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The Crystal Structure of Eu_3O_4*

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The crystal structure of trieuropium tetroxide, Eu_3O_4, has been determined from single-crystal X-ray diffraction data. This compound, containing both divalent and trivalent europium ions, is isomorphous with $CaFe_2O_4$. It crystallizes in the orthorhombic system, space group *Pnam*. The unit cell has dimensions $a=10{\cdot}085$, $b=12{\cdot}054$, $c=3{\cdot}502$ Å, and contains four formula units. The structure is layered along the short *c* axis, having all atoms on mirror planes at $z=\frac{1}{4}$ and $z=\frac{3}{4}$. Least-squares refinement of *x* and *y* positional parameters and isotropic temperature factors was based on 955 observed independent *hk*0 and *hk*1 reflections, and established the structure with a final *R* of 0·089. The coordination of oxygens around trivalent europium is sixfold, forming a distorted octahedron around each Eu^{3+} ion. Around divalent europium the coordination is eightfold, with each Eu^{2+} ion lying at the center of a triangular prism of six oxygen atoms. Two oxygen atoms lying out from the centers of two of the prism faces complete the coordination.

Introduction

In the search for more efficient nuclear reactor control materials, ceramic compounds containing some of the rare earth ions having high neutron capture cross sections have been studied under conditions simulating possible reactor environments. During high-temperature tests of monoclinic europium sesquioxide (Eu_2O_3) under reducing conditions, it was found that this normally yellowish-white colored oxide could be reduced to a dark red-brown to blackish material. Powder X-ray diffraction patterns showed that this material was not the NaCl-type cubic divalent monoxide, EuO, reported by Eick, Baenziger & Eyring (1956), but indicated a more complex structure. Subsequent single-crystal studies indicated that this new compund was orthorhombic, having approximate unit-cell dimensions of $a=10{\cdot}07$, $b=12{\cdot}01$, and $c=3{\cdot}50$ Å, and had a measured density of 8·03 g.cm^{-3}. By comparison of this measured density with that calculated with various possible combinations of europium and oxygen in the unit cell, the compound was deduced to be trieuropium tetroxide, Eu_3O_4, containing both divalent and trivalent cations.

The existence of a compound corresponding to the composition Eu_3O_4 was first reported by Achard (1960) He obtained an intermediate phase, having an oxygen to europium ratio of approximately 1·3, during his studies of carbon reduction of Eu_2O_3 to EuO. Later, Bärnighausen & Brauer (1962) reported the preparation of Eu_3O_4 by heating an equimolar mixture of EuO and Eu_2O_3 at 900°C in an inert atmosphere. Although these authors reported the lattice parameters and space group for Eu_3O_4 and the isomorphous compound $SrEu_2O_4$, and showed that these compounds are structurally related to calcium ferrite, $CaFe_2O_4$ (Decker & Kasper, 1957), they did not carry out the complete crystal structure analysis. Recently, Schieber & Holmes (1964) prepared mixtures of Eu_3O_4 in Eu_2O_3 during attempts to reduce the sesquioxide in carbon monoxide atmosphere.

Preparation of Eu_3O_4

For the present study, Eu_3O_4 was prepared by several methods. The first preparation occurred accidentally when Eu_3O_4 was formed as a granular black layer approximately one millimeter thick surrounding a core of Eu_2O_3 which had been hot-pressed in a graphite die at 3·5 kg.cm^{-2} (50 lb.in^{-2}) at 1700°C. Single-crystal fragments chipped from this layer were used for the present structure analysis.

Subsequent to this initial preparation, a reliable method of producing single-phase Eu_3O_4 was developed consisting of hydrogen reduction of the sesquioxide or the hydroxide. This method, which involved heating Eu_2O_3 or $Eu(OH)_3$ in a hydrogen atmosphere at 1650°C, yielded coarsely polycrystalline black chunks of Eu_3O_4. Single-crystal fragments from these chunks appeared dark red under the polarizing miscroscope, and were found to be biaxial with refractive indices near 2·12. Grinding chunks of Eu_3O_4 produced a red-brown powder.

Preliminary analyses

Preliminary Weissenberg and precession photographs established the orthorhombic symmetry, and showed reflections present for the following conditions:

*h*00, 0*k*0, 00*l* only when $h, k, l=2n$
*h*0*l* only when $h=2n$
0*kl* only when $k+l=2n$
*hk*0, *hkl* without regular extinctions.

These conditions are satisfied by space groups $Pna2_1$ (No. 33) and *Pnam* (*Pnma*, No. 62). Assignment of the

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centrosymmetric space group was based upon consideration of the reflection intensities. As pointed out by Bärnighausen & Brauer (1962), alternate layers along the short *c* axis exhibit similar intensities, thus indicating that all atoms must lie on two planes separated by $\frac{1}{2}$ in *z*. This condition is fulfilled only by the special fourfold positions (*c*) in the space group *Pnam*, where all atoms have $z=\frac{1}{4}$ or $\frac{3}{4}$.

Lattice parameters derived from the single-crystal films were refined by means of powder data. The Eu_3O_4 powder pattern was obtained with iron *Kα* radiation on a Norelco diffractometer (Rau, 1964). Indexed back-reflection lines from that pattern were used to calculate the lattice parameters, using the computer program of Mueller, Heaton & Miller (1960). The values obtained are listed in Table 1, and are seen to agree closely with those reported by Bärnighausen & Brauer (1962). With these values, and assuming four formula units per unit cell, the theoretical density of Eu_3O_4 is 8·11 g.cm^{-3}, in good agreement with the measured value of 8·03 g.cm^{-3}.

Table 1. *Lattice parameters of* Eu_3O_4

	This study	Bärnighausen & Brauer (1962)
a	10·085 ± 0·002 Å	10·094 ± 0·003 Å
b	12·054 ± 0·002	12·068 ± 0·003
c	3·502 ± 0·001	3·500 ± 0·001

Computing procedures

For the structure analysis of Eu_3O_4, the 'X-ray 63' crystal structure calculation system of Stewart & High (1964) was used on an IBM 7094 computer. This system is composed of an integrated set of computer programs for preparing the data and making the many different calculations involved in crystal structure analysis. Interconnection of the links of the system makes it possible to use the programs individually or in continuous sequence, with the output of one program serving as input to the next.

Collection of data

Although a preliminary set of Weissenberg photographs was obtained using copper radiation, these photographs were felt to be unsuitable for the structure analysis, since the extremely high absorption coefficient ($\mu=3033{\cdot}95$ cm^{-1}) of Eu_3O_4 for Cu *Kα* radiation would cause large errors in measured intensities. Accordingly, Mo *Kα* radiation was chosen ($\mu=438{\cdot}75$ cm^{-1}). The crystal used for intensity collection was approximately needle-shaped, being elongated along the *c* axis. Its cross-section was nearly square, with an average radius of 0·005 cm.

Equi-inclination Weissenberg photographs were taken of the (*hk*0) and (*hk*1) levels. Since the preliminary analysis had indicated a layered structure with all atoms on mirror planes at $z=\frac{1}{4}$ and $z=\frac{3}{4}$, no *z* parameter refinement was planned, and additional level data were not collected.

Intensities were collected with the use of the multiple film technique. Two film packs, composed of three sheets of Kodak No-Screen film separated by nickel foil, were exposed for 48 hours and 3 hours, respectively, for each level of data. Intensities were estimated visually by comparison with a calibrated intensity strip prepared using the 920 reflection of the crystal under investigation. All zones of the Weissenberg films were read, and intensities of crystallographically equivalent reflections were averaged. In all, 955 of a possible 1463 crystallographically different reflections had measurable intensities.

The averaged intensities were then correlated and scaled to the most heavily exposed film. For (*hk*0) and (*hk*1) films the average inter-film correlation factors within the film packs were 2·75 and 2·68, respectively, and the inter-pack factors were 14·68 and 13·80, respectively. The intensities were converted to experimental structure factors, F_o, in the usual way, with corrections being applied for the Lorentz and polarization effects, as well as for sample absorption. The absorption corrections used were based on a cylindrical crystal having $\mu R=2{\cdot}2$ (Bond, 1959).

The trial structure

In their work on Eu_3O_4, Bärnighausen & Brauer (1962) found that the strong intensities showed general agreement with the strong reflections of calcium ferrite, $CaFe_2O_4$ (Decker & Kasper, 1957), thus indicating that the heavy atoms in Eu_3O_4 were probably located in positions similar to those occupied by the metal atoms in the reported structure of that compound. In the present study, good intensity agreement was found not only between the strong reflections, but also between many of the weaker reflections as well. Based on this agreement, a trial Eu_3O_4 structure containing trivalent europium ions in the iron positions and divalent europium ions in the calcium positions of $CaFe_2O_4$ was proposed.

To check this trial structure, calculations of structure factors and Fourier summations were made with the unit cell containing only europium atoms, using an over-all isotropic temperature factor of $B=0{\cdot}55$ Å^2 and the scattering factors of Cromer & Waber (1965). Fourier maps appeared reasonable, and sections at $z=\frac{1}{4}$ and $\frac{3}{4}$ showed not only the three strong europium peaks of the asymmetric unit, but also showed evidence of four weak peaks at locations equivalent to oxygen positions in $CaFe_2O_4$. One anomalous intensity spike was present at a location related to that of the Eu(3) atom by a translation of $y\pm\frac{1}{2}$, but this was removed by subsequent refinement. The agreement index at this time, calculated with no oxygen atoms in the cell, was $R=0{\cdot}34$.

The refinement

Refinement was carried out with the X-ray 63 system version of the Busing, Martin & Levy (1962) full-matrix least-squares program, ORFLS. The function minimized was $\Sigma w(F_o-F_c)^2$, with $w=50/F_o$ when $F_o>50$ and $w=1$ when $F_o\le 50$. Unobserved reflections were entered as the minimum observable threshold values, and were weighted $w=1$ when $F_c>F_{\min}$ and $w=0$ when $F_c<F_{\min}$. Refinement was carried out on 23 variables, including the x, y, and B parameters for each of the seven atoms in the asymmetric unit, and two scale factors for the two levels of data. Starting x and y positional parameters were derived from the Fourier map, and individual isotropic temperature factors $B=0{\cdot}55$ Å^2 were assigned to each atom. Ionic scattering factors were used, with those for Eu^{2+} and Eu^{3+} being taken from Cromer & Waber (1965), and those for O^{2-} being taken from Suzuki (1960).

The R value of the observed reflections with oxygen ions inserted in the lattice was 0·325; this was reduced to 0·195 after two least-squares cycles. Shifts in all parameters were appreciable, especially for the oxygen temperature factors. A Fourier map computed at this time showed sharpening of the electron density peaks, and reduction of the anomalous intensity spike to a negligible value.

Eight additional least-squares cycles produced convergence to an R of 0·095. A Fourier map computed at this time was quite similar to the one computed with $R=0{\cdot}195$, except that the anomalous spike was completely absent.

At this point, it was noticed that low-angle reflections with $(\sin\theta)/\lambda<0{\cdot}30$ were systematically stronger than their calculated F_c values. Inspection of the Weissenberg films showed this to be related to a noticeable background which fell off abruptly at this angle. Accordingly, the 41 observed reflections within the affected range were given an empirical correction derived from a plot of their F_c/F_o ratios. Also at this time, nine reflections which were judged to be affected by secondary extinction were given zero weight. In addition, the 400 and 240 reflections, which lay on strong white radiation streaks, were also weighted zero. Two additional cycles of least-squares with the corrected data produced only slight changes in the parameters, and lowered R to 0·089.

The final parameters derived from the last least-squares cycle are listed in Table 2, together with their errors, which were derived from the diagonal elements of the inverse least-squares matrix. All parameter shifts during the last least-squares cycle were less than $0{\cdot}12\sigma$, the average shift/error ratio being 0·039. The observed structure factors are compared with those calculated from the final parameters in Table 3. The final R, omitting unobserved reflections, was 0·089, while the weighted R was 0·119 and R of the unobserved reflections was 0·091.

Two types of Fourier map were computed with the final parameters listed in Table 2, one being a difference map and the other a standard electron density map. The difference map showed that all ions were located at positions with nearly zero gradient, and no areas of appreciable electron density remained in the unit cell. As expected, the standard electron density map was little different from the one computed when R was 0·095.

Discussion

Differentiation of the cation positions

As mentioned previously, assignment of the Eu^{2+} and Eu^{3+} positions was based on the cation locations in $CaFe_2O_4$. These ions could not be differentiated in the final electron density map, even though ionic scattering factors were used, but their assignments were verified by packing considerations in the final structure. Fig. 1 shows a cross section of the structure at $z=\frac{1}{4}$, with the ions drawn to the same scale as the cell edges. Eu^{2+} and Eu^{3+} radii of 1·17 and 0·95 Å, respectively, were calculated from the lattice parameters of EuO and cubic-phase Eu_2O_3 (Rau, 1964). These calculations were made assuming an O^{2-} radius of 1·40 Å (Pauling, 1960), and assuming europium–oxygen contact in the EuO and Eu_2O_3 structures. As shown by Fig. 1, an interchange of the divalent cation, Eu(3), for either of the trivalent cations, Eu(1) and Eu(2), would be impossible without changing some of the positional parameters.

A further check on the cation position assignments was made by means of a cursory X-ray study of the isomorphous compound $SrEu_2O_4$ (Glasser, Glasser & Schieber, 1965), which contains strontium in place of the divalent europium. A sample of this material produced a powder diffraction pattern which was found to be almost identical with that of Eu_3O_4, the only notable differences being in the intensities of some of the lines. A set of 32 $SrEu_2O_4$ powder reflections which could be unequivocally indexed with unique indices was used to carry out three successive structure factor calculations, with the Sr^{2+} ion successively substituted in each of the three possible europium locations. Positional and thermal parameters listed in Table 2 were used for these calculations, and Sr^{2+} scat-

Table 2. *Final parameters for* Eu_3O_4

Eu(1) and Eu(2) are the trivalent ions. Eu(3) is the divalent ion.

	x	$\sigma(x)$	y	$\sigma(y)$	z	B	$\sigma(B)$
Eu(1)	0·4280	0·0001	0·6140	0·0001	0·250	0·476	0·008
Eu(2)	0·4136	0·0001	0·1106	0·0001	0·250	0·466	0·008
Eu(3)	0·2481	0·0001	0·3525	0·0001	0·250	0·594	0·009
O(1)	0·2150	0·0013	0·6824	0·0011	0·250	0·845	0·143
O(2)	0·1334	0·0011	0·9841	0·0009	0·250	0·606	0·111
O(3)	0·0055	0·0014	0·2151	0·0012	0·250	0·947	0·161
O(4)	0·4297	0·0013	0·9207	0·0012	0·250	0·843	0·139

Table 3. *Observed and calculated structure factors*

Each group of three columns list h, $10F_o$, and $10F_c$ respectively. E indicates reflections affected by extinction. * indicates unobserved reflections whose $10F_o$ are listed as ten times the minimum observable threshold.

H,0,0		
4	774	511
6	4577E	-5041
8	399	-322
10	557	-572
12	2357E	2721
14	468	453
16	724	610
18	1373	-1320
20	257	-135
22	421	-373
24	568	599
26	126*	-33
28	187	240
H,1,0		
3	331	334
4	431	-445
5	324	321
6	651	-644
7	155*	144
8	485	-422
9	802	-810
10	179*	157
11	535	-576
12	760	763
13	199*	11
14	361	395
15	853	815
16	212*	14
17	550	526
18	770	-673
19	213*	32
20	314	-376
21	644	-527
22	192*	-126
23	440	-397
24	478	423
25	146*	-116
26	245	276
27	264	329
28	71*	112
H,2,0		
2	925	987
3	4432E	-5809
4	1378	-1336
5	402	-388
6	156	-174
7	559	-519
8	630	-703
9	3208E	3609
10	247	309
11	209	291
12	193*	-43
13	549	575
14	280	386
15	2009	-1902
16	290	-191
17	294	-164
18	215*	-40
19	570	-456
20	209*	-241
21	964	856
22	192*	118
23	179*	38
24	163*	-40
25	282	272
26	125*	85
27	262	-356
28	69*	-65
H,3,0		
1	100*	-82
2	108*	76
3	881	-831
4	249	-289
5	140*	-109
6	994	-910
7	158*	61
8	438	-470
9	782	726
10	213	239
11	188*	96
12	894	969
13	200*	-34
14	583	665
15	514	-592
16	212*	-27
17	294	-310
18	885	-723
19	213*	-93
20	639	-588
21	436	425
22	191*	-58
23	244	262
24	463	496
25	144*	86
26	391	444
27	209	-288
28	66*	114
H,4,0		
0	3728E	-5596
1	1167	-1352
2	492	-288
3	127*	-79
4	136*	-208
5	1481	-1408
6	4254E	4461
7	1180	1138
8	680	693
9	176*	25
10	463	483
11	876	992
12	2111	-2410
13	636	-680
14	252	-328
15	209*	81
16	337	-419
17	565	-517
18	1291	1150
19	319	346
20	208*	160
21	200*	-48
22	411	367
23	187	270
24	492	-492
25	142*	-145
26	122*	-22
27	98*	39
H,5,0		
1	433	428
2	129*	88
3	340	-308
4	142*	119
5	662	-579
6	278	285
7	383	391
8	172*	95
9	818	880
10	185*	-38
11	662	741
12	479	-514
13	202*	-75
14	206*	-145
15	820	-743
16	213*	-47
17	667	-657
18	395	422
19	212*	-45
20	207*	102
21	630	617
22	188*	87
23	548	564
24	238	-278
25	140*	90
26	119*	-110
27	323	-368
H,6,0		
0	313	-242
1	328	330
2	2507	-2566
3	4209E	4390
4	2021	1863
5	608	558
6	371	288
7	168*	98
8	1626	1781
9	2498	-2680
10	1032	-1111
11	513	-593
12	199*	-174
13	324	-363
14	1040	-1005
15	1511	1388
16	525	545
17	280	336
18	214*	-43
19	274	293
20	540	539
21	640	-672
22	186*	-262
23	172*	-115
24	155*	80
25	137*	-218
26	297	-285
27	136	248
H,7,0		
1	288	288
2	146*	-28
3	150*	-23
4	155*	123
5	378	-359
6	728	755
7	259	-248
8	566	574
9	451	-437
10	190*	-165
11	195*	-36
12	819	-923
13	205*	18
14	884	-781
15	290	379
16	214*	136
17	215*	-6
18	780	701
19	210*	-2
20	722	682
21	292	-280
22	183*	1
23	169*	-39
24	489	-443
25	133*	-85
26	485	-511
27	98	153
H,8,0		
0	3030E	3194
1	2318	2412
2	824	761
3	443	441
4	544	-459
5	2085	2138
6	2469	-2560
7	1664	-1680
8	732	-656
9	187*	-124
10	193*	-129
11	1579	-1487
12	1426	1527
13	977	940
14	473	461
15	213*	48
16	295	238
17	994	916
18	860	-784
19	541	-494
20	276	-250
21	192*	37
22	180*	-164
23	442	-430
24	321	305
25	177	267
26	107*	74
27	79*	-67
H,9,0		
1	240	239
2	181	-131
3	333	371
4	168*	-67
5	508	506
6	293	-240
7	422	-236
8	376	267
9	616	-684
10	196*	48
11	822	-726
12	205*	169
13	285	251
14	211*	-153
15	857	810
16	215*	37
17	768	742
18	212*	-112
19	207*	-52
20	199*	51
21	565	-545
22	176*	-31
23	536	-576
24	144*	114
25	124*	-45
26	101*	-35
27	233	334
H,10,0		
0	874	832
1	645	-618
2	2300	2462
3	2003	-2199
4	1902	-2057
5	887	-997
6	394	-467
7	207	247
8	1757	-1931
9	1285	1477
10	1106	1313
11	712	790
12	231	217
13	210*	-56
14	1303	1325
15	841	-740
16	677	-665
17	552	-459
18	210*	-32
19	204*	-130
20	668	-703
21	212	285
22	394	359
23	214	205
24	138*	-42
25	118*	120
26	291	326
H,11,0		
1	381	-360
2	195	245
3	177*	-69
4	179*	-214
5	204	204
6	534	-597
7	232	243
8	523	-546
9	198*	4
10	226	291
11	230	-278
12	662	654
13	211*	-112
14	728	665
15	215*	-76
16	215*	-132
17	212*	177
18	577	-574
19	202*	-26
20	677	-672
21	181*	62
22	167*	8
23	151*	-125
24	407	402
25	112*	12
26	406	493
H,12,0		
0	1196	-1206
1	2078	-2191
2	875	-980
3	640	-700
4	490	562
5	2046	-2235
6	886	940
7	1416	1550
8	741	808
9	513	579
10	229	-310
11	1557	1575
12	589	-637
13	912	-887
14	632	-582
15	247	-225
16	214*	37
17	893	-903
18	236	240
19	403	442
20	364	309
21	176*	9
22	161*	20
23	466	512
24	126*	-75
25	143	-221
26	77*	-158
H,13,0		
1	185*	-145
2	417	384
3	210	-302
4	190*	154
5	192*	-198
6	195*	-68
7	297	362
8	225	-324
9	575	662
10	207*	-21
11	411	546
12	212*	60
13	246	-268
14	215*	271
15	586	-602
16	212*	88
17	696	-647
18	202*	-58
19	194*	127
20	183*	-214
21	495	454
22	155*	-32
23	514	566
24	119*	80
25	96*	-5
H,14,0		
0	915	-917
1	843	935
2	1655	-1831
3	479	550
4	1429	1654
5	839	925
6	746	825
7	493	-550
8	1698	1728
9	284	-295
10	1124	-1044
11	839	-758
12	359	-381
13	247	169
14	1133	-1133
15	245	132
16	668	609
17	595	514
18	198*	162
19	189*	-57
20	654	661
21	164*	-16
22	272	-272
23	196	-255
24	110*	-14
25	86*	13
H,15,0		
1	219	238
2	197*	-11
3	198*	-77
4	199*	251
5	225	-308
6	203*	266
7	205*	-123
8	422	417
9	240	190
10	212*	-284
11	293	338
12	480	-523
13	215*	78
14	606	-569
15	242	-185
16	207*	179
17	201*	-294
18	464	458
19	183*	-51
20	479	479
21	156*	151
22	140*	-61
23	167	228
24	294	-303
25	72*	43
H,16,0		
0	201*	-43
1	1730	1617
2	906	791
3	1190	1101
4	773	-710
5	1672	1587
6	207*	16
7	1145	-1113
8	908	-842
9	831	-732
10	321	400
11	1124	-1259
12	215*	-150
13	550	544
14	594	580
15	286	390
16	279	-222
17	819	820
18	187*	125
19	241	-288
20	300	-363
21	148*	-146
22	132*	62
23	372	-420
24	90*	-120
H,17,0		
1	205*	177
2	235	-234
3	206*	184
4	207*	-229
5	208*	44
6	210*	158
7	242	-335
8	291	353
9	293	-461
10	215*	185
11	295	-351
12	294	-266
13	291	254
14	287	-349
15	344	422
16	199*	-57
17	466	457
18	247	243
19	169*	-148
20	212	277
21	302	-330
22	122*	64
23	362	-427
24	147	-150
H,18,0		
0	1339	1133
1	853	-716
2	1423	1278
3	511	487
4	1024	-981
5	881	-789
6	1022	-937
7	434	511
8	1149	-1128
9	323	-318
10	621	639
11	686	594
12	632	633
13	288	-302
14	860	825
15	274	280
16	264	-298
17	414	-364
18	237	-281
19	160*	141
20	489	-476
21	178	-226
22	112*	138
23	230	253
H,19,0		
1	211*	-123
2	212*	-55
3	212*	147
4	213*	-296
5	321	326
6	294	-282
7	215*	60
8	215*	-149
9	323	-262
10	293	318
11	291	-320
12	287	328
13	206*	-41
14	275	293
15	421	345
16	255	-174
17	295	331
18	318	-311
19	151*	100
20	333	-366
21	286	-280
22	99*	65
23	149	-262
H,20,0		
0	690	573
1	875	-803
2	673	-620
3	1233	-1155
4	466	525
5	1099	-983
6	605	-581
7	578	534
8	665	565
9	1042	872
10	260	-360
11	847	819
12	450	474
13	275	-308
14	486	-462
15	495	-483
16	178*	191
17	542	-532
18	314	-334
19	140*	82
20	316	286
21	218	192
22	85*	-98
H,21,0		
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2	295	238
3	215*	-105
4	215*	149
5	215*	-3
6	246	-275
7	214*	248
8	213*	-260
9	211*	206
10	208*	-86
11	205*	155
12	368	327
13	194*	-237
14	256	306
15	244	-293
16	168*	96
17	180	-249
18	311	-302
19	129*	116
20	169	-312
21	140	208
H,22,0		
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1	395	438
2	740	-667
3	889	-753
4	477	486
5	414	394
6	1144	985
7	317	-349
8	614	625
9	748	671
10	249	-192
11	365	-334
12	744	-681
13	213	224
14	530	-492
15	468	-454
16	158*	22
17	318	272
18	351	373
19	116*	-134
20	284	299
21	238	290
H,23,0		
1	213*	104
2	212*	216
3	212*	-85
4	211*	258
5	210*	-174
6	208*	157
7	206*	-36
8	204*	-25
9	301	324
10	196*	-227
11	261	316
12	211	-241
13	176*	61
14	168*	-127
15	374	-372
16	179	186
17	182	-290
18	163	205
19	102*	-62
20	99	173
H,24,0		
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1	425	323
2	465	319
3	1165	1046
4	206*	-238
5	417	401
6	805	711
7	200*	-156
8	295	-273
9	920	-782
10	187*	202
11	453	-407
12	548	-518
13	166*	-12
14	179	198
15	514	483
16	133*	-118
17	297	289
18	371	382
19	85*	62
H,25,0		
1	203*	176
2	202*	-99
3	201*	43
4	200*	-37
5	198*	-99
6	207	203
7	204	-267
8	188*	218
9	183*	-127
10	177*	26
11	170*	5
12	384	-354
13	153*	168
14	271	-280
15	137*	124
16	119*	-46
17	104*	57
18	333	343
H,26,0		
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1	195*	-92
2	194*	217
3	846	738
4	191*	-78
5	189*	-111
6	1000	-886
7	182*	115
8	352	-315
9	671	-613
10	165*	-59
11	158*	109
12	646	614
13	140*	-115
14	207	222
15	461	453
16	103*	116
17	86*	-77
H,27,0		
1	185*	-56
2	239	-189
3	183*	141
4	192	-225
5	178*	130
6	174*	-89
7	170*	6
8	165*	127
9	301	-288
10	152*	204
11	144*	-181
12	135*	113
13	125*	-16
14	114*	-29
15	299	314
16	84*	-120
H,28,0		
0	826	691
1	173*	-28
2	172*	17
3	845	-777
4	168*	47
5	165*	-124
6	624	-621
7	157*	-86
8	151*	-27
9	647	642
10	137*	-1
11	129*	133
12	487	490
13	115	153
14	95*	13
15	347	-415
H,29,0		
1	160*	-202
2	159*	37
3	157*	-7
4	154*	-48
5	151*	175
6	156	-187
7	142*	159
8	136*	-137
9	129*	51
10	121*	44
11	112*	-92
12	233	288
13	89*	-127
14	141	193
H,30,0		
0	772	-730
1	144*	-101
2	143*	-0
3	593	-566
4	138*	-95
5	135*	-119
6	590	605
7	125*	63
8	119*	46
9	475	476
10	134	167
11	92*	98
12	363	-431
H,31,0		
1	127*	-31
2	134	170
3	124*	-79
4	128	173
5	117*	-46
6	112*	10
7	107*	20
8	99*	-141
9	147	210
10	80*	-133
H,32,0		
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1	108*	-84
2	161	-197
3	449	506
4	176	180
5	97*	-15
6	423	457
7	126	163
8	168	191
H,33,0		
1	111	155
2	84*	21
3	80*	24
4	76*	72
5	126	-160
H,0,1		
4	3506E	3863
6	502	418
8	1734	-1856
10	2298	-2461
12	416	-409
14	705	765
16	1279	1185
18	460	278
20	205*	-215
22	587	-558
24	159*	-166
26	121*	0
H,1,1		
2	1546	1537
3	1621	-1658
4	1272	-1227
5	1740	1571
6	1176	1163
7	154*	-178
8	1752	-1738
9	955	917
10	178*	236
11	1042	-1130
12	1000	-1060
13	197*	-202
14	1042	1101
15	685	-741
16	209*	49
17	744	675
18	725	685
19	315	344
20	764	-654
21	587	570
22	187*	-202
23	429	-420
24	464	-481
25	212	-299
26	246	308
27	305	-378
H,2,1		
2	533	513
3	111*	169
4	544	566
5	2730	-2675
6	416	350
7	2599	-2647
8	476	-456
9	476	-458
10	297	-328
11	1085	1178
12	192*	-90
13	1346	1587
14	202*	247
15	253	301
16	209*	143
17	431	-429
18	212*	71
19	923	-851
20	205*	-36
21	197*	-156
22	187*	-44
23	174*	85
24	158*	-53
25	258	356
26	120*	40
27	96*	40
H,3,1		
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1	1992	-2281
2	1341	1281
3	1824	1741
4	129*	-85
5	2043	-1988
6	837	727
7	1019	995
8	1056	-1047
9	1218	-1244
10	452	-453
11	1269	1347
12	510	-573
13	198*	-186
14	821	872
15	763	811
16	645	647
17	887	-847
18	520	545
19	209*	18
20	514	-494
21	524	-529
22	518	-487
23	410	464
24	340	-426
25	139*	46
26	268	256
27	300	388
H,4,1		
1	1111	1153
2	3073	-3239
3	126*	36
4	3190	-3126
5	682	-612
6	316	-282
7	643	-637
8	1638	1621
9	175*	-20
10	1911	1990
11	467	480
12	402	430
13	366	397
14	580	-673
15	207*	189
16	1167	-1161
17	318	-273
18	318	-309
19	209*	-130
20	203*	217
21	195*	-101
22	492	520
23	171*	168
24	155*	103
25	137*	41
26	116*	-19
27	92*	53
H,5,1		
0	1542	1706
1	124*	116
2	1982	-1957
3	149	162
4	1479	1332
5	444	-404
6	1514	-1445
7	714	-657
8	1542	1575
9	468	-495
10	776	-824
11	622	647
12	868	948
13	769	817
14	864	-1041
15	394	441
16	289	320
17	576	-540
18	677	-663
19	770	-701
20	591	575
21	291	-387
22	183*	-84
23	254	250
24	371	398
25	470	493
26	210	-314
27	245	315
H,6,1		
1	2804	-2895
2	1775	-1656
3	380	-356
4	1346	-1272
5	1988	1841
6	312	-269
7	2313	2258
8	1042	1001
9	384	317
10	703	747
11	933	-1056
12	334	362
13	1324	-1412
14	446	-480
15	377	-350
16	409	-431
17	291	346
18	211*	-226
19	654	643
20	302	249
21	192*	201
22	181*	171
23	167*	-81
24	150*	108
25	180	-295
26	111*	-109
27	85*	-84
H,7,1		
0	142*	-98
1	1618	1659
2	146*	-24
3	1246	-1227
4	896	-807
5	1880	1792
6	185	143
7	1169	-1078
8	430	410
9	809	898
10	971	1111
11	1112	-1202
12	199*	60
13	560	626
14	392	-356
15	622	-625
16	1010	-1002
17	669	715
18	288	-274
19	282	-229
20	273	263
21	471	446
22	790	745
23	317	-389
24	270	308
25	128*	96
26	160	-155
27	207	-247
H,8,1		
1	1360	-1368
2	1947	1943
3	157*	-83
4	1981	1996
5	1422	1359
6	470	423
7	1280	1299
8	1342	-1295
9	309	345
10	1364	-1445
11	756	-824
12	387	-341
13	534	-630
14	509	569
15	210*	-214
16	868	811
17	504	469
18	209*	221
19	280	286
20	197*	-133
21	187*	203
22	321	-387
23	160*	-201
24	143*	-129
25	124*	-93
26	102*	12
27	72*	-98
H,9,1		
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1	949	-907
2	1415	1455
3	637	622
4	1276	-1315
5	171*	-124
6	1013	970
7	1203	1239
8	987	-986
9	300	-311
10	787	800
11	253	-239
12	525	-597
13	973	-1179
14	626	692
15	211*	-77
16	390	-423
17	211*	194
18	285	349
19	985	938
20	358	-397
21	184*	201
22	234	272
23	156*	-137
24	208	-222
25	562	-671
26	177	210
H,10,1		
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2	1580	1601
3	170*	12
4	1579	1622
5	1403	-1366
6	350	293
7	1512	-1547
8	1132	-1195
9	305	-357
10	1013	-1115
11	508	587
12	229	-349
13	829	914
14	663	680
15	352	360
16	441	521
17	210*	-282
18	206*	272
19	465	-484
20	262	-334
21	180*	-237
22	167*	-212
23	151*	65
24	133*	-182
25	113*	162
26	89*	151
H,11,1		
0	831	868
1	1011	-1025
2	776	-760
3	419	447
4	1056	1095
5	812	-904
6	605	-665
7	854	886
8	215	181
9	372	-437
10	1247	-1383
11	692	708
12	206*	195
13	549	-576
14	211*	59
15	331	303
16	1113	1123
17	404	-423
18	204*	-10
19	362	361
20	187*	-95
21	176*	-144
22	783	-800
23	146*	211
24	175	-145
25	146	-190
26	81*	15
H,12,1		
1	1733	1782
2	1079	-1108
3	203	182
4	1003	-1084
5	1388	-1527
6	211	-212
7	1159	-1266
8	727	730
9	299	-366
10	804	804
11	870	935
12	329	316
13	835	841
14	290	-314
15	331	385
16	427	-465
17	491	-469
18	276	-220
19	468	-430
20	183*	120
21	171*	-206
22	214	222
23	139*	237
24	166	135
25	99*	136
H,13,1		
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1	963	910
2	623	-633
3	897	-1001
4	674	724
5	415	416
6	194*	-140
7	1171	-1300
8	454	530
9	554	628
10	510	-567
11	208*	-89
12	210*	84
13	1201	1275
14	212*	-194
15	259	-241
16	504	451
17	204*	-39
18	198*	-38
19	954	-980
20	244	140
21	165*	-25
22	225	-257
23	133*	22
24	113*	19
25	495	650
H,14,1		
1	757	-793
2	1467	-1532
3	214	-190
4	1400	-1549
5	630	639
6	221	-212
7	730	753
8	965	1091
9	324	309
10	911	1088
11	331	-403
12	211	311
13	493	-458
14	668	-674
15	287	-251
16	634	-605
17	246	119
18	193*	-297
19	184*	196
20	334	341
21	217	202
22	214	242
23	125*	1
24	144	160
25	80*	-74
H,15,1		
0	987	-1032
1	378	368
2	736	722
3	196*	64
4	1164	-1229
5	316	216
6	728	790
7	422	-457
8	252	-305
9	207*	-91
10	951	1104
11	211*	-88
12	390	-462
13	431	425
14	210*	62
15	208*	103
16	1002	-976
17	197*	20
18	188*	82
19	327	-329
20	166*	-36
21	151*	-105
22	669	742
23	117*	-5
24	96*	31
H,16,1		
1	1438	-1525
2	426	413
3	201*	-223
4	448	474
5	1176	1295
6	205*	145
7	1224	1334
8	255	-241
9	257	358
10	259	-329
11	967	-892
12	260	-217
13	908	-862
14	208*	135
15	280	-312
16	244	166
17	390	412
18	250	228
19	408	413
20	158*	-35
21	143*	228
22	126*	-34
23	107*	-169
24	126	-141
H,17,1		
0	518	452
1	736	-726
2	203*	61
3	908	925
4	205*	-209
5	342	-381
6	232	-290
7	900	1000
8	210*	127
9	565	-648
10	237	315
11	212*	149
12	258	265
13	993	-991
14	205*	-57
15	246	320
16	266	-280
17	186*	-27
18	175*	-237
19	778	788
20	150*	87
21	134*	-59
22	215	263
23	97*	17
H,18,1		
1	206*	214
2	1226	1276
3	207*	87
4	1179	1264
5	209*	-163
6	235	204
7	211*	-41
8	1051	-945
9	212*	-169
10	1069	-964
11	211*	71
12	373	-299
13	206*	49
14	491	531
15	268	223
16	581	579
17	179*	1
18	252	234
19	155*	-29
20	211	-264
21	124*	-131
22	307	-278
23	84*	-5
H,19,1		
0	985	873
1	209*	67
2	557	-480
3	407	-382
4	681	659
5	211*	238
6	818	-714
7	212*	110
8	212*	206
9	482	410
10	895	-825
11	256	-335
12	345	384
13	276	-241
14	196*	-35
15	367	-378
16	736	719
17	234	262
18	218	-184
19	146*	246
20	131*	0
21	209	279
22	466	-528
H,20,1		
1	1416	1192
2	211*	32
3	212*	39
4	212*	-7
5	1145	-1017
6	212*	-112
7	1242	-1085
8	211*	-32
9	210*	-255
10	208*	-4
11	557	572
12	201*	159
13	811	722
14	190*	36
15	284	280
16	172*	65
17	222	-330
18	149*	-159
19	413	-415
20	119*	-41
21	102*	-198
22	79*	-67
H,21,1		
0	735	-541
1	546	433
2	318	313
3	740	-650
4	212*	-136
5	212*	193
6	659	542
7	684	-555
8	313	-349
9	540	490
10	204*	-118
11	200*	-34
12	521	-463
13	665	556
14	360	347
15	271	-232
16	163*	217
17	151*	10
18	318	359
19	432	-472
20	246	-253
21	87*	73
H,22,1		
1	290	256
2	1102	-931
3	211*	-28
4	1164	-970
5	210*	-169
6	208*	-211
7	207*	-162
8	800	706
9	202*	106
10	945	792
11	194*	121
12	258	238
13	248	182
14	419	-380
15	163*	-73
16	562	-499
17	140*	-71
18	126*	-187
19	152	-130
20	127	135
21	67*	105
H,23,1		
0	638	-506
1	209*	-263
2	209*	105
3	706	515
4	284	-282
5	499	-465
6	607	489
7	202*	43
8	199*	28
9	545	-476
10	396	386
11	558	463
12	347	-324
13	171*	94
14	163*	-25
15	462	430
16	407	-373
17	391	-359
18	113*	128
19	197	-194
20	74*	33
H,24,1		
1	1025	-818
2	280	-237
3	203*	-98
4	339	-294
5	721	621
6	198*	44
7	938	775
8	192*	206
9	188*	158
10	223	264
11	463	-426
12	169*	-98
13	705	-571
14	151*	-162
15	140*	-188
16	175	-173
17	114*	180
18	135	83
19	324	304
H,25,1		
0	688	474
1	198*	-67
2	450	-405
3	457	389
4	195*	165
5	193*	0
6	638	-475
7	187*	151
8	522	483
9	178*	-244
10	172*	-8
11	165*	-73
12	467	426
13	148*	-200
14	453	-431
15	127*	144
16	114*	-134
17	99*	87
18	338	-393
H,26,1		
1	453	-345
2	788	645
3	188*	-5
4	848	680
5	395	336
6	181*	111
7	359	347
8	489	-413
9	167*	3
10	701	-558
11	256	-240
12	144*	-188
13	248	-261
14	124*	198
15	112*	48
16	422	396
17	134	136
H,27,1		
0	350	298
1	247	320
2	179*	129
3	536	-413
4	175*	-33
5	460	412
6	284	-226
7	165*	-101
8	160*	-124
9	464	412
10	147*	-39
11	491	-426
12	130*	164
13	147	-95
14	108*	134
15	366	-361
16	106	92
H,28,1		
1	636	497
2	454	394
3	165*	48
4	457	397
5	418	-399
6	156*	-26
7	580	-476
8	389	-287
9	191	-128
10	345	-330
11	193	215
12	114*	-9
13	408	374
14	219	185
15	132	137
H,29,1		
0	399	-287
1	154*	-144
2	329	317
3	151*	-143
4	149*	-179
5	199	-194
6	337	287
7	136*	98
8	428	-424
9	152	136
10	116*	-12
11	146	159
12	307	-323
13	83*	-65
H,30,1		
1	450	392
2	367	-323
3	136*	5
4	475	-413
5	446	-354
6	125*	-88
7	366	-365
8	203	214
9	106*	-24
10	415	379
11	278	252
12	98	115
H,31,1		
0	122*	-87
1	167	-198
2	182	-196
3	263	232
4	207	199
5	315	-328
6	131	86
7	101*	47
8	182	201
9	222	-210
10	109	-155
H,32,1		
1	228	-256
2	412	-370
3	99*	-34
4	413	-394
5	177	198
6	85*	-56
7	282	270
8	282	311
H,33,1		
0	109	96
1	261	254
2	184	-221
3	74*	42
4	68*	90

tering factors (Cromer & Waber, 1965) were used in place of the Eu^{2+} scattering factors. The best structure factor agreement ($R=0{\cdot}17$) was obtained with Sr^{2+} in the location assigned to the divalent europium ion, Eu(3), of the Eu_3O_4 structure. The poorer agreement ($R=0{\cdot}22$ and $R=0{\cdot}21$) when Sr^{2+} was assigned to the other two possible europium locations was taken as evidence to rule out those lattice sites for possible occupancy by the divalent cation.

Bonding and coordination

A stereoscopic illustration of the Eu_3O_4 structure, suitable for three-dimensional viewing with a standard 3-D viewer, is shown in Fig. 2. This illustration was prepared by Dr C. K. Johnson of Oak Ridge National Laboratory, using his crystal structure plotting program, ORTEP (Johnson, 1965). The view is along the short *c* axis, and shows the two atom layers and their relationship to the unit cell edges. Bond lengths shown in the figure were obtained when R was 0·095, and in some cases differ slightly from the final bond lengths.

As may be deduced from Fig. 2, each europium cation is coordinated with oxygen atoms at three levels along the *c* axis, *i.e.* for europium ions with $z=\frac{1}{4}$, coordinated oxygen atoms are at $z=-\frac{1}{4}$, $\frac{1}{4}$, and $\frac{3}{4}$. The coordination polyhedra are shown in Fig. 3, where the drawings are tilted somewhat about the *x* axis to separate the projected images of oxygen ions at $z=-\frac{1}{4}$ and $z=\frac{3}{4}$. Bond lengths and angles within these polyhedra, as well as nearest europium–europium distances, are listed in Table 4. Average standard deviations of the distances are 0·001 Å for Eu–Eu, 0·011 Å for Eu–O, and 0·017 Å for O–O, while the deviations of the angles average about 0·3°.

As shown in Fig. 3(*a*) and (*b*), the trivalent europium atoms, Eu(1) and Eu(2), are coordinated to six oxygen atoms forming distorted octahedra, the Eu(2) octahedron showing the greatest deviation from regularity. Average Eu^{3+}–O^{2-} distances are 2·337 and 2·343 Å, respectively, in the Eu(1) and Eu(2) polyhedra, while average O^{2-}–O^{2-} distances are 3·295 Å in the former and 3·280 Å in the latter. Both the shortest (2·955 Å) and the longest (3·892 Å) significant oxygen–oxygen distances in Eu_3O_4 occur in the Eu(2) polyhedron. The average bond angle involving two adjacent oxygen atoms and europium is 89·9° in the Eu(1) polyhedron and 89·5° in the Eu(2) polyhedron, both very close to the undistorted octahedral value of 90°.

In the divalent Eu(3) polyhedron [Fig. 3(*c*)] the europium ion is located in the center of a triangular prism whose interfacial angles are 49·8°, 62·9°, and 67·3°. Six oxygen ions, three at $z=-\frac{1}{4}$ and three at $z=\frac{3}{4}$, make up this prism, and two additional oxygen ions, located out from the two wide faces of the prism on the $z=\frac{1}{4}$

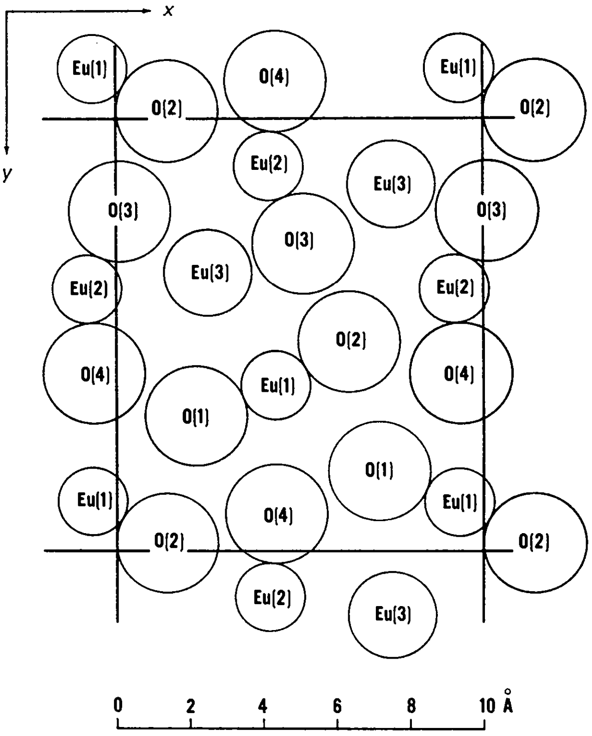

Fig. 1. Cross section of the Eu_3O_4 structure at $z=\frac{1}{4}$. The ions are drawn to the same scale as the cell edges.

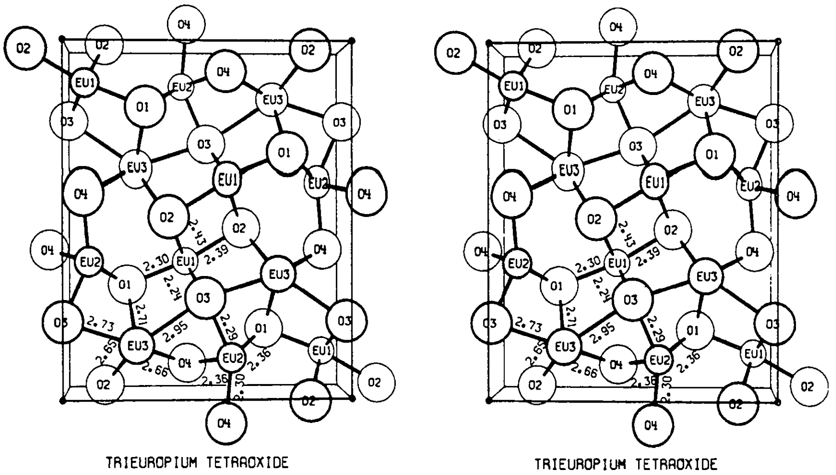

Fig. 2. Stereoscopic illustration of the Eu_3O_4 structure viewed along the *c* axis. The box represents one unit cell.

Table 4. *Bond lengths and angles in* Eu_3O_4

Primed ions have $z=\frac{3}{4}$ or $z=-\frac{1}{4}$, unprimed ions have $z=\frac{1}{4}$. The second column in each grouping indicates the bond or angle multiplicity. Average standard deviations of the distances are 0·001 Å for Eu–Eu, 0·011 Å for Eu–O, and 0·017 Å for O–O; the deviations of the angles average about 0·3°.

Within the trivalent Eu(1) polyhedron

Eu(1)–O(1)	1	2·301 Å	O(1) –Eu(1)–O(2)	1	171·3°
Eu(1)–O(2)	1	2·386	O(2′)–Eu(1)–O(3′)	2	172·8
Eu(1)–O(2′)	2	2·430	O(1) –Eu(1)–O(2′)	2	89·6
Eu(1)–O(3′)	2	2·236	O(1) –Eu(1)–O(3′)	2	94·9
O(1) –O(2′)	2	3·334	O(2) –Eu(1)–O(2′)	2	84·4
O(1) –O(3′)	2	3·342	O(2) –Eu(1)–O(3′)	2	90·5
O(2) –O(2′)	2	3·234	O(2′)–Eu(1)–O(2′)	1	92·2
O(2) –O(3′)	2	3·285	O(2′)–Eu(1)–O(3′)	2	82·1
O(2′)–O(2′)	1	3·502	O(3′)–Eu(1)–O(3′)	1	103·1
O(2′)–O(3′)	2	3·069			
O(3′)–O(3′)	1	3·502			

Within the trivalent Eu(2) polyhedron

Eu(2)–O(3)	1	2·297 Å	O(3) –Eu(2)–O(4)	1	152·2°
Eu(2)–O(4)	1	2·295	O(1′)–Eu(2)–O(4′)	2	166·3
Eu(2)–O(1′)	2	2·345	O(3) –Eu(2)–O(1′)	2	83·4
Eu(2)–O(4′)	2	2·388	O(3) –Eu(2)–O(4′)	2	83·0
O(3) –O(1′)	2	3·088	O(4) –Eu(2)–O(1′)	2	114·0
O(3) –O(4′)	2	3·104	O(4) –Eu(2)–O(4′)	2	78·2
O(4) –O(1′)	2	3·892	O(1′)–Eu(2)–O(1′)	1	96·6
O(4) –O(4′)	2	2·955	O(1′)–Eu(2)–O(4′)	2	82·9
O(1′)–O(1′)	1	3·502	O(4′)–Eu(2)–O(4′)	1	94·3
O(1′)–O(4′)	2	3·136			
O(4′)–O(4′)	1	3·502			

Within the divalent Eu(3) polyhedron

Eu(3)–O(4′)	2	2·638 Å	O(3) –Eu(3)–O(3)	1	128·5°
Eu(3)–O(3)	1	2·955	O(3) –Eu(3)–O(1)*	1	112·2
Eu(3)–O(1′)	2	2·722	O(1) –Eu(3)–O(3)*	1	119·3
Eu(3)–O(3)	1	2·720	O(3) –Eu(3)–O(4′)	2	67·2
Eu(3)–O(2′)	2	2·648	O(3) –Eu(3)–O(1′)	2	72·0
Eu(3)–O(1)*	1	3·991	O(3) –Eu(3)–O(1′)	2	69·2
O(3) –O(4)′	2	3·104	O(3) –Eu(3)–O(2′)	2	75·5
O(3) –O(1′)	2	3·342	O(4′)–Eu(3)–O(1′)	2	84·3
O(3) –O(1′)	2	3·088	O(1′)–Eu(3)–O(1′)	1	80·1
O(3) –O(2′)	2	3·285	O(4′)–Eu(3)–O(4′)	1	83·2
O(4′)–O(4′)	1	3·502	O(1′)–Eu(3)–O(2′)	2	87·9
O(4′)–O(1′)	2	3·597	O(2′)–Eu(3)–O(2′)	1	82·8
O(1′)–O(1′)	1	3·502	O(2′)–Eu(3)–O(4′)	2	71·4
O(1′)–O(2′)	2	3·728	O(4′)–O(1′)–O(2′)	2	49·8
O(2′)–O(2′)	1	3·502	O(1′)–O(2′)–O(4′)	2	62·9
O(2′)–O(4′)	2	3·084	O(2′)–O(4′)–O(1′)	2	67·3

* Quantities involving the ninth 'non-coordinated' oxygen ion.

Nearest europium-europium distances

Eu(1)–Eu(3)	1	3·638 Å
Eu(1)–Eu(1′)	2	3·568
Eu(1)–Eu(3′)	2	3·728
Eu(1)–Eu(2′)	2	4·079
Eu(1)–Eu(3′)	2	3·805
Eu(1)–Eu(2′)	2	3·865
Eu(1)–Eu(1)	2	3·502
Eu(2)–Eu(3)	1	3·360
Eu(2)–Eu(1′)	2	3·865
Eu(2)–Eu(3′)	2	3·925
Eu(2)–Eu(2′)	2	3·634
Eu(2)–Eu(3)	1	3·403
Eu(2)–Eu(1′)	2	4·079
Eu(2)–Eu(2)	2	3·502
Eu(3)–Eu(3)	1	3·403
Eu(3)–Eu(1′)	2	3·805
Eu(3)–Eu(2)	1	3·360
Eu(3)–Eu(1′)	2	3·728
Eu(3)–Eu(1)	1	3·638
Eu(3)–Eu(2′)	2	3·925
Eu(3)–Eu(3)	2	3·502

level, complete the eightfold coordination. A ninth oxygen ion, located out from the third prism face on the $z=\frac{1}{4}$ level, is 3·991 Å from the central europium ion and is probably too distant to be considered in the primary coordination shell. This ninth oxygen ion is indicated by the dashed bond in Fig. 3(*c*), and the few quantities involving it are marked with an asterisk in Table 4. The average Eu^{2+}–O^{2-} distance, omitting this ninth oxygen ion, is 2·711 Å, and the average O^{2-}–O^{2-} distance is 3·351 Å, both slightly greater than similar distances in the trivalent europium polyhedra.

The metal ions form a pseudo-hexagonal network, with half the europium ions on $z=\frac{1}{4}$ levels and half on $z=\frac{3}{4}$ levels. Each Eu(1) ion has 13 nearest europium neighbors at an average distance of 3·749 Å, each Eu(2) ion has 12 nearest europium neighbors at an average distance of 3·731 Å, and each Eu(3) ion has 11 nearest europium neighbors at an average distance of 3·666 Å.

Most MN_2O_4 compounds (where M is a divalent metal and N is a trivalent metal) crystallize in structures which are characterized by close-packing of the anions (*i.e.* spinel structures, *etc.*). In the case of Eu_3O_4 the cations are too large to be accommodated interstitially in a close-packed oxygen lattice, and cation size therefore plays an important role in determining the structure. If cation/anion radius ratios are considered, that of Eu^{3+}/O^{2-} (ratio = 0·68) predicts sixfold coordination, and that of Eu^{2+}/O^{2-} (ratio = 0·84) predicts eight- or ninefold coordination (Pauling, 1960). The fact that these predicted coordinations coincide with those observed for the two types of europium in Eu_3O_4 further tends to confirm the assignment of cation locations in the structure.

Other similar structures

The structural similarity of Eu_3O_4 and $CaFe_2O_4$ has already been pointed out. It should be mentioned that β-$CaCr_2O_4$ (Hill, Peiser & Rait, 1956) and $PbBi_2S_4$ (Wickman, 1951) are also similar. However, in the reported structure analysis of the latter compound the cation locations were probably incorrectly assigned. In particular, it seems unlikely that one of the trivalent bismuth ions should occupy the position of eightfold coordination, while the other trivalent bismuth ion and the divalent lead ion occupy the two octahedral sites.

An interesting variation of the Eu_3O_4 structure is exhibited by Rh_4P_3 (Rundqvist & Hede, 1960). In this compound, half the atoms are moved one half of a translation distance along the short axis of the unit cell, resulting in a structure having each phosphorus atom at the center of a trigonal prism of rhodium atoms.

A number of people contributed vitally to the present study. These include especially Dr S. F. Bartram of the writer's laboratory, who assisted throughout the course of the structure determination and provided many valuable discussions; Dr J. M. Stewart of the University of Maryland, who furnished the X-ray 63 computer program and provided much information on its use; Dr M. Schieber of the Massachusetts Institute of Technology National Magnet Laboratory, who provided a specimen of $SrEu_2O_4$; and Dr C. K. Johnson of the Oak Ridge National Laboratory, who provided the stereoscopic illustration of Fig. 3. The writer is deeply grateful to these persons for their assistance.

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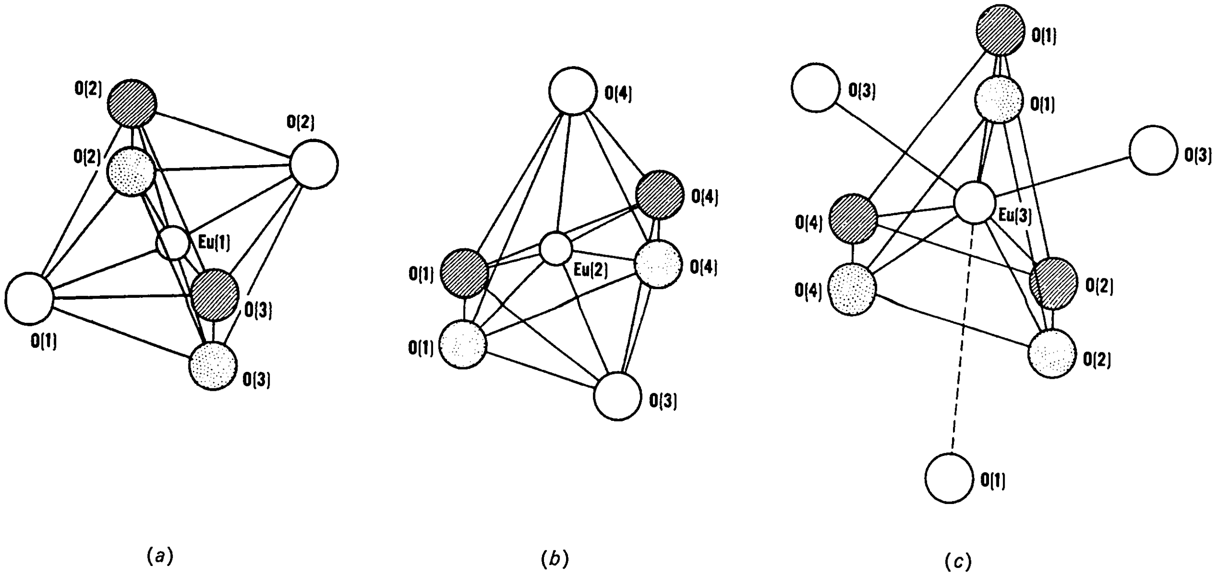

Fig. 3. Europium coordination polyhedra in Eu_3O_4. Open circles have $z=\frac{1}{4}$, dashed circles have $z=-\frac{1}{4}$, and stippled circles have $z=\frac{3}{4}$. (*a*) Trivalent Eu(1) polyhedron. (*b*) Trivalent Eu(2) polyhedron. (*c*) Divalent Eu(3) polyhedron.

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Refinement of the Crystal Structure of In_2O_3 at two Wavelengths

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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