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Note on the crystallography of Eu_2SiO_4 . By ROBERT C. RAU, *General Electric Company, Nuclear Materials and Propulsion Operation, Cincinnati 15, Ohio, U.S.A.*

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Recent crystallographic studies of europium-oxygen compounds reported at the Third Rare Earth Conference (Rau, 1963) revealed an unknown orthorhombic phase, designated Ortho I, which was believed to be a reduced oxide containing divalent and trivalent europium. This compound was produced both as yellow powder and as well-formed orange-yellow crystals during various tests of Eu_2O_3 under reducing atmospheres. Garton & Hukin (1963) reported forming a similar yellow compound, in the presence of silica, which gave an X-ray powder pattern identical with that of Ortho I, and which they believed to have a composition near Eu_3O_4 . In recent work which included several of the writer's Ortho I crystals, Shafer, McGuire & Suits (1963) identified this material as europium orthosilicate, Eu_2SiO_4 . This composition was subsequently verified in this laboratory by electron microprobe analysis.

Although a crystal structure determination of Eu_2SiO_4 has not yet been carried out, single-crystal X-ray data have been used to determine the lattice parameters and

index the powder pattern. Rotation and Weissenberg photographs were obtained for two different axes, with copper $K\alpha$ radiation, and powder data were obtained from both Debye-Scherrer photographs and diffractometer traces, with iron $K\alpha$ radiation. To aid in indexing the powder pattern, several double-exposure photographs were made by recording both the single-crystal rotation pattern and the Debye-Scherrer powder pattern on the same piece of film, with iron $K\alpha$ radiation.

The powder diffraction pattern and lattice parameters are given in Table 1. Back reflection lines from this pattern were used to calculate the lattice parameters, by the computer method of Mueller, Heaton & Miller (1960), and the accuracy of the indexing was checked by computing theoretical d -values by means of the computer program of Mueller, Meyer & Simonsen (1962).

Eu_2SiO_4 appears to have a very unusual crystal structure, the long b axis being of particular interest. On first examination of rotation photographs taken about this axis, strong layer lines were seen which gave

Table 1. X-ray data for Eu_2SiO_4

d	I/I_0	hkl	d	I/I_0	hkl
4.87	20	101	1.500	3	0,28,2; 3,28,1
4.011	50	171; 270	1.482	2	1,28,2
3.317	10	1,14,0	1.458	3	473
3.262	70	271	1.433	5	2,28,2
2.995	35	0,14,1	1.424	3	6,14,1
2.940	16	370	1.414	9	004
2.862	100	1,14,1; 2,14,0	1.406	6	602
2.824	80	002	1.361	6	3,28,2
2.807	100	301	1.360	6	1,35,1; 2,35,0
2.718	3	052*	1.353	3	503; 701
2.549	12	2,14,1	1.306	6	6,14,2
2.428	3	400	1.299	3	1,14,4
2.386	12	3,14,0	1.290	2	0,28,3
2.309	20	272	1.279	10	1,28,3
2.294	25	470	1.275	6	374
2.291	40	1,21,0	1.260	5	4,21,3
2.207	5	0,14,2	1.225	2	2,35,2
2.152	7	1,14,2	1.204	5	474; 1,21,4
2.126	20	471	1.196	5	4,35,1
2.039	25	372	1.180	14	0,42,0
2.010	25	2,14,2	1.129	3	574
1.906	5	3,21,0	1.123	4	4,35,2
1.873	6	570	1.102	8	2,35,3; 872
1.836	5	501	1.089	7	0,42,2
1.824	14	3,14,2	1.088	10	275; 3,42,1; 5,14,4
1.780	12	472; 1,21,2; 571	1.078	3	0,14,5; 2,28,4
1.753	2	223*	1.072	3	1,14,5
1.705	8	273; 5,14,0	1.069	8	305
1.663	18	1,28,1; 0,14,3; 2,28,0	1.062	2	5,35,2
1.640	16	1,14,3	1.046	2	3,28,4
1.629	18	303	1.020	2	6,14,4
1.621	25	4,21,1; 600	1.016	3	9,14,1
1.581	4	3,21,2	1.008	2	873
1.562	14	572	0.9915	6	1,49,1; 2,49,0
1.520	7	671	0.9769	5	505; 2,49,1

* Reflections from weak layers with $k \neq 7n$.

Orthorhombic: $a=9.713$, $b=49.56$, $c=5.652 \text{ \AA}$.

a lattice spacing of about 7.07 Å. However, close examination always showed the presence of two weak layer lines positioned in such a way between each pair of strong lines that the pattern could only be indexed by designating the strong layers $k=7n$ and the weak layers $k=7n \pm 2$. Thus the observed layer lines follow the numerical sequence $k=0, 2, 5, 7, 9, 12, 14, \dots$, and the true repeat distance along the b axis is seven times 7.07 Å, *i.e.* ~ 49.5 Å. This same effect was seen in Weissenberg photographs obtained from crystals rotated about the a axis, and was especially noticeable at high angles on upper level photographs. However, only two reflections from the weak $k=7n \pm 2$ layers appeared in powder patterns, these being the 052 and 223 reflections.

The significance of these unusual diffraction effects is not yet completely understood. Similar effects have been reported for various plagioclase feldspars by Chao & Taylor (1940) and Cole, Sörum & Taylor (1951), and have been attributed to layering in the crystal structure. Thus it is believed that the structure of Eu_2SiO_4 may be layered along the b axis, with the layering, and hence the true b parameter, repeating every seven layers. Such a structure would contain 4 formula units of Eu_2SiO_4 in each pseudo-cell layer, and 28 units in the complete unit cell. This leads to a theoretical density of 6.77 g.cm⁻³, in very good agreement with the value of 6.74 g.cm⁻³ measured from single crystals.

Petrographic analyses of the orange-yellow crystals

showed Eu_2SiO_4 to be biaxial positive, having an optic angle $2V=25^\circ$ and refractive indices $N_x=1.89$ and $N_z=1.92$. N_y is approximately 1.90.

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References

- CHAO, S. H. & TAYLOR, W. H. (1940). *Proc. Roy. Soc. A*, **176**, 76.
 COLE, W. F., SÖRUM, H. & TAYLOR, W. H. (1951). *Acta Cryst.* **4**, 20.
 GARTON, G. & HUKIN, D. A. (1963). Third Rare Earth Conference, Clearwater, Florida, 22-24 April, 1963. To be published in *Rare Earth Research*, Vol. III.
 MUELLER, M. H., HEATON, L. & MILLER, K. T. (1960). *Acta Cryst.* **13**, 828.
 MUELLER, M. H., MEYER, E. F. H. & SIMONSEN, S. H. (1962). Argonne National Laboratory Report ANL-6519.
 RAU, R. C. (1963). Third Rare Earth Conference, Clearwater, Florida, 22-24 April, 1963. To be published in *Rare Earth Research*, Vol. III.
 SHAFER, M. W., MCGUIRE, T. R. & SUITS, J. C. (1963). *Phys. Rev. Letters*, **11**, 251.

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X-ray absorption corrections for single crystals. By GINO OGNIBEN and SERGIO QUARENI, *Istituto di Mineralogia dell'Università, Padova, Italy*

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Evans (1952) determined the corrections for absorption for prismatic crystals dividing the cross section into triangular and parallelogram-shaped areas within which can be integrated the original equation:

$$T = \frac{\int^v \exp(-\mu t) dV}{V}$$

Nothing has been said for the special case when the angle between the X-ray beam and a crystal face is equal to θ (Bragg angle).

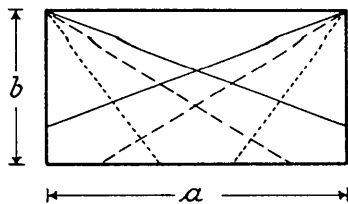


Fig. 1. Case (1) full line; case (2) dashed line; case (3) dotted line.

When such a relation is established between the X-ray beam and the crystal face, and the cross section of the crystal is rectangular (Fig. 1), then there are three possible solutions for the original integral according to: (1) $\cot \theta > a/b$; (2) $\cot \theta > a/2b$; (3) $\cot \theta < a/2b$.

(1) When $\cot \theta > a/b$,

$$T = \frac{1 + \mu A + [-1 - 2\mu A + (2AB - \frac{3}{2}A^2)\mu^2] \exp(-\mu A)}{2\mu^2 AB}$$

(2) When $\cot \theta > a/2b$,

$$T = \frac{1 + \mu A + [3 + 2\mu A - 4\mu B + \frac{1}{2}\mu^2(2B - A)^2] \times \exp(-\mu A) - 4 \exp(-\mu B)}{2\mu^2 AB}$$

(3) When $\cot \theta < a/2b$,

$$T = \frac{(3 - \mu A + 2\mu B) \exp(-2\mu B) + 1 - 4 \exp(-\mu B) + \mu A}{2\mu^2 AB}$$

where $A = a/\cos \theta$ and $B = b/\sin \theta$.

Reference

- EVANS, H. T., Jr. (1952). *J. Appl. Phys.* **23**, 663.