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The Crystal Structure of $Eu_4Al_2O_9$[1]

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The phase $2(RE)_2O_3 \cdot Al_2O_3$ occurs in rare earth aluminates for the series Sm–Lu. All compounds are isostructural, and $Eu_4Al_2O_9$ was selected for detailed structural analysis. The compound is monoclinic, $a = 7.608\,(4)$ Å, $b = 10.616\,(5)$ Å, $c = 11.101\,(8)$ Å, $\beta = 108.50\,(9)°$, space group $P2_1/c$, and there are 4 formula weights in the unit cell with a calculated $\rho = 6.29$ g/cm³. The integrated intensities of 3184 independent reflections were measured using a scintillation counter and monochromatic Mo Kα radiation. The structure was refined by least-squares calculations with isotropic temperature factors to a conventional R of 0.053. The Al^{3+} is in tetrahedral coordination, and Al–O bond distances are approximately 1.73 Å as expected for tetrahedral aluminum. The europium ions are in sixfold and sevenfold coordination. The sixfold-coordinated ion has oxygen ions at about 2.32 Å at the corners of a distorted octahedron; the sevenfold ion has five bonds at an average distance of 2.33 Å and two at about 2.5–2.6 Å. The articulation of the polyhedra forms a cavity in the structure. The summation of ionic bond strengths shows that one oxygen ion has a local positive charge imbalance of $^1/_2$ and two other ones have a negative imbalance of $^1/_4$. This structure is representative for the isostructural series $2(RE)_2O_3 \cdot Al_2O_3$, RE = Sm–Lu, and $2(RE)_2O \cdot Ga_2O_3$, RE = La–Gd.

Introduction

The phase diagrams for the systems $(RE)_2O_3$–Al_2O_3 and $(RE)_2O_3$–Ga_2O_3 (RE = rare earth) have been studied by several investigators.[2,3] Usually three compounds have been observed with compositions $3(RE)_2O_3 \cdot 5Al_2O_3$ having the garnet structure, $(RE)_2O_3 \cdot Al_2O_3$ with the perovskite structure, and $2(RE)_2O_3 \cdot Al_2O_3$ of unknown structure. Warshaw and Roy[3] have reported that the 2:1 phase is formed with Al_2O_3 in the systems from Gd_2O_3 through Yb_2O_3 and with Ga_2O_3 in the systems La_2O_3 through Gd_2O_3. We have found that this structure type also exists in the samarium–, europium–, and lutetium–alumina systems. Warshaw and Roy concluded that the aluminum atoms exist in fourfold coordination because silicon can be substituted for it over a complete range of solid solution. Reed and Chase[4] have reported that the composition $2Y_2O_3 \cdot Al_2O_3$ has a monoclinic cell, with space group $P2_1/c$, $a = 7.323$ Å, $b = 10.467$ Å, $c = 11.121$ Å, and $\beta = 108.53°$. The rare earth aluminates with composition $2(RE)_2O_3 \cdot Al_2O_3$ are isostructural and this paper presents a detailed analysis of $Eu_4Al_2O_9$ ($2Eu_2O_3 \cdot Al_2O_3$).

Experimental Section

The appropriate weights of the oxides were arc melted together on a water-cooled copper hearth under an argon atmosphere and quickly cooled. The resulting button was crushed and examined optically and by X-ray powder diffraction methods for the presence of other phases besides the desired rare earth aluminate. All buttons showed a large degree of crystallinity. The crystals were needle shaped; the needle axis was later identified as the a axis of the primitive unit cell. All mixtures from samarium through lutetium formed a single phase whose powder patterns were identical with that reported by Schneider, Roth, and Waring[2] except for the shift in d spacings due to the varying size of the rare earth radius. Several attempts were made to form the composition $2Nd_2O_3 \cdot Al_2O_3$ but in every case two phases, $NdAl_2O_3$ and Nd_2O_3, were observed in the X-ray diffraction powder patterns. Thus the formation of this phase with Al_2O_3 is strongly dependent upon the rare earth radius with the upper limit being about 1.0 Å.

When the initial preparations of the various aluminates were examined for single-crystal fragments, the europium compound exhibited the best formed crystals and one of them was selected for analysis. A wedge-shaped crystal of dimensions 0.16 × 0.096 × 0.015 mm was mounted parallel to the a axis, which was the long dimension of the crystal, and aligned on PAILRED (Philips Automatic Indexing Linear Reciprocal Space Exploring Diffractometer). The lattice parameters were determined from a least-squares refinement of 40 measurements of Υ made on the PAILRED instrument with monochromatic Mo Kα radiation, λ 0.71069 Å ($\Upsilon = 2\theta$ for the zero level). The angles of the diffraction spectra were read to 0.05° and with each least-squares cycle the μ angle was adjusted for the change in the lattice constants. This process was repeated until the parameters were refined. The lattice parameters of the primitive cell are $a = 7.608\,(4)$ Å, $b = 10.616\,(5)$ Å, $c = 11.101\,(8)$ Å, and $\beta = 108.50\,(9)°$. There are 4 formula weights in the unit cell and the calculated density is 6.29 g/cm³. The diffraction symmetry was obtained from Weissenberg and precession photographs and was 2/m; the systematic absences were $h0l$, l odd, and $0k0$, k odd, uniquely characteristic of space group $P2_1/c$. None of the atoms needs to be in special positions due to symmetry requirements. The choice of a B-centered unit cell with dimensions $a = 7.608$ Å, $b = 10.616$ Å, $c = 21.063$ Å, and $\beta = 89.22°$, which is related to the monoclinic primitive cell by the transformation

$$\begin{pmatrix} a_B \\ b_B \\ c_B \end{pmatrix} = \begin{pmatrix} 100 \\ 010 \\ 102 \end{pmatrix} \begin{pmatrix} a_P \\ b_P \\ c_P \end{pmatrix}$$

yields a cell which is almost orthogonal. Table I presents the unit cell dimensions for several compounds in the isostructural series in terms of the primitive as well as the B-centered cells. The lattice constants for $Dy_4Al_2O_9$ were obtained from a least-squares refinement of Weissenberg film data. Those of the other materials were obtained from precession films. It was also observed on Weissenberg and precession photographs that all levels in which h was odd were extremely weak, indicating a subcell whose a parameter is half the true a unit cell value.

Three-dimensional data to $(\sin\theta)/\lambda = 0.648$ were collected with the automatic single-crystal diffractometer using crystal-monochromatized Mo Kα radiation. The integrated intensity was measured by an ω scan at 1°/min over a 2° interval, and background was counted for 100 sec on each side of the peak.

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[1] This work was sponsored by a grant from the National Science Foundation.

[2] S. V. Schneider, R. S. Roth, and U. L. Waring, *J. Res. Natl. Bur. Std.*, **A65**, 345 (1961).

[3] I. Warshaw and R. Roy, *J. Am. Ceram. Soc.*, **42**, 434 (1959).

[4] J. W. Reed and A. B. Chase, *Acta Cryst.*, **15**, 812 (1962).

TABLE I

UNIT CELL PARAMETERS FOR $2(RE)O_3 \cdot Al_2O_3$ FOR THE MONOCLINIC PRIMITIVE AND B-CENTERED CELLS[a]

	$P2_1/c$				B-centered cell			
Compn	a_P, Å	b_P, Å	c_P, Å	β_P, deg	a_B, Å	b_B, Å	c_B, Å	β_B, deg
$Sm_4Al_2O_9$	7.62	10.68	11.15	108.5	7.62	10.68	21.17	89.3
$Gd_4Al_2O_9$	7.59	10.61	11.12	108.5	7.59	10.61	21.11	89.6
$Eu_4Al_2O_9$	7.608 (4)	10.616 (5)	11.101 (8)	108.50 (9)	7.608 (4)	10.616 (5)	21.063 (16)	89.22 (8)
$Dy_4Al_2O_9$	7.432 (6)	10.533 (1)	11.089 (2)	108.16 (19)	7.432 (6)	10.533 (1)	21.081 (3)	89.26 (8)
$Ho_4Al_2O_9$	7.37	10.50	10.99	108.1	7.37	10.50	20.91	89.4

[a] Numbers in parentheses after cell dimensions are standard deviations, $10^3\sigma$; after angle values they are $10^2\sigma$.

The levels $0kl$–$10,k,l$ were collected. A total of 3342 reflections were measured and 3184 were independent. The basis for accepting an intensity as statistically nonzero was a value of $\Delta I/I \leq 0.1$, where $\Delta I/I = (T + t^2B)^{1/2}/(T - tB)$ (T = total counts in time t_T for the ω scan; B = total background counts; $t = t_T/(t_1 + t_2)$, t_1, and t_2 are background counting times[5]), and 2267 intensities satisfying this requirement were used in the structure determination. The data were corrected for Lorentz and polarization factors and for absorption and were reduced to structure factors F_o. For the absorption correction the crystal shape was described by 5 plane faces, and 64 sampling points were used in the evaluation of the absorption factor ($\mu_{Mo\ K\alpha} = 304.53\ cm^{-1}$). The transmission factors varied from about 0.2 to about 0.75. The empirical equation

$$\sigma^2(F) = \frac{F^2}{4(T - B)^2}[T + B + 0.0009(T - B)^2]$$

was used to estimate the variance for each structure factor where T = total count, B = average background count, and the additive term involving $T - B$ is to allow for errors proportional to the net count, such as variation in the beam intensity and absorption errors. A standard reflection was used throughout the data gathering to check on intensity drift which would affect the scale factors used in bringing the various levels to the same scale. The standard reflection maintained a constant intensity during the data collection for levels $0kl$–$2kl$ but displayed a small change between successive levels thereafter. Separate scale factors were therefore used in the refinement of the structure for $0kl$–$2kl$, $3kl$, etc., for a total of nine different values.

Structure Determination

The direct method for the determination of phases was used in the solution of the structure. A Wilson plot was constructed which provided an approximate scale factor and temperature factor for the calculation of normalized structure factors, $E(hkl)$. A program written by Dewar[6] making use of the symbolic addition method yielded approximately 160 signed $E(hkl)$'s. All E values had even h indexes because of the presence of the previously mentioned subcell. The calculated E map displayed four high peaks which were interpreted as being Eu^{3+} but the pseudo a glide related the x parameters of two crystallographically independent atoms so that instead of four independent europium atoms the map showed only two. Several cycles of least-squares refinement were calculated in which the europium atoms were considered independent, and after the first iteration the x parameter began to deviate from the exact $^1/_2a$ separation and phases could now be assigned to the h odd structure factors.

A three-dimensional Fourier map based on the signs from Eu^{3+} contribution to $F(hkl)$ showed peaks which could be assigned to Al^{3+} ions. These additional ions were used in a new calculation of phases but the new electron density map displayed numerous peaks of varying height which made the assignment of O^{2-} ions difficult. A knowledge of approximate bond distances and coordination to be expected around aluminum and europium was used for the oxygen position determination. Various oxygen parameters corresponding to observed peaks in the electron density maps were tried in least-squares refinements. The coordinates of some of these atoms did not converge, indicating that atoms did not exist at these positions. Slowly the oxygen positions were determined, and this process accelerated considerably once a few of the oxygen ions were correctly located. The least-squares program used was XFLS, a modification of ORFLS.[7] The structure factors were weighted as $1/\sigma^2$ and the quantity $\Sigma w(|F_o| - |F_c|)^2$ was minimized with the summation taken over all independent reflections.

TABLE II

COORDINATES AND TEMPERATURE FACTORS FOR $Eu_4Al_2O_9$[a]

Atom	x	y	z	B, Å^2
Al(1)	0.2223 (7)	0.1880 (4)	0.1299 (5)	−0.01 (6)
Al(2)	0.6538 (7)	0.1855 (4)	0.1174 (5)	0.03(6)
Eu(1)	0.5242 (1)	0.1035 (1)	0.7870 (1)	0.17 (1)
Eu(2)	0.0252 (1)	0.0890 (1)	0.8088 (1)	0.16 (1)
Eu(3)	0.3349 (1)	0.1251 (1)	0.4310 (1)	0.23 (1)
Eu(4)	0.8366 (1)	0.1226 (1)	0.4144 (12)	0.19 (1)
O(1)	0.7866 (16)	0.2276 (11)	0.7481 (12)	0.35 (15)
O(2)	0.2320 (18)	0.2291 (12)	0.7651 (14)	0.32 (15)
O(3)	0.2156 (19)	0.0280 (13)	0.1640 (15)	0.42 (16)
O(4)	0.0739 (16)	0.2345 (11)	0.9803 (13)	0.40 (16)
O(5)	0.4311 (19)	0.2403 (11)	0.1151 (14)	0.23 (14)
O(6)	0.6372 (18)	0.2292 (12)	0.9624 (14)	0.28 (15)
O(7)	0.6987 (20)	0.0297 (13)	0.1668 (15)	0.49 (16)
O(8)	0.0774 (22)	−0.0061 (13)	0.3915 (16)	0.50 (16)
O(9)	0.5655 (21)	0.0063 (12)	0.3937 (15)	0.47 (16)

[a] Numbers in parentheses are standard deviations.

The least-squares procedure was used to refine each scale factor separately and then the spatial parameters and isotropic temperature factors. The best positional and temperature parameters were used to redetermine the nine scale factors and this iterative procedure was carried out until no further changes in the scale factors occurred. The best parameters were then used to scale all reflections to their absolute values. The last cycle of refinement varied all parameters simultaneously. The refinement was based on F_o; the discrepancy value R is 0.053 for all reflections used in the refinement, and

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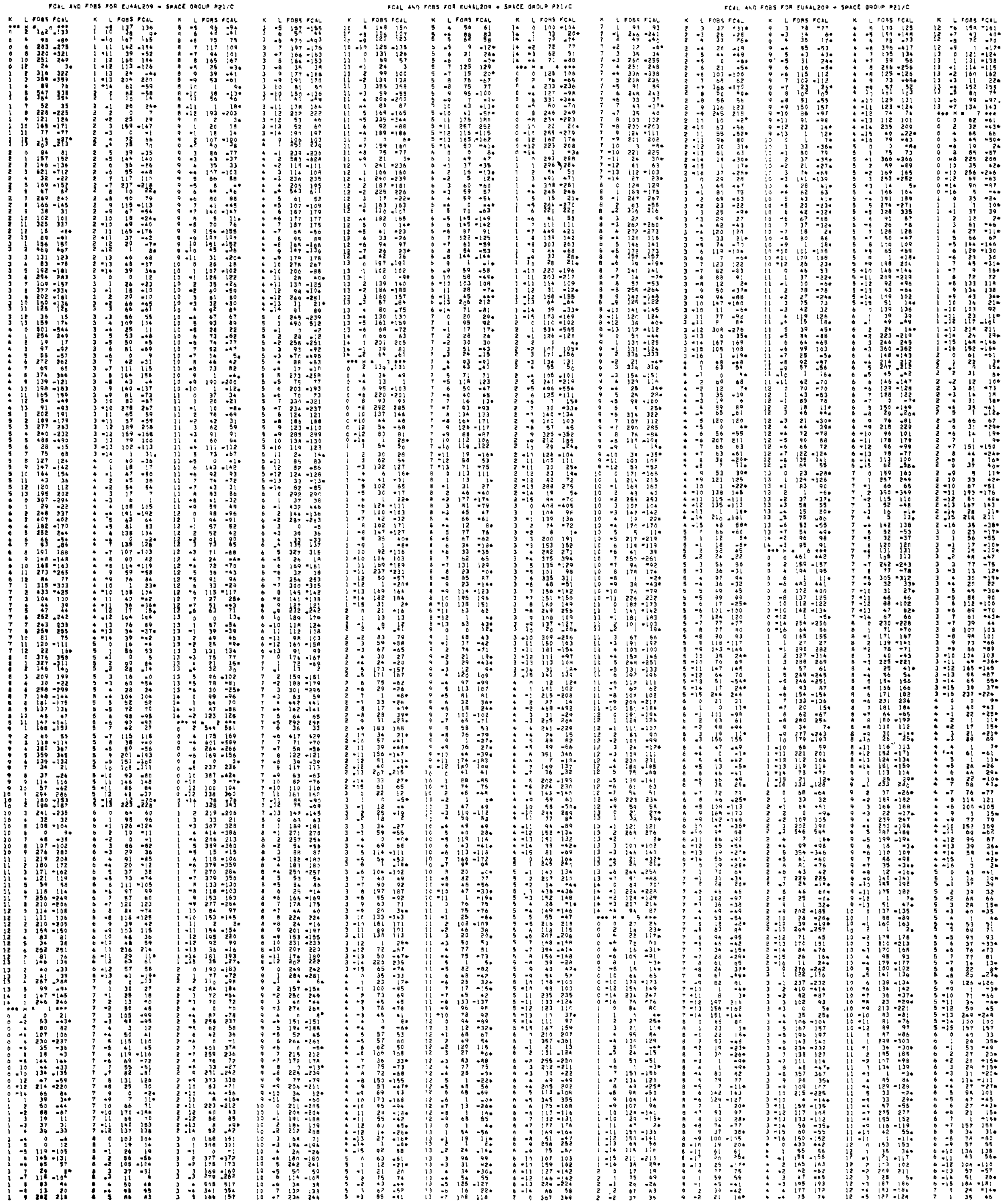
(5) M. Mack, *Norelco Reptr.*, **12**, 40 (1965).

(6) R. Dewar and A. Stone, University of Chicago, 1966.

(7) W. R. Busing, K. O. Martin, and H. A. Levy, USAEC Report ORNL-TM 305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.

Table III

List of Observed and Calculated Structure Factors for $Eu_4Al_2O_9$[a]


FCAL AND FOBS FOR EU4AL2O9 - SPACE GROUP P21/C

the weighted R is 0.054. An anisotropic least-squares refinement was also carried out. None of the positional parameters shifted significantly; Eu(2) and Eu(4) had isotropic thermal parameters while Eu(1) and Eu(3) had $\beta_{11} = \beta_{22}$ and β_{33} was near zero. The thermal parameter anisotropies for the lighter atoms appeared not to be physically meaningful. The R for this refinement was 0.050, and the weighted R was 0.051. Because no physical significance is associated with the anisotropic thermal parameters, only the isotropic values are shown in Table II. A three-dimensional difference electron density map was calculated from the final isotropic refinement and the largest peaks were about 0.5 e$^-$/Å^3 and occurred at the Eu^{3+} positions. The standard deviation of an observation of unit weight $[\Sigma w(|F_o| - |F_c|)^2/(n_o - n_v)]^{1/2}$ is 2.15 (n_o is the number of reflections and n_v the number of variables). Dispersion corrected scattering factors based on the Thomas–Fermi–Dirac statistical model using $\Delta f'$ and $\Delta f''$ for Eu[8] were used in the calculation of F. The oxygen and aluminum scattering factors were obtained from a self-consistent field model using values listed in ref 8.

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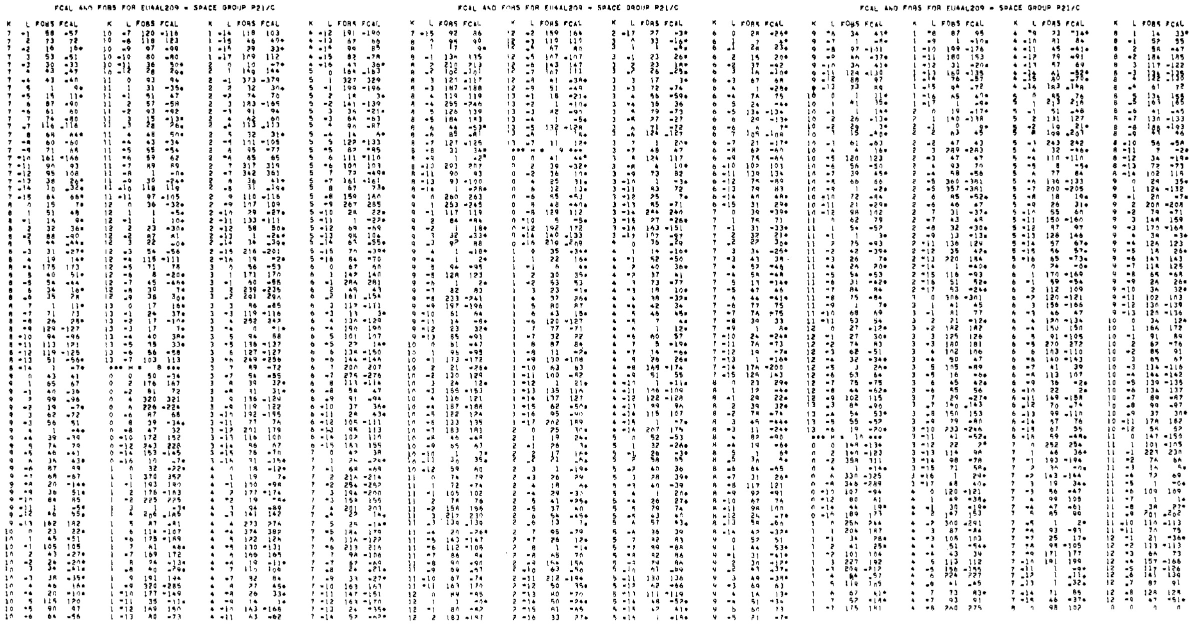
(8) "International Tables for X-Ray Crystallography," Vol. 1, The Kynoch Press, Birmingham, England, 1952, pp 202, 211.

TABLE III (*Continued*)



FCAL AND FOBS FOR EU4AL2O9 - SPACE GROUP P21/C

K L FOBS FCAL

[a] The starred entries were not used in the structure refinement.

TABLE IV

INTERATOMIC DISTANCES AND ANGLES IN $Eu_4Al_2O_9$[a]

Distances, Å

Al(1)–O(2)	1.72 (2)	Eu(2)–O(3)	2.32 (2)
Al(1)–O(5)	1.74 (2)	Eu(2)–O(2)	2.32 (2)
Al(1)–O(3)	1.74 (2)	Eu(2)–O(7)	2.38 (2)
Al(1)–O(4)	1.75 (2)	Eu(2)–O(4)	2.38 (2)
Al(2)–O(1)	1.74 (2)	Eu(2)–O(9)	2.31 (2)
Al(2)–O(7)	1.74 (2)	Eu(3)–O(9)	2.31 (2)
Al(2)–O(6)	1.75 (2)	Eu(3)–O(8)	2.33 (2)
Al(2)–O(5)	1.77 (2)	Eu(3)–O(2)	2.33 (2)
Eu(1)–O(9)	2.23 (2)	Eu(3)–O(5)	2.40 (2)
Eu(1)–O(6)	2.28 (2)	Eu(3)–O(4)	2.67 (2)
Eu(1)–O(3)	2.33 (2)	Eu(3)–O(6)	2.70 (2)
Eu(1)–O(7)	2.39 (2)	Eu(4)–O(4)	2.28 (2)
Eu(1)–O(5)	2.45 (2)	Eu(4)–O(9)	2.33 (2)
Eu(1)–O(2)	2.53 (2)	Eu(4)–O(8)	2.36 (2)
Eu(1)–O(1)	2.53 (2)	Eu(4)–O(6)	2.36 (2)
Eu(2)–O(1)	2.26 (2)	Eu(4)–O(1)	2.37 (2)
Eu(2)–O(8)	2.28 (2)	Eu(4)–O(8)	2.38 (2)

Angles, Deg

O(2)–Al(1)–O(5)	98 (1)	O(1)–Al(2)–O(7)	104 (1)
O(2)–Al(1)–O(3)	108 (1)	O(1)–Al(2)–O(6)	121 (1)
O(2)–Al(1)–O(4)	121 (1)	O(1)–Al(2)–O(5)	97 (1)
O(5)–Al(1)–O(3)	115 (1)	O(7)–Al(2)–O(6)	120 (1)
O(5)–Al(1)–O(4)	98 (1)	O(7)–Al(2)–O(5)	114 (1)
O(3)–Al(1)–O(4)	115 (1)	O(6)–Al(2)–O(5)	98 (1)

[a] Numbers in parentheses are standard deviations.

The F_o and F_c values are listed in Table III, and the signs are those from the real part of F_c. The starred values were not used in the refinement. Table IV lists the bond distances and angles found in this compound.

Discussion

The aluminum ions are in tetrahedral positions as had been deduced previously from the crystal chemical behavior.[3] The bond distances Al–O are in the range reported for tetrahedrally coordinated Al.[9] The angles are distorted from the ideal tetrahedral values, varying from 98 to 121°. The Eu^{3+} ions display irregular coordination. The Eu(1) and Eu(3) atoms are bonded to seven O^{2-}; five bond distances are short and four of these are nearly coplanar. One short and the two long bonds are in a plane nearly normal to the plane formed by the four short bonds. The Eu(2) and Eu(4) ions are in sixfold coordination with the O^{2-} ions which form a distorted octahedron. In this case Eu–O distances are approximately equal and their sum is close to the sum of their ionic radii. The values of the short distances are similar to the Eu–O values found in $Eu_2(WO_4)_3$[10] where Eu is in eightfold coordination and the long distances are close to the values found in $EuAlO_3$[11] where Eu is in twelvefold coordination. The linkages of europium heptaverticons and hexaverticons with aluminum tetrahedra create a channel in the structure as shown in Figure 1 which extends through the crystal with its axis nearly parallel to the [100] direction.

The examination of the structure in terms of the cation coordination around the various oxygen ions as illustrated in Figure 2 provides a better insight into the reasons for the unequal bond lengths between europium and oxygen and their division into sets of two long bonds and five normal bonds for Eu(1) and Eu(3). If the Eu–O normal bond distance of about 2.4 Å is considered to have a bond strength of $^1/_2$ and the long distance of approximately 2.6 Å is considered to have the bond strength of $^1/_4$ (in $EuAlO_3$ (perovskite structure type[11]) the Eu–O distance is 2.639 Å and Eu is in 12-fold coordination so that the electrostatic bond strength is $^1/_4$ in that compound), then the summation of bond strengths around each crystallographically independent oxygen ion provides the following results: O(1), O(2), O(4), and O(6) are coordinated to two

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(9) J. V. Smith and S. W. Bailey, *Acta Cryst.*, **16**, 801 (1963).

(10) D. H. Templeton and Zalkin, *ibid.*, **16**, 762 (1963).

(11) S. Geller and V. B. Bala, *ibid.*, **9**, 1019 (1956).

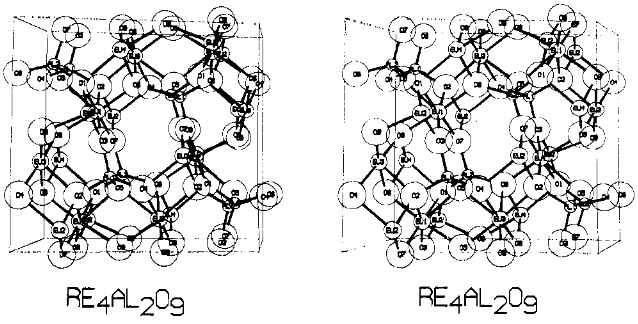

Figure 1.—Stereoscopic view of the $Eu_4Al_2O_9$ structure which is representative for the isostructural series. The positive *a* axis points away from the observer, *b* is vertical, and *c* is horizontal.

europiums at the normal distances, to one Eu^{3+} with a long bond, and to one aluminum, so that the summation of bond strengths provides for electrical neutrality; O(8) and O(9) are tetrahedrally coordinated by four europium ions at the normal distance thus again preserving local electrical neutrality; O(5) is coordinated to Eu(1) and Eu(3) at the normal distance and to Al(1) and Al(2) giving rise to an excess positive charge of $^1/_2$; O(7) and O(3) each are coordinated to two europium ions and one aluminum ion in a planar triangular configuration with the Eu–O bond distances normal and thus each oxygen has a charge deficiency, or an excess negative charge, of $^1/_4$. The local charge imbalances on O(5), O(7), and O(3) thus cancel when summed over the total crystal volume and electrical neutrality is preserved. The lengthening of two bonds, Eu(3)–O(4) and Eu(3)–O(6), is thus seen to result from the electrostatic neutrality requirements which must be preserved in the structure.

The channel in the structure can be considered as formed by two octagonal rings one above the other each having a chair configuration. The ring closest to the observer in Figure 1 consists of O(6)–Al(2)–O(7)–Eu(2)–O(4)–Al(1)–O(3)–Eu(1)–O(6). The lower ring is related to the upper one by a center of symmetry which exists in the center of the channel. The channel cross section has dimensions approximately 1.2 × 2.1 Å so that diffusion of outside atoms along these channels is not likely. The diffusion of small cations such as Mg^{2+} or Li^+ toward sites of excess negative charge is a possibility although the modes of over-all charge compensation that would be required might prevent such a process.

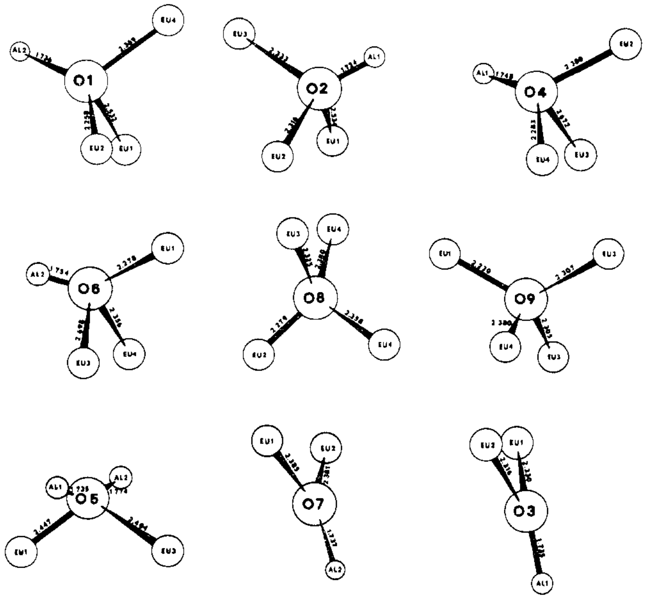

Figure 2.—The cation coordination around the crystallographically independent O^{2-}: the bond strengths around O(1), O(2), O(4), O(6), O(8), and O(9) preserve electrical neutrality around the anions; O(5) has an excess positive charge of $^1/_2$ and O(7) and O(3) each have an excess negative charge of $^1/_4$.

There are few structures of compounds $A_4B_2O_9$ known. Several of these—$Sr_4Sb_2O_9$, $Ba_4Nb_2O_9$, $Ba_4Ta_2O_9$—have a distorted perovskite structure[12,13] and the structure of $Ca_4P_2O_9$ is unknown. This structure appears to be unique to the series of compounds formed in the rare earth–alumina and rare earth–gallia systems.

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(12) G. Blasse, *J. Inorg. Nucl. Chem.*, **27**, 993 (1965).

(13) F. S. Galasso, J. R. Barrante, and L. Katz, *J. Am. Chem. Soc.*, **83**, 2830 (1961).