

Europium Arsenic Oxide $\text{Eu}_4\text{As}_2\text{O}$: A Filled La_2Sb Structure and its Relation to the K_2NiF_4 and GeTeU Types*

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$\text{Eu}_4\text{As}_2\text{O}$, tetragonal, $I4/mmm$ (D_{4h}^{17}); $Z = 2$, FW 773.68, $a = 4.7924$ (4), $c = 16.1933$ (9) Å, $c/a = 3.379$, $U = 371.9$ Å³; $F(000) = 649$, $D_x = 6.71$ g cm⁻³; $\mu = 439$ cm⁻¹ (Mo $K\alpha$). Diffraction data from a crystal $\sim 0.03 \times 0.07 \times 0.03$ mm with Mo $K\alpha$ radiation and a graphite monochromator gave $R_p = 3.8\%$ for 529 observed hkl when corrected for absorption and refined by full-matrix least squares with allowance for anomalous dispersion. The structure is a filled version of the La_2Sb type with O atoms occupying the octahedral holes at $2(b)$ ($0, 0, \frac{1}{2}$), As atoms in $4(e)$ [$z = 0.1354$ (2)] and Eu atoms in $4(e)$ with $z = 0.3261$ (1) and $4(c)$ ($0, \frac{1}{2}, 0$). The average O–Eu distance is 2.54 Å but the individual distances O–Eu(1) = 2.40 (×4) and O–Eu(2) = 2.82 Å (×2) may indicate the different nature of the two independent Eu atoms. The As atom has nine Eu atoms as nearest neighbors with an average As–Eu of 3.35 Å; this arrangement is usually described in terms of a tricapped trigonal prism but the description in terms of a monocapped square antiprism is more convenient in this case because there is an As contact of 4.39 Å opposite the uncapped square face. Both Eu atoms can be described as 14-coordinated with Eu(1) clearly occupying less volume; average distances for CN = 14 are Eu(1) = 3.30 and Eu(2) = 3.66 Å. This structure is closely related to the K_2NiF_4 and GeTeU types.

Introduction

The structure analysis of $\text{Eu}_4\text{As}_2\text{O}$ was undertaken to resolve a difficulty encountered in a study of the binary EuAs system (Taylor, Calvert, Utsonomiya & Wang, 1977). Samples containing less than 42 at.% As which were slowly cooled from above the liquidus in sealed Ta tubes were frequently found to contain minor amounts of a phase which could not be placed in the phase diagram. This phase was not obtained as a major component, and was also found in unmelted samples containing 38–42 at.% As, prepared in silica, Ta and Mo crucibles, if the preparation temperature exceeded 1100°C. It was found as well-formed crystals in arc-melted samples with nominal compositions in the range 39–41 at.% As. Although it was suspected prior to the structure analysis that this was a ternary phase, no conclusive proof of its nature was obtained from chemical analysis or by synthetic methods, because it was never obtained as a single phase. The total overall O and Ta content of the samples was ~ 1000 p.p.m.a. (parts per million atomic) and 30 p.p.m.a. respectively as compared with 1200 p.p.m.a. O and 10 p.p.m.a. Ta in the Eu used in preparing the samples. The best crystals were obtained from a sample, with nominal composition ~ 38 at.% As, cooled from the liquidus ($\sim 1700^\circ\text{C}$) in a sealed Ta crucible. Debye–Scherrer

and Guinier photographs confirmed that these crystals were of the desired phase and precession photographs yielded the diffraction symbol $4/mmm.I^{***}$ ($h + k + l = 2n$ for all observed reflections) with cell parameters which could be used to index the Guinier photographs. The crystals were sealed in thin-walled glass capillaries in an argon-atmosphere dry box which was used for all specimen preparation operations (Ono, Hui, Despault, Calvert & Taylor, 1971). A well-formed crystal which gave satisfactory Laue photographs was used to collect intensity data on a four-circle computer-controlled diffractometer with local programs (Wang, Gabe, Calvert & Taylor, 1976). The lattice parameters, obtained by centering 30 hkl reflections with $2\theta > 70^\circ$, were $a = 4.7927$ (5), $b = 4.7920$ (4), $c = 16.1932$ (9) Å, $\alpha = 89.969$ (6), $\beta = 89.959$ (6) and $\gamma = 89.976$ (7)° when refined as triclinic. The values used in the structure refinement are those given in the Abstract. Intensities were measured with a θ – 2θ scan technique [width = $(0.7 + 0.7 \tan \theta + 0.7)^\circ$; background measured for a time equal to scan time]; the 1264 accessible reflections with $2\theta < 100^\circ$ were measured. These measurements were averaged over 632 symmetry-related pairs, corrected for Lorentz and polarization factors and absorption effects yielding 529 independent hkl with $I > 2\sigma$ (84% observed). The internal consistency between symmetry-related sets, $\Sigma|I|/\Sigma I$, was 0.06. The diffraction data indicated that the structure was of the La_2Sb type although the nominal composition was $\sim \text{Eu}_5\text{As}_3$. A full-matrix least-

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Table 1. Atomic parameters for $\text{Eu}_4\text{As}_2\text{O}$ ($B_{ij} \times 10^4$)

	<i>x</i>	<i>y</i>	<i>z</i>	β_{11}^*	β_{22}	β_{33}	B_{iso}^\dagger
Eu(1) in 4(c)	0	$\frac{1}{2}$	0	30 (2)	104 (3)	13 (1)	0.91 (2)
Eu(2) in 4(e)	0	0	0.3261 (1)	149 (2)	149 (2)	8 (1)	1.19 (3)
As in 4(e)	0	0	0.1356 (1)	91 (3)	91 (3)	6 (1)	0.81 (5)
O in 2(b)	0	0	$\frac{1}{2}$	40 (25)	40 (25)	42 (7)	0.41 (—)

* $T = \exp[-(h^2\beta_{11}^2 + \dots + hk\beta_{12} \dots)]$; $\beta_{12} = \beta_{23} = \beta_{13} = 0$.

† $B_{\text{iso}} = \text{equivalent isotropic } B$; $T = \exp[-B(\sin \theta/\lambda)^2]$.

Table 2. Interatomic distances in $\text{Eu}_4\text{As}_2\text{O}$ (Å)

Eu(1)—O	2.3962 (1) (×2)	Eu(2)—O	2.8162 (6)
—As	3.2499 (8) (×4)	—As	3.085 (1)
—Eu(1)	3.3887 (1) (×4)	—As	3.4451 (3) (×4)
—Eu(2)	3.6977 (5) (×4)	—Eu(1)	3.6977 (5) (×4)
As—As	4.391 (2) (×4)	—Eu(2)	4.1900 (7) (×4)

Average values

Eu(1)—Eu	3.54	Eu(2)—Eu	3.93
Eu(1)—As	3.25	Eu(2)—As	3.37
Eu(1)—all	3.30	Eu(2)—all	3.66
As—Eu	3.35	O—Eu	2.54

Table 3. Guinier focusing-camera pattern of $\text{Eu}_4\text{As}_2\text{O}$

Diameter = 80 mm, Cu $K\alpha_1$, $\lambda\alpha_1 = 1.54060$ Å, 22°C, silicon standard $a = 5.43052$ Å, d_c from refined parameters $a = 4.7939$ (7), $c = 16.1936$ (24) Å gave $M_{20} = 70$ (de Wolff, 1968). I_c are integrated intensities based on the parameters of Table 1.

d_o (Å)	d_c (Å)	<i>hkl</i>	I_o	I_c
8.11	8.10	0 0 2	<i>w</i>	17
3.586	3.586	1 0 3	<i>w</i>	13
3.390	3.390	1 1 0	<i>w</i>	10
3.127	3.127	1 1 2	<i>vs</i>	100
2.700	2.699	0 0 6	<i>m</i>	33
2.684	2.684	1 0 5	<i>m</i>	25
2.600	2.599	1 1 4	<i>vs</i>	77
2.398	2.397	2 0 0	<i>s</i>	63
1.792	1.792	2 0 6	<i>m</i>	35
	1.788	2 1 5	<i>w</i>	13
1.737	1.738	1 1 8	<i>w</i>	10
1.695	1.695	2 2 0	<i>m</i>	19
1.690	1.685	1 0 9	<i>w</i>	5
1.4903	1.4901	3 1 2	<i>w</i>	18
1.4612	1.4612	1 1 1 0	<i>w</i>	6
1.436	1.4353	2 2 6	<i>m</i>	15
1.4191	1.4197	3 1 4	<i>m</i>	19

squares refinement starting from the La_2Sb coordinates (Stassen, Sato & Calvert, 1970) converged to $R_2 = 0.11$. A difference Fourier map showed anisotropic thermal motion and revealed a large peak at $(0, 0, \frac{1}{2})$. Continued refinement with anisotropic thermal parameters and allowance for anomalous dispersion gave $R_2 = 0.069$ but the large peak at $(0, 0, \frac{1}{2})$ remained. Refinements with partial occupancy of this site by Ta, Eu or As were unsuccessful. However, a refinement

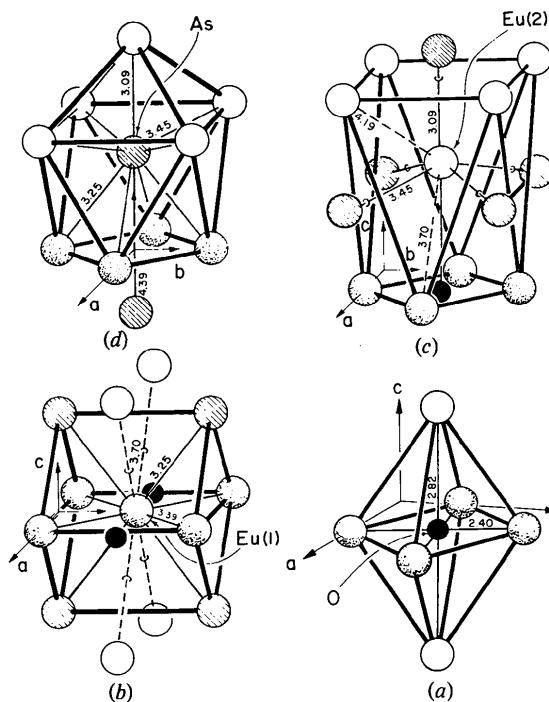


Fig. 1. Atomic coordinations in $\text{Eu}_4\text{As}_2\text{O}$. (a) O atom at $(\frac{1}{2}, \frac{1}{2}, 0)$ [2(b)]. (b) Eu(1) atom at $(0, \frac{1}{2}, 0)$ [4(c)]. (c) Eu(2) atom at $(\frac{1}{2}, \frac{1}{2}, 0.1379)$ [4(e)]. (d) As atom at $(0, 0, 0.1356)$ [4(e)]. The origin is indicated in each case; O is represented by small solid circles, Eu(1) by stippled circles, Eu(2) by open circles and As by hatched circles.

with full occupancy by O converged and showed no significant detail in the final difference Fourier map. The parameters, interatomic distances and an indexed powder pattern are given in Tables 1, and 2 and 3.* The final agreement factors are $R_1 = \Sigma |\Delta F| / \Sigma F_o = 0.050$, $R_2 = [\omega \Delta F^2 / \omega F_o^2]^{1/2} = 0.038$, goodness of fit $[\Sigma \omega (\Delta F)^2 / (N - V)]^{1/2} = 1.37$ where $N = 529$ and $V = 11$ (Wang *et al.*, 1976). All calculations were carried out on the laboratory PDP-8e computer with local programs. For reasons given below a refinement based

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32600 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

on the K_2NiF_4 arrangement was tried but was found to be unsuccessful. It should be noted that the X-ray refinement does not exclude the possibility that the 2(*b*) site is occupied by N (or by N and O in a disordered manner); the chemical analysis shows about ten times as much O as N in the samples and this supports the occupancy by O atoms. Subsequent to this structure analysis, microprobe analyses were carried out in the laboratories of the Department of Energy, Mines and Resources. Attempts to analyze the actual crystal used failed, but six grains in two ingots which contained this phase were analyzed. With EuAs and Eu_3As_3 used as standards, the analysis sums for Eu and As were less than 100% – if the difference is taken to be O the average values for each ingot are $\text{Eu}_{4.00}\text{As}_{2.00}\text{O}_{0.84}$ and $\text{Eu}_{4.01}\text{As}_{1.99}\text{O}_{1.34}$. This is consistent with, and indeed supports the structure analysis.

Description

The O at $(0,0,\frac{1}{2})$ (Fig. 1*a*) is bonded to four Eu(1) and two Eu(2) which form a distorted octahedron (Table 2). Eu(1) has CN = 14 with its neighbors forming an irregular polyhedron (Fig. 1*b*) with 12 vertices, with the two O lying along two of the sides of the square formed by Eu(1) atoms. Eu(2) is also 14-coordinated with As and O as strongly bonded neighbors (3.09 and 2.82 Å) and four Eu(2) at 4.19 Å with weak interactions. This coordination polyhedron is an irregular figure (Fig. 1*c*) having 13 vertices with the O lying at the center of the square face; this polyhedron can be derived by taking a square antiprism, formed by the four Eu(1) and four Eu(2), placing four As alternately opposite four of its eight

triangular faces and then adding an As, capping the Eu(2) square face, and an O in the center of the other square face. The As have nine near neighbors forming the tri-capped trigonal prism common among transition-metal pnictides and chalcogenides; the alternative description as a mono-capped square antiprism (Fig. 1*d*) is convenient here because there is a tenth neighbor (As at 4.39 Å) at what amounts to a van der Waals contact opposite the remaining square face.

Discussion

The La_2Sb structure type has, since its first description (Stassen *et al.*, 1970), been found and described for a number of other phases: Ba_2Bi (Martinez-Ripoll, Haase & Brauer, 1974), Sr_2Sb (Martinez-Ripoll & Brauer, 1973), Ca_2Sb and Ca_2Bi (Eisenmann & Schäfer, 1974; Hamon, Marchand, L'Haridon & Laurent, 1975) and Ca_2As (Hutz & Nagorsen, 1974) so that no detailed geometrical description is necessary. One feature will be discussed here. These structures (Table 4) are all characterized by *c/a* values between 3.3 and 3.9 and z_1 and z_2 values ≈ 0.135 and 0.325 respectively, values essentially identical with those of $\text{Eu}_4\text{As}_2\text{O}$. Thus, they all have two kinds of metal-atom environment, *M*(1) and *M*(2) with *M*(1) on the 4(*c*) site occupying much less volume. For $\text{Eu}_4\text{As}_2\text{O}$ the domain volumes (Frank & Kasper, 1958) unique to Eu(1) and Eu(2) are, respectively, 22.5 and 33.3 Å³ with the corresponding average interatomic distances 3.30 and 3.66 Å. To explain this difference in the case of $\text{Eu}_4\text{As}_2\text{O}$, two arguments may be advanced. On the one hand Eu(1) may be smaller because of the tight bonding to O [Eu(1)–O($\times 2$) = 2.40 Å], but if this is so, then a different explanation would be required for the other phases of this type in Table 4. However, these phases may contain O which was not detected in the structure analysis; we have canvassed this possibility for the La_2Sb data used by Stassen *et al.* (1970) and conclude that their photographic data would not be accurate enough to show the presence of O and do not warrant reprocessing and refining. For the other compounds of this type in Table 3 a study of the *R* values and the refinements does not rule out the possibility that O was present but not detected; because in particular, no difference Fourier maps were calculated and the elements involved are either heavy or reactive or both. It therefore seems desirable to reexamine one of these structures again and we plan to do this. On the other hand, the difference between *M*(1) and *M*(2) for the $\text{Eu}_4\text{As}_2\text{O}$ case may be ascribed to the presence of Eu^{3+} ($r \approx 1.80$ Å) and Eu^{2+} ($r \approx 2.04$ Å). Both the difference ($\Delta = 0.36$ Å) between the average *M*(1) and *M*(2)-neighbor distances and their absolute values, Eu(1)–*X* = 3.30, Eu(2)–*X* = 3.66 Å, are compatible with this explanation, but for the other phases of this

Table 4. Structures in *I4/mmm* closely related to $\text{Eu}_4\text{As}_2\text{O}$

<i>c/a</i>	Formula	Average distances (Å)*			z_1 ($\times 10^3$)	z_2 ($\times 10^3$)	<i>R</i> (%)
		4(<i>e</i>) z_1	4(<i>e</i>) z_2	4(<i>c</i>) –			
3.26	$\text{F}_4\text{K}_2\text{Ni}$	2.59	2.98	2.52	151	352	11
3.36	Ca_4As_2	3.16	3.60	3.31	135	328	—
3.37	$\text{Eu}_4\text{As}_2\text{O}$	3.32	3.66	3.30	136	326	3.8
3.48	Sr_4Sb_2	3.47	3.93	3.63	137	328	9.5
3.49	Ca_4Sb_2	3.25	3.69	3.38	139	334	15
3.49	Ca_4Sb_2	3.29†	3.94†	3.40	—	—	—
3.51	Ca_4Bi_2	3.28	3.74	3.42	140	334	15
3.55	Ba_4Bi_2	3.67	4.17	3.85	137	327	7
3.90	La_4Sb_2	3.35	3.78	3.55	138	320	14
4.15	$\text{P}_2\text{Te}_2\text{U}_2$	3.04	3.50	2.52	115	310	11
4.16	$\text{As}_2\text{Te}_2\text{U}_2$	3.07	3.55	2.93	120	315	6
4.28	$\text{Ge}_2\text{Te}_2\text{U}_2$	3.08	3.53	2.94	123	312	5
3.58	$\text{Ti}_2\text{Bi}_2\text{Ti}_2$	2.87	2.93	2.86	133	353	—

* Average of all distances from central atom to its neighbors.

† Average values over two independent Ca atoms; this structure is refined in *I4mm* (Hamon *et al.*, 1975).

type in Table 4 no such variable valency is known to occur. Nevertheless the average As—Eu distance (3.35 Å) is closer to that predicted for Eu^{2+} —As (3.43 Å) than that predicted for Eu^{3+} —As (3.19 Å) (based on CN = 12 radii) suggesting the nominal valence formulation $\text{Eu}_4^{2+}\text{As}_2^{3-}\text{O}^{2-}$, consistent with divalency for all compounds in the second group of Table 4 and with the first explanation given above. Detailed discussion is more appropriate after one of these structures has been reexamined.

Related structure types

Table 4 lists selected data for other structures closely related to that of $\text{Eu}_4\text{As}_2\text{O}$. Only one representative of the K_2NiF_4 type is listed as this structure is well known (Muller & Roy, 1974; Baltz & Plieth, 1954, 1955). The UGeTe structure type was first reported and described by Haneveld & Jelinek (1969) and UPTe and UAsTe were described by Zygmunt, Murasik, Ligenza & Leciejewicz (1974). Although all structures are similar in a formal geometrical sense, the z_1 and z_2 coordinates and the distribution of atoms among the site sets clearly divide them into groups. The K_2NiF_4 structure has F(1) and K atoms in the $M(1)4(c)$ and $M(2)4(e)$ ($z \sim 0.35$) sites of the La_2Sb type whereas the UGeTe type has U in the trigonal prismatic site 4(e) ($z \sim 0.1$) occupied by the Group V element in the La_2Sb type and Ge and Te occupying the $M(1)$ and $M(2)$ sites respectively. Their relation to the parent type Cu_2Sb (PbFCl , SiZrSe) has been discussed by Haneveld & Jelinek (1969) and also by Zygmunt *et al.* (1974) and for the La_2Sb type this comparison has been discussed by Stassen *et al.* (1970). In Table 4, Ti_2Bi (Auer-Welsbach, Nowotny & Kohl, 1958) appears to hold an anomalous position although closely similar to K_2NiF_4 . It has been discussed by Haneveld & Jelinek (1969) and Stassen *et al.* (1970) but the structure may deserve further study.

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