

Fig. 2. A projection of the structure of WO_2 on to the (010) plane.

such as VO_2 , TcO_2 and NbO_2 (Rogers, Shannon, Sleight & Gillson, 1969) as well as in AlWO_4 (Doumerc, Vlasse, Pouchard & Hagenmuller, 1975) and GaWO_4 (Palmer, 1977).

There is no evidence for the space group $P2_1$, as suggested by Magnéli & Andersson (1955) from either the X-ray or neutron powder profiles: the symmetry

and size of the unit cell of WO_2 are such that there would be no fully resolved peaks $h0l$, $l = 2n + 1$ in the 2θ range investigated. However, refinement was attempted in $P2_1$; no improvement in the agreement between observed and calculated profiles was seen, and indeed the atomic coordinates refined effectively to the symmetry-equivalent positions in $P2_1/c$.

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Dieuropium(III) Germanate Oxide

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Abstract. $\text{Eu}_2(\text{GeO}_4)_2\text{O}$, monoclinic, $P2_1/c$, $a = 9.977(7)$, $b = 7.136(4)$, $c = 6.854(4)$ Å, $\beta = 115.78(6)^\circ$, $Z = 8$, $D_m = 6.84(2)$, $D_x = 6.90$ Mg m^{-3} . Crystals were prepared by melting a pre-sintered mixture of Eu_2O_3 and GeO_2 in an image furnace with a tungsten halogen lamp as heat source. The seven-coordination polyhedra of Eu^{3+} ions in a set of

equivalent sites form slabs parallel to (100) by edge-sharing. These slabs are connected to the corrugated layers of the edge-shared polyhedra of seven-coordinated Eu^{3+} ions in other equivalent positions through common edges of the polyhedra and O–Ge–O bonds of the GeO_4 tetrahedra.

Introduction. Of the germanates and silicates of the rare-earth elements Ln_2XO_5 ($\text{Ln} = \text{Sc}, \text{Y}, \text{La}, \text{Ce}, \dots$, © 1979 International Union of Crystallography

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Lu; $X = \text{Si, Ge}$), the crystal structures have been determined for Sc_2GeO_5 (Gorbunov, Maksimov, Kharitonov & Belov, 1974) and Y_2SiO_5 (Michel, Buisson & Bertaut, 1967). The germanates of Lu, Yb, Er, Ho, Dy, Tb and Y are isomorphous with Y_2SiO_5 (Buisson & Michel, 1968). Leonov & Bondar (1973) classified the compounds Ln_2GeO_5 into two subgroups of different structure types and stated that the germanates, Ln_2GeO_5 , of La, Ce, Pr, Nd, Sm and Eu with larger ionic radii than Gd^{3+} are orthorhombic while those of Tb, Dy, Ho, Y, Er, Tm, Yb, Lu and Sc with smaller ionic radii are monoclinic. The crystal structure of Eu_2GeO_5 was investigated because the crystals prepared by the present authors were found to be monoclinic and to adopt an unknown structure which is evidently not isotopic with those of Sc_2GeO_5 and Y_2SiO_5 .

The lattice constants were refined by least squares from the 2θ values of 19 reflections measured on a four-circle diffractometer (Rigaku) with $\text{Mo K}\alpha$ radiation [$\lambda(\text{Mo K}\alpha) = 0.70926 \text{ \AA}$] monochromatized with a pyrolytic-graphite crystal ($2\theta_M = 12.17^\circ$). The systematic absences $h0l$ with $l \neq 0 \pmod{2}$ and $0k0$ with $k \neq 0 \pmod{2}$ indicated space group $P2_1/c$. Within the limits of $2\theta \leq 90^\circ$, $h \geq 0$ and $k \geq 0$, the intensities of 3782 reflections were collected on the same diffractometer operated in the 2θ - ω -scanning (when $2\theta \geq 30^\circ$) or in the ω -scanning mode ($2\theta < 30^\circ$). Those reflections whose net intensities (I_o) did not exceed the e.s.d.'s (σ_I) were considered to be unobserved. The 2806 observed reflections were corrected for absorption [numerical integration with $8 \times 8 \times 4$ Gaussian points in the specimen bounded by six faces; specimen size $0.10 \times 0.07 \times 0.02 \text{ mm}$, $\mu(\text{Mo K}\alpha) = 33.5 \text{ mm}^{-1}$] and then reduced to a set of 2706 independent reflections.

The positions of the Eu and Ge atoms were determined from the Patterson function by means of a minimum function (Buerger, 1959). The O atoms were located by a difference synthesis. The least-squares refinement of the coordinates and anisotropic thermal parameters of the atoms was performed with a program written by one of the authors. The sum of $w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2$ and $\sigma = \sigma_I F_o / (2I_o)$ was minimized. The scattering factors given by Cromer & Mann (1968) were used with corrections for dispersion (Cromer & Liberman, 1970). A correction was also made for extinction with the formula of Zachariasen (1968) in the following simplified form, modified for the partially polarized incident beam:

$$F_c = sF[1 + (g/\sin 2\theta)(1 + \cos^4 2\theta \cos^4 2\theta_M) \times (1 + \cos^2 2\theta \cos^2 2\theta_M)^{-1} (sF)^2]^{-1/4},$$

where $g = 2.7(1) \times 10^{-6}$, $s = 1.267(4)$. The coefficient g was treated as one of the free parameters to be refined; s is a scale factor. The atomic coordinates

and isotropic thermal parameters calculated from the anisotropic ones are listed in Table 1.* $R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.050$ for the 2706 non-zero reflections. The parameter shifts in the last cycle were $< 0.6\%$ of the e.s.d.'s. The last difference syntheses with $\Delta F = F'(|F_o| - |F_c|) / |F_c|$, where F_c and F' represent the structure factors calculated with and without the extinction and dispersion corrections respectively, revealed no further significant details of the structure, except that ripples of electron density within the limits of $\pm 8 \text{ e \AA}^{-3}$

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34519 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates and isotropic thermal parameters of Eu_2GeO_5

| | x | y | z | B (\AA^2) |
|-------|--------------|--------------|--------------|----------------------|
| Eu(1) | 0.13006 (6) | 0.13492 (9) | 0.18212 (8) | 0.38 (1) |
| Eu(2) | 0.47725 (6) | 0.12804 (9) | 0.70949 (8) | 0.39 (1) |
| Ge | 0.80231 (14) | 0.08932 (18) | 0.27673 (18) | 0.37 (2) |
| O(1) | 0.1086 (11) | 0.0543 (15) | 0.8315 (14) | 0.81 (17) |
| O(2) | 0.2146 (9) | 0.0790 (14) | 0.5483 (13) | 0.60 (19) |
| O(3) | 0.3904 (9) | 0.1176 (14) | 0.3218 (12) | 0.52 (22) |
| O(4) | 0.6107 (10) | 0.1347 (16) | 0.1166 (13) | 0.59 (37) |
| O(5) | 0.8894 (11) | 0.2092 (13) | 0.8931 (15) | 0.58 (38) |

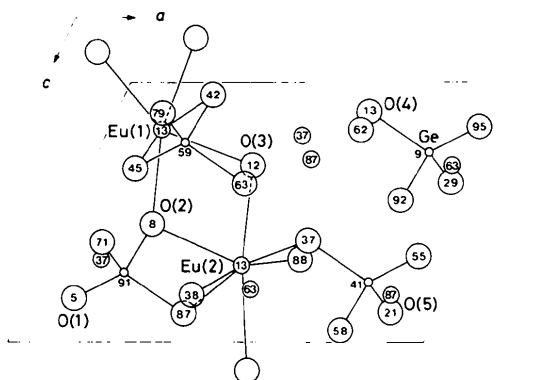


Fig. 1. Projection of the Eu_2GeO_5 structure on to (010). Numbers indicate the heights of atoms in hundredths of the b axis.

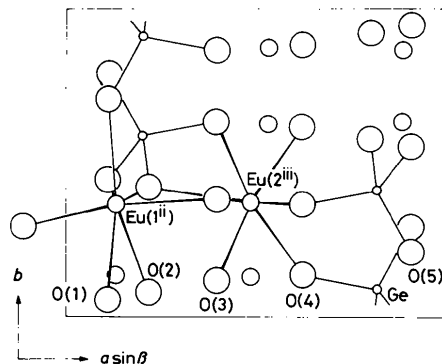


Fig. 2. Structure of Eu_2GeO_5 viewed along c .

were found around both Eu positions. These ripples might be due to the small systematic errors introduced by the extinction and/or the absorption correction(s).

Discussion. Figs. 1 and 2 show the Eu_2GeO_5 structure projected parallel to [010] and [001] respectively. While the small Sc^{3+} ions [$r(\text{VI}\text{Sc}^{3+}) = 0.745 \text{ \AA}$; Shannon & Prewitt (1970)] in Sc_2GeO_5 are each surrounded octahedrally by six O atoms (Gorbunov *et al.*, 1974), there are two crystallographically independent Y^{3+} ions [$r(\text{VI}\text{Y}^{3+}) = 0.900 \text{ \AA}$] in Y_2SiO_5 , one of which is coordinated to six and the other to seven O atoms (Michel *et al.*, 1967). In Eu_2GeO_5 , both Eu(1) and Eu(2) have seven O-atom nearest neighbours in accordance with their larger ionic radii [$r(\text{VI}\text{Eu}^{3+}) = 0.947$, $r(\text{VII}\text{Eu}^{3+}) = 1.03 \text{ \AA}$]. The coordination polyhedra [monocapped octahedra (Wells, 1975)] of Eu(2) are joined by edge-sharing to form a slab with quasi-close-packed O-atom layers parallel to (100) (Fig. 3). The coordination around Eu(1) can be regarded as a distorted monocapped trigonal prism. The coordination polyhedra of Eu(1) are connected to each other through common edges and form a corrugated layer parallel to (100) together with the equivalent polyhedra in the neighbouring unit cells (Fig. 4). The slabs

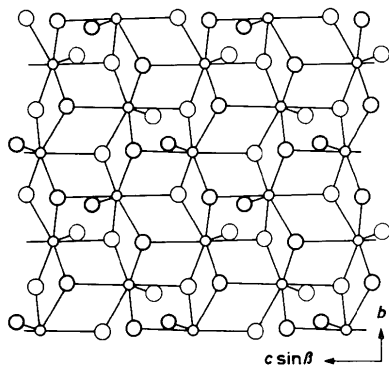


Fig. 3. Slab of the edge-shared coordination polyhedra of Eu(2) viewed along *a*.

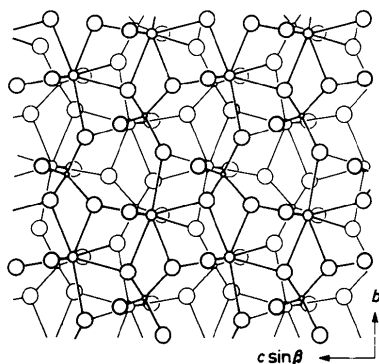


Fig. 4. Corrugated layer of the edge-shared coordination polyhedra of Eu(1) and the GeO_4 tetrahedra viewed along *a*.

Table 2. Eu—O distances (\AA)

E.s.d.'s are in parentheses.

| Symmetry code | | | |
|---------------------------|------------------------------------|---------------------|-----------------|
| (i) | $1-x, 1-y, 1-z$ | (v) | $x, y, 1+z$ |
| (ii) | $x, \frac{1}{2}-y, \frac{1}{2}+z$ | (vi) | $-1+x, y, -1+z$ |
| (iii) | $x, \frac{1}{2}-y, -\frac{1}{2}+z$ | (vii) | $x, y, -1+z$ |
| (iv) | $1-x, -y, 1-z$ | | |
| Eu(1)—O(1 ^{iv}) | 2.389 (9) | Eu(2)—O(2) | 2.386 (9) |
| O(1 ⁱⁱⁱ) | 2.491 (10) | O(3) | 2.412 (7) |
| O(2) | 2.308 (8) | O(3 ^{iv}) | 2.260 (10) |
| O(2 ⁱⁱⁱ) | 2.529 (9) | O(3 ⁱⁱ) | 2.284 (10) |
| O(3) | 2.349 (9) | O(4 ^{iv}) | 2.572 (10) |
| O(5 ^{iv}) | 2.500 (10) | O(4 ⁱⁱ) | 2.404 (10) |
| O(5 ^{vi}) | 2.415 (10) | O(4 ^v) | 2.516 (8) |
| Mean | 2.426 | Mean | 2.404 |

Table 3. Bond lengths (\AA) and angles ($^\circ$) around the Ge atom

Ge—O distances are given on the diagonal; O—O distances and O—Ge—O angles in the upper-right and the lower-left triangles respectively. E.s.d.'s are in parentheses. The symmetry code is given in Table 2.

| | O(1 ^{iv}) | O(2 ^{iv}) | O(4) | O(5 ⁱⁱⁱ) |
|----------------------|---------------------|---------------------|-----------|----------------------|
| O(1 ^{iv}) | 1.721 (9) | 2.59 (1) | 2.99 (1) | 2.91 (1) |
| O(2 ^{iv}) | 96.2 (4) | 1.757 (9) | 2.68 (1) | 2.93 (1) |
| O(4) | 117.5 (4) | 98.6 (4) | 1.772 (9) | 2.82 (1) |
| O(5 ⁱⁱⁱ) | 117.0 (5) | 116.2 (4) | 109.4 (5) | 1.690 (9) |

Mean Ge—O 1.735

of Eu(2) and the corrugated layers of Eu(1) are linked through a common edge O(2)—O(3) and further by O—Ge—O bonding of the GeO_4 tetrahedra.

It can be seen from Figs. 1 or 2 that there exist only four Eu—O bonds across the unit-cell boundary parallel to (100), suggesting the relative weakness of the bonding in this direction as compared with the other directions. Moreover, the electrical neutrality can always be maintained when the crystal is divided into two parts at any unit-cell boundary. These facts might well explain the perfect cleavage of the crystal parallel to (100). Prior to the structure determination, measurements of emission and absorption spectra of Eu_2GeO_5 had been carried out by one of the authors. The results had predicted that the Eu^{3+} ions occupy two sets of equivalent positions with low point symmetry. The bond lengths and angles were calculated by means of a local version of the ORFFE program (Busing, Martin & Levy, 1964), and are tabulated in Tables 2 and 3.

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