References

AMBERGER, E. (1977). Private communication.

AMBERGER, E., DRUMINSKI, M. & PLOOG, K. (1971). *J. Less-Common Met.* **23**, 43–52.

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee.

CLARK, K. H. & HOARD, J. L. (1943). *J. Am. Chem. Soc.* **65**, 2115–2119.

GUPTA, A., KIRFEL, A. & WILL, G. (1977). *Acta Cryst.* B**33**, 637–641.

HAREL, M. & HIRSHFELD, F. L. (1975). *Acta Cryst.* B**31**, 162–172.

HIRSHFELD, F. L. (1971). *Acta Cryst.* B**27**, 769–781.

HIRSHFELD, F. L. (1976). *Acta Cryst.* A**32**, 239–244.

HOARD, J. L., SULLENGER, D. B., KENNARD, C. H. & HUGHES, R. E. (1970). *J. Solid State Chem.* **1**, 268–277.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

LONGUET-HIGGINS, H. C. & ROBERTS, M. DE V. (1955). *Proc. R. Soc. London, Ser. A*, **230**, 110–119.

MATKOVICH, V. I. & ECONOMY, J. (1977). *Boron and Refractory Borides*, pp. 98–114. Berlin: Springer-Verlag.

WILL, G. (1967). *Acta Cryst.* **23**, 1071–1079.

WILL, G. (1969). *Acta Cryst.* B**25**, 1219–1222.

WILL, G. & KOSSOBUTZKI, K. H. (1976*a*). *J. Less-Common Met.* **44**, 87–97.

WILL, G. & KOSSOBUTZKI, K. H. (1976*b*). *J. Less-Common Met.* **47**, 43–48.

ZACHARIASEN, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.

Acta Cryst. (1979). B**35**, 1059–1062

Refinement of the Sr_2EuFeO_5 and Sr_2EuAlO_5 Structures

BY M. DROFENIK* AND L. GOLIČ

Institute 'Jožef Stefan', Chemistry Department, University of Ljubljana,
61000 *Ljubljana, Yugoslavia*

(*Received* 8 *November* 1978; *accepted* 7 *February* 1979)

Abstract

Crystals of Sr_2EuFeO_5 and Sr_2EuAlO_5 are tetragonal, space group $I4/mcm$ and $Z = 4$. Cell parameters for Sr_2EuFeO_5 are $a = 6{\cdot}812\,(3)$, $c = 11{\cdot}263\,(3)$ Å, and for Sr_2EuAlO_5 $a = 6{\cdot}742\,(1)$, $c = 10{\cdot}970\,(1)$ Å. The two compounds are isostructural with Cs_3CoCl_5. The structures were refined to final R values of 0·021 and 0·022 respectively. The structures contain FeO_4 or AlO_4 tetrahedra. The Sr and Eu atoms are statistically distributed over one position, 8(*h*). The O atom which is not a part of the tetrahedron is octahedrally coordinated by Sr and Eu.

Introduction

In our study of the ternary system $SrO–Eu_2O_3–Fe_2O_3$ (Drofenik, Kolar & Golič, 1974*a*) we reported the occurrence of the ternary phase Sr_2EuFeO_5. Monocrystals of the compounds Sr_2EuFeO_5 and Sr_2EuAlO_5 have been grown (Drofenik, Kolar & Golič, 1974*b*, 1979) and the structure model has been proposed. The present work describes the refinement of this structure.

This group of compounds belongs to a group of alkaline-earth pentaoxometallates, with strontium substituted by a rare-earth atom.

During his extensive work Scholder (1958) prepared a series of isotypic compounds with the general formula Ba_3MO_5 (M = Ti, V, Cr, Mn, Fe, Co, Si, Ge). Later, Gotsmann (1962) and Letzelter (1960) prepared some ternary compounds Sr_2LaAlO_5 and Ba_2LaMO_5 (M = Mn, Fe, Co, Al, Ga).

During their study of silicates, Dent Glasser & Glasser (1965), and Dent Glasser (1965) solved the structure of Sr_3SiO_5 and described the structural relationship between Sr_3SiO_5, Cd_3SiO_5 and Ca_3SiO_5. Mansmann (1965) found that three barium pentaoxometallates Ba_3MO_5 were isotypic with Cs_3CoCl_5 (Powell & Wells, 1935), and reported that the structure of Sr_3SiO_5 ($P4/ncc$) is isotypic with Cs_3CoCl_5 ($I4/mcm$) up to the second non-metal position, which causes the transition from a centrosymmetric to a primitive lattice. Also Eysel (1970) has reported the structures of two pentafluoroberyllates, K_3BeF_5 and Rb_3BeF_5, which are isotypic with Cs_3CoCl_5, and reviewed this group of compounds.

---

* To whom correspondence should be addressed.

0567-7408/79/051059-04$01.00

Experimental

Monocrystals of Sr_2EuFeO_5 and Sr_2EuAlO_5 were prepared by high-temperature solution methods. The monocrystals of Sr_2EuFeO_5 were brown, of a block-like habit, while those of Sr_2EuAlO_5 were colourless transparent plates. Empirical formulae were derived from atomic-absorption spectroscopy. The density was measured pycnometrically.

Crystal data: Sr_2EuFeO_5, $M_r = 463{\cdot}044$, tetragonal, $a = 6{\cdot}812\ (3)$, $c = 11{\cdot}263\ (3)$ Å, $V = 522{\cdot}6$ Å^3, $D_o = 5{\cdot}90$, $D_c = 5{\cdot}88$ Mg m^{-3}, $Z = 4$, space group: $I4/mcm$ (No. 140). Sr_2EuAlO_5, $M_r = 434{\cdot}178$, tetragonal, $a = 6{\cdot}742\ (1)$, $c = 10{\cdot}970\ (1)$ Å, $V = 498{\cdot}6$ Å^3, $D_o = 5{\cdot}79$, $D_c = 5{\cdot}78$ Mg m^{-3}, $Z = 4$, space group: $I4/mcm$ (No. 140).

Single crystals of Sr_2EuFeO_5 (Sr_2EuAlO_5)* with approximate dimensions 0·5 mm were used for the data collection on an automatic computer-controlled CAD-4 diffractometer by the use of an ω–2θ scan with a variable scan rate and Mo $K\alpha$ radiation. The full sphere in the range $1{\cdot}5 < \theta < 35°$ was measured. After the absorption correction of 4282 (4089) reflections, 332 (320) unique reflections were obtained by averaging, with a discrepancy of 3·7 (3·9)%.

Structure refinement

The structures were solved by trial methods and refined using a full-matrix least-squares program with anisotropic temperature factors assigned to Eu, Sr, O and Fe(Al). Further refinements were carried out: (*a*) by putting the Eu atoms at the 8(*h*) positions, and (*b*) by putting the Sr and Eu atoms (distributed statistically) at the 8(*h*) positions.

In trial (*a*), the population of Eu at the 8(*h*) position was refined to 0·747 (3) [0·746 (4)]. For this model the *R* values were finally reduced to 0·018 (0·020). In trial (*b*), the occupancies of Sr and Eu in positions 8(*h*) were fixed at 0·5 each. In this case *R* values of 0·021 (0·022) were obtained. For the structures of the title compound, model (*b*) was chosen over model (*a*) because of the better match with the stoichiometry and with density measurements despite the lower *R* values for model (*a*). The largest peaks in the final difference maps were of height 0·1 (0·2) e Å^{-3}.

The atomic scattering factors and dispersion correction factor were taken from Cromer & Mann (1968) and Cromer & Liberman (1970). The final positional parameters are listed in Table 1.†

Description of the structure

Fig. 1 shows a stereoscopic view of the Sr_2EuAlO_5 structure. The unit cell contains eight Sr, four Eu, four Fe(Al) and twenty O atoms. The atoms are numbered according to the system set forth in Table 1. Bond lengths and coordination polyhedra are presented in Table 2.

The Fe(Al) atoms at 4(*b*) sites are coordinated tetrahedrally by O atoms at 16(*l*) sites with four equal Fe(Al)—O distances of 1·851 (3) [1·753 (2)] Å. The tetrahedra are not linked together and are angularly distorted. Two edges of the tetrahedra are parallel to the base-plane diagonal.

Table 1. *Population factors and fractional coordinates* ($\times 10^5$), *for the models* (*b*), *with e.s.d.'s in parentheses*

	Population factor	x	y	z
Sr_2EuFeO_5				
Eu	0·5	32144 (5)	17856 (5)	0
Sr(1)	0·5	32144 (5)	17856 (5)	0
Sr(2)	1·0	0	0	25000
Fe	1·0	50000	0	25000
O(1)	1·0	0	0	0
O(2)	1·0	14496 (43)	35504 (43)	14216 (32)
Sr_2EuAlO_5				
Eu	0·5	32075 (4)	17925 (4)	0
Sr(1)	0·5	32075 (4)	17925 (4)	0
Sr(2)	1·0	0	0	25000
Al	1·0	50000	0	25000
O(1)	1·0	0	0	0
O(2)	1·0	14025 (30)	35975 (30)	14663 (27)

Table 2. *Bond lengths* (Å) *for* Sr_2EuFeO_5 *and* Sr_2EuAlO_5

Symmetry code

(o)	x,	y,	z	(viii)	$\frac{1}{2}+x$,	$\frac{1}{2}-y$,	z
(i)	$-x$,	$-y$,	$-z$	(ix)	$-\frac{1}{2}+x$,	$\frac{1}{2}-y$,	z
(ii)	$\frac{1}{2}-x$,	$\frac{1}{2}-y$,	$\frac{1}{2}-z$	(x)	$-x$,	y,	$\frac{1}{2}-z$
(iii)	$-x$,	$-y$,	z	(xi)	$\frac{1}{2}-x$,	$-\frac{1}{2}+y$,	$-z$
(iv)	x,	y,	$-z$	(xii)	$\frac{1}{2}-x$,	$-\frac{1}{2}+y$,	z
(v)	$\frac{1}{2}+x$,	$-\frac{1}{2}+y$,	$\frac{1}{2}-z$	(xiii)	x,	$-y$,	$\frac{1}{2}-z$
(vi)	$-\frac{1}{2}+x$,	$-\frac{1}{2}+y$,	$\frac{1}{2}-z$	(xiv)	$\frac{1}{2}+x$,	$\frac{1}{2}-y$,	$-z$
(vii)	x,	$-y$,	$\frac{1}{2}+z$				

Sr_2EuFeO_5					
$Sr(2)O_{10}$ polyhedra					
Sr(2)—O(1)$^{(o,vii)}$	2·816	× 2	FeO_4 tetrahedra		
Sr(2)—O(2)$^{(o,ii,iii,vi,ix,x,xii,xiii)}$	2·881 (3)	× 8	Fe—O(2)$^{(ii,v,viii,xii)}$	1·851 (3)	×4
EuO_8 polyhedra			O(1)(Eu,Sr)$_6$ octahedra		
Eu—O(2)$^{(o,iv)}$	2·335 (3)	× 2	O(1)—[Eu,Sr(1)]$^{(o,i,ix,xi)}$	2·505 (1)	× 4
Eu—O(1)$^{(o,viii)}$	2·505	× 2	O(1)—Sr(2)$^{(o,i)}$	2·816	× 2
Eu—O(2)$^{(viii,xi,xii,xiv)}$	2·734 (3)	× 4			
Sr_2EuAlO_5					
$Sr(2)O_{10}$ polyhedra					
Sr(2)—O(1)$^{(o,vii)}$	2·743	× 2	AlO_4 tetrahedra		
Sr(2)—O(2)$^{(o,ii,iii,vi,ix,x,xii,xiii)}$	2·840 (2)	× 8	Al—O(2)$^{(ii,v,viii,xii)}$	1·753 (2)	× 4
EuO_8 polyhedra			O(1)(Eu,Sr)$_6$ octahedra		
Eu—O(2)$^{(o,iv)}$	2·356 (3)	× 2	O(1)—[Eu,Sr(1)]$^{(o,i,ix,xi)}$	2·477 (1)	× 4
Eu—O(1)$^{(o,viii)}$	2·477 (1)	× 2	O(1)—Sr(2)$^{(o,i)}$	2·743	× 2
Eu—O(2)$^{(viii,xi,xii,xiv)}$	2·701 (2)	× 4			

---

* The details in parentheses refer to Sr_2EuAlO_5.

† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34264 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

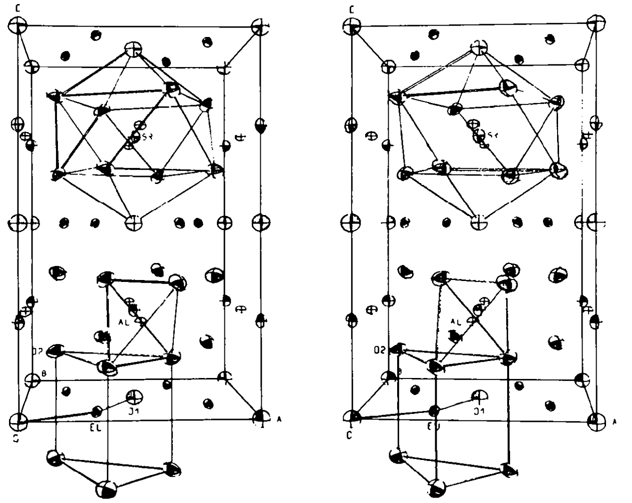

Fig. 1. Stereoscopic view of the Sr_2EuAlO_5 structure.

The strontium atoms at the 4(*a*) position are coordinated by ten O atoms. Eight of them form a regular Archimedes antiprism with equal Sr(2)—O(2) distances of 2·881 (3) [2·840 (2)] Å. The ninth and the tenth O atoms are outside the centres of the rectangular faces parallel to the base plane. The Sr(2)—O(1) distances are 2·816 (2·743) Å.

Eu and Sr atoms which are statistically distributed at 8(*h*) sites are coordinated by six O atoms in the form of a trigonal prism, with four equal Sr(1),Eu—O(2) distances of 2·734 (3) [2·701 (2)] Å and two shorter ones of 2·335 (3) [2·356 (3)] Å. The seventh and the eighth O(1) atoms cap two of the rectangular faces of the prism parallel to the *c* axes. The distances Sr(1), Eu—O(1) are 2·505 (2·477) Å.

The O(1) atoms at the 4(*c*) position, which are not a part of the coordination tetrahedra around Fe(Al), are octahedrally surrounded by Sr(1), Eu and Sr(2) atoms. The Sr(1) and Eu atoms form a square-planar arrangement with four equal distances of 2·505 (2·477) Å. The Sr(2) atoms form the top and bottom of the octahedron with O(1)—Sr(2) distances of 2·816 (2·743) Å.

Discussion

The structures Sr_2EuFeO_5 and Sr_2EuAlO_5 are isotypic with the Cs_3CoCl_5 structure.

The structure contains isolated $FeO_4(AlO_4)$ tetrahedra arranged about the (001) plane. The tetrahedra are angularly distorted with two O—Fe—O angles of 98·0 (1) [99·4 (1)]° and four of 115·5 (1) [114·7 (1)]°, which causes distortion from tetrahedral symmetry of the O atom arrangement around Fe(Al). The origin of the distortion lies in the crystal packing conditions, as is the case for Cs_3CoCl_5 (Figgis, Gerloch & Mason, 1964). The $FeO_4(AlO_4)$ tetrahedra interact strongly in the $x(y)$ direction; along this direction flattening of the tetrahedra is observed.

The second series of groups in the structures are 'octahedra' of cations around O(1), forming an infinite three-dimensional array with common corners. The octahedra are nearly perfect with a fourfold axis parallel to the *c* axis. The octahedra are elongated along the *c* axis because the 4(*a*) positions are filled with Sr(2) atoms, in comparison with 8(*h*) positions where Sr(1) and Eu atoms statistically surround O(1) in an equidistant planar arrangement, but with a shorter O(1)—Sr(1),Eu distance than O(1)—Sr(2). The coordination of the Sr(1),Eu ions is completed with O atoms belonging to $FeO_4(AlO_4)$ tetrahedra.

The mean ${}^{\mathrm{iv}}Fe^{3+}$—O^{2-} distance for the tetrahedrally coordinated Fe atom in the Sr_2EuFeO_5 structure is 1·851 Å. This value is somewhat shorter than the calculated distance of 1·88 Å, using the ionic-radii tables of Shannon & Prewitt (1969), but is in agreement with the observed ${}^{\mathrm{iv}}Fe^{3+}$—O^{2-} distance for $Na_3Fe_5O_9$: average 1·85 (8) Å, single values 1·83 (4)–1·89 (5) Å (Romers, Rooymans & de Graaff, 1967).

The ${}^{\mathrm{iv}}Al^{3+}$—O^{2-} distance of 1·753 Å for the $[AlO_4]^-$ tetrahedra is in fair agreement with the sum of the ionic radii for tetrahedrally coordinated ${}^{\mathrm{iv}}Al^{3+}$ and octahedrally coordinated ${}^{\mathrm{vi}}O^{2-}$, *i.e.* 1·78 Å (Shannon & Prewitt, 1969). The ${}^{\mathrm{iv}}Al^{3+}$—O^{2-} distance is important in the crystal chemistry of aluminium silicates and has been the subject of intensive study.

Smith & Bailey (1963), in their second review of Al—O tetrahedral distances, reported that the most reliable values were in the range 1·75–1·80 Å and suggested the value of 1·75 Å. Using the data from 13 feldspar structures, Ribbe & Gibbs (1967) and Jones (1968) gave values of 1·757 and 1·760 Å, respectively, for ${}^{\mathrm{iv}}Al^{3+}$—O^{2-}. Our distance (1·753 Å) is in agreement with these values and with ${}^{\mathrm{iv}}Al^{3+}$—O^{2-} distances reported recently for $Ca_{8\cdot5}NaAl_6O_{18}$; average 1·751 Å (Nishi & Takéuchi, 1975) and $Ca_3Al_2O_6$: average 1·750, 1·754 Å (Mondal & Jeffery, 1975).

We thank Professor D. Kolar for his interest in this work and the Boris Kidrič Foundation for financial support.

References

Cromer, D. T. & Liberman, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.

Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* A**24**, 321–324.

Dent Glasser, L. S. (1965). *Acta Cryst.* **18**, 455–457.

Dent Glasser, L. S. & Glasser, F. P. (1965). *Acta Cryst.* **18**, 453–454.

Drofenik, M., Kolar, D. & Golič, L. (1974*a*). *J. Less-Common Met.* **37**, 281–284.

Drofenik, M., Kolar, D. & Golič, L. (1974*b*). *J. Cryst. Growth.* **21**, 305–306.

Drofenik, M., Kolar, D. & Golič, L. (1979). To be published.

Eysel, W. (1970). *Neues Jahrb. Mineral. Monatsh.* **12**, 534–547.

Figgis, B. N., Gerloch, M. & Mason, R. (1964). *Acta Cryst.* **17**, 506–508.

Gotsmann, G. (1962). Dissertation TH Karlsruhe.

Jones, J. B. (1968). *Acta Cryst.* B**24**, 355–358.

Letzelter, L. (1960). Dissertation TH Karlsruhe.

Mansmann, M. (1965). *Z. Anorg. Allg. Chem.* **339**, 52–56.

Mondal, P. & Jeffery, J. W. (1975). *Acta Cryst.* B**31**, 689–697.

Nishi, F. & Takéuchi, Y. (1975). *Acta Cryst.* B**31**, 1169–1173.

Powell, H. M. & Wells, A. F. (1935). *J. Chem. Soc.* pp. 359–362.

Ribbe, P. H. & Gibbs, G. V. (1967). *Trans. Am. Geophys. Union*, **48**, 229.

Romers, C., Rooymans, C. J. M. & de Graaff, R. A. G. (1967). *Acta Cryst.* **22**, 766–771.

Scholder, R. (1958). *Angew. Chem.* **70**, 583–614.

Shannon, R. D. & Prewitt, C. T. (1969). *Acta Cryst.* B**25**, 925–946.

Smith, J. V. & Bailey, S. W. (1963). *Acta Cryst.* **16**, 801–811.

Acta Cryst. (1979). B**35**, 1062–1067

Structure Cristalline du Disulfate d'Antimoine(III) $Sb_2(S_2O_7)_3$

Par Jacques Douglade et René Mercier

Laboratoire de Chimie-Physique, Faculté des Sciences et des Techniques, Université de Franche-Comté,
25030 *Besançon CEDEX, France*

(*Reçu le* 13 *septembre* 1978, *accepté le* 8 *février* 1979)

Abstract

The title compound, $Sb_2(S_2O_7)_3$, forms crystals belonging to the triclinic system, space groupe $P1$. The unit cell has the following dimensions: $a = 6{\cdot}644$ (1), $b = 12{\cdot}390$ (3), $c = 9{\cdot}678$ (4) Å, $\alpha = 92{\cdot}69$ (2), $\beta = 82{\cdot}29$ (2), $\gamma = 96{\cdot}88$ (2)°, $V = 783{\cdot}4$ Å^3, $Z = 2$, $D_m = 3{\cdot}25 \pm 0{\cdot}05$, $D_x = 3{\cdot}27$ Mg m^{-3}. The structure determination was based on 4587 independent reflexions. Refinement of parameters of all atoms by block-diagonal least-squares methods with anisotropic temperature factors gave an unweighted R factor of 0·032. There are three S_2O_7 groups with mean bond lengths: S—O (bridge) = 1·618 Å, $S<O_2$ (terminal) = 1·423 Å, S—O···Sb = 1·48 Å, the average value of the S—O—S angle being 121·4°. The two ends of the third S_2O_7 group are linked to the same Sb (thus a bidentate ligand) to form a hexagonal ring. The coordination polyhedra of Sb atoms are distorted trigonal bipyramids, SbO_4E (E being the lone pair of Sb), with a weak axial fourth Sb—O (2·32–2·42 Å).

Introduction

La détermination de la structure de $Sb_2(S_2O_7)_3$ fait suite à diverses études de la coordination de Sb^{III} par des atomes d'oxygène dans des sulfates: $Sb_2O(SO_4)_2$ (Mercier, Douglade & Théobald, 1975); $Sb_2(SO_4)_3$ (Mercier, Douglade & Bernard, 1976); $Sb_2(OH)_2(SO_4)_2.2H_2O$ (Douglade, Mercier & Vivier, 1978); $Sb_6O_7(SO_4)_2$ (Bovin, 1976), dont l'objet est de préciser l'influence de la paire d'électrons non liée de Sb^{III}.

A la différence du groupe P_2O_7, la géométrie du groupe pyrosulfate S_2O_7 est mal connue, puisqu'un seul disulfate $K_2S_2O_7$ (Lynton & Truter, 1960) a vu sa structure déterminée ainsi que deux hydrogénodisulfates: $Se_4(HS_2O_7)_2$ (Brown, Crump & Gillespie, 1971); $NO_2(HS_2O_7)$ (Steeman & MacGillavry, 1954). La connaissance précise de la configuration de ce groupement devrait permettre de vérifier les calculs de Brown (1973) sur les angles de liaison et d'affiner les calculs de champs de forces relatifs à ce groupe.

Signalons qu'aucun composé répondant à cette formule n'est signalé dans la littérature.

Résultats expérimentaux

La dissolution à 393 K de Sb_2O_3 (25 g l^{-1}) dans un oléum riche en SO_3 (~65% SO_3), en tube scellé conduit, après refoidissement à 293 K, à la formation de cristaux incolores pouvant atteindre quelques millimètres. Leur manipulation, en atmosphère anhydre, permet de les isoler en tubes de Lindemann scellés ensuite pour leur étude radiocristallographique. Les dosages de Sb^{3+} (par BrO_3^-) et de SO_4^{2-} (par précipitation de $BaSO_4$), après mise en solution dans HCl 3 M, correspondent à la formule dualistique:

0567-7408/79/051062-06$01.00