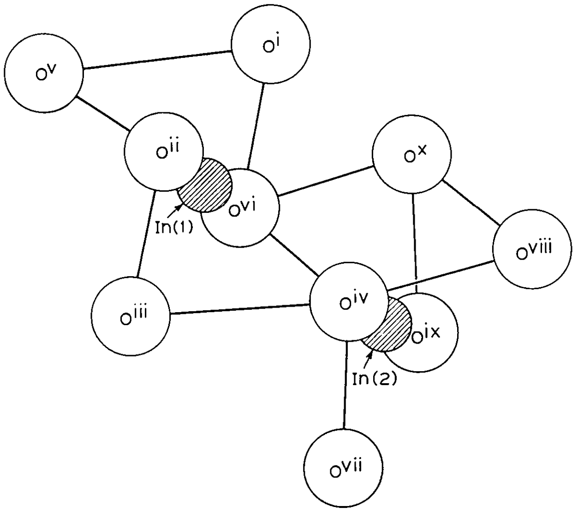

Fig. 1. The coordination arrangement around the indium atoms.

This feature should be common to all the sesquioxides with the *C* modification structure. Those which have been refined are: Ho_2O_3, Mn_2O_3, Y_2O_3, Er_2O_3, Yb_2O_3, Pr_2O_3 and $(Fe,Mn)_2O_3$. The metal–oxygen distances present in these structures are compared in Table 5. It can be seen that the feature discussed above has been observed only in Ho_2O_3. It has also been observed in Pr_2O_3 but in this case the average of the Pr(2)–O distances is much shorter than the Pr(1)–O distance. The failure to reveal this feature by the previous studies may be due to the fact that their refinements were based on powder data.

Possible existence of a high-pressure phase of In_2O_3

Recently Hoekstra & Gingerich (1964), have shown that the *B* modification of yttrium and of the rare-earth sesquioxides can be obtained from the *C* modification by applying high pressure (25–40 kbar) and high temperature (900–1050°) and quenching to ambient conditions. It seems possible that In_2O_3 will undergo a similar phase transition. A powder sample of In_2O_3 was subjected to 40 kbar and 850° using a piston-cylinder device. After quenching, X-ray powder analysis showed that In_2O_3 still had the *C* modification structure. Further work is contemplated to see if other modifications of In_2O_3 exist.

Table 5. *Cation-oxygen distances* (Å) *in C sesquioxides*

		M(1)–O		M(2)–O	
In_2O_3	Present work	2·18	2·23	2·13	2·19
Mn_2O_3	Fert (1962)	2·11	2·18	2·02	2·21
$(Fe, Mn)_2O_3$	Dachs (1956)	2·01	2·24	1·90	1·92
Y_2O_3	Fert (1962)	2·25	2·34	2·27	2·25
Pr_2O_3*		2·47	2·46	2·28	2·40
Ho_2O_3	Fert (1962)	2·27	2·33	2·20	2·31
Er_2O_3	Fert (1962)	2·28	2·33	2·23	2·20
Yb_2O_3	Fert (1962)	2·25	2·31	2·23	2·21

* These values were calculated from the values for the positional parameters quoted by Eyring & Baenziger (1962).

The writer wishes to thank J.P. Remeika and E.G. Spencer for making this work possible by supplying the crystals of In_2O_3, S.C. Abrahams for suggesting the use of Mo $K\alpha$ radiation, Mrs V.B. Compton, R.D. Burbank and D.B. McWhan for their comments on this manuscript and Professor W.H. Zachariasen for many valuable discussions.

References

Burbank, R. D. (1965). *Acta Cryst.* **18**, 88.

Busing, W. R. & Levy, H. A. (1959). ORNL Report 59-12-3. Oak Ridge National Laboratory, Tennessee.

Busing, W. R., Martin, K. O. & Levy, H. A. (1962). ORNL Report TM-305. Oak Ridge National Laboratory, Tennessee.

Cromer, D. T. (1965). *Acta Cryst.* **18**, 17.

Cromer, D. T. & Waber, J. T. (1965). *Acta Cryst.* **18**, 104.

Dachs, H. (1956). *Z. Kristallogr.* **107**, 370.

Eyring, L. & Baenziger, N. C. (1962). *J. Appl. Phys.* **33**, 428.

Fert, A. (1962). *Bull. Soc. franç. Miner. Crist.* **85**, 267.

Hoekstra, H. R. & Gingerich, K. A. (1964). *Science*, **146**, 1163.

International Tables for X-ray Crystallography (1959). Vol. II. Birmingham: Kynoch Press.

Pauling, L. & Shappell, M. D. (1930). *Z. Kristallogr.* **75**, 128.

Remeika, J. P. & Spencer, E. G. (1964). *J. Appl. Phys.* **35**, 2803.

Roth, R. S. (1957). *J. Res. Nat. Bur. Stand.*, **58**, 75.

Zachariasen, W. H. (1927). *Norsk Geol. Tidssk.* **9**, 310.

Zachariasen, W. H. (1963). *Acta Cryst.* **16**, 1139.

Acta Cryst. (1966). **20**, 728

The Crystal Structure of Tutton's Salts.
IV. Cadmium Ammonium Sulfate Hexahydrate

By H. Montgomery,

Canadian Services College, Royal Roads, Victoria, B.C., Canada

and E. C. Lingafelter,

Department of Chemistry, University of Washington, Seattle, Washington 98105, *U.S.A.*

(*Received* 27 *September* 1965)

The crystal structure of cadmium ammonium sulfate hexahydrate, $Cd(NH_4)_2(SO_4)_2 . 6H_2O$, has been determined by a three-dimensional X-ray analysis with the use of Cu $K\alpha$ radiation ($\lambda = 1\cdot5418$ Å). The crystals are monoclinic, space group $P2_1/a$, with 2 molecules per unit cell. The cell dimensions are $a = 9\cdot43$, $b = 12\cdot82$, $c = 6\cdot29$ Å; $\beta = 106°52'$. The water molecules are arranged about the cadmium ion in an almost regular octahedron, the average metal–oxygen distance being 2·28 Å.

Introduction

Cadmium ammonium sulfate hexahydrate is the only reported Tutton salt in which the metal ion belongs to the second long period in the periodic system. Its structure was therefore examined to see if it followed the pattern of the other Tutton's salts whose structures have already been established (Montgomery & Lingafelter, 1964*a*, 1964*b*, 1966).

Experimental

The procedure followed was essentially that for the isomorphous zinc salt (Montgomery & Lingafelter, 1964*a*) except that the crystal needle was ground to approximate a cylinder along *c* ($\mu = 78\cdot5$ cm^{-1}; $\mu R = 0\cdot40$). The cell dimensions were determined from rotation and zero-level (*hk*0) Weissenberg photographs (calibrated with $a_0 = 5\cdot6387$ Å for NaCl) and a precession photograph of the a^*c^* net (Mo $K\alpha$ radiation, $\lambda = 0\cdot7107$). The results and their estimated standard deviations are $a_0 = 9\cdot433 \pm 0\cdot010$, $b = 12\cdot823 \pm 0\cdot015$, $c = 6\cdot286 \pm 0\cdot006$ Å, $\beta = 106°52' \pm 6'$. Systematic absences: *h*0*l* when *h* is odd; 0*k*0 when *k* is odd; space group $P2_1/a$, $Z = 2$.

The raw intensities were collected by photometer from singly-integrated equi-inclination Weissenberg photographs (*hk*0 through *hk*4) and were corrected for Lorentz and polarization factors and for absorption after Bond's (1959) method. The resulting structure factors were then scaled by levels to correspond to the calculated values, using the parameters of the isomorphous zinc salt. (It should be recognized that this procedure precludes physical interpretation of the anisotropic thermal parameters.) In all, 1136 reflections were used, of which 162 were below minimum observed value and 20 were given zero weight in the refinement because of secondary extinction effects. The intensities of the remainder varied from 1 to 1300.

The initial atomic parameters were taken from the isomorphous zinc salt for the heavy atoms and from the magnesium salt (Montgomery & Lingafelter, 1964*b*)