Acta Cryst. (1978). B**34**, 1962–1965

Structure of Europium Arsenide Eu_5As_4: A More Symmetrical Version of the Sm_5Ge_4-Type Structure*

By Yu Wang, L. D. Calvert,† E. J. Gabe and J. B. Taylor

Division of Chemistry, National Research Council of Canada, Ottawa K1A 0R9, Canada

(*Received* 28 *October* 1977; *accepted* 23 *January* 1978)

Abstract. Eu_5As_4, orthorhombic, *Ccmb* (D_{2h}^{18}), $Z = 4$, FW 1059·6, $a = 8{\cdot}021\,(1)$, $b = 15{\cdot}802\,(3)$, $c = 8{\cdot}058\,(1)$ Å, $U = 1021$ Å^3, $F(000) = 1788$, $D_m = 6{\cdot}85$, $D_x = 6{\cdot}89$ g cm^{-3}, $\mu(\text{Mo } K\alpha) = 439{\cdot}7$ cm^{-1}. Diffractometer data gave $R = 4{\cdot}7\%$ for 942 independent observed *hkl*, for the model described below, when refined by full-matrix least squares with allowance for anomalous dispersion. The structure is a more symmetrical version of the Sm_5Ge_4 type, with trigonal-prismatic coordination of two independent As atoms by six Eu; one As prism is monocapped, while the other is tricapped; one Eu atom is 10-coordinated (to six As atoms arranged octahedrally plus four Eu atoms arranged tetrahedrally) while the other Eu atom is 14-coordinated (to eight Eu atoms forming a square prism plus six As atoms which cap the prism faces). The average interatomic distances are Eu—As = 3·21 Å and Eu—Eu = 3·76 Å, indicating Eu^{3+}. There is a distinctive structural unit composed of four $[Eu_6As]$ trigonal prisms in which pairs of As atoms occur (As—As = 2·54 Å). The structure can thus be considered to be polyanionic.

Introduction. This structural study was undertaken in order to characterize a new phase found in the Eu–As system (Taylor, Calvert, Utsunomiya, Wang & Despault, 1978; Ono, Hui, Despault, Calvert & Taylor, 1971). The phase had a composition close to 57 at.% Eu and its formula was thought to be Eu_5As_4 from consideration of the density and cell volume. Intensity data were collected on a four-circle computer-controlled diffractometer using local programs (for details see Wang, Gabe, Calvert & Taylor, 1976). The crystal used was a fragment 0·04 × 0·07 × 0·08 mm from an Eu–As alloy of composition 60 at.% Eu which had been melted at 1675 K and then slowly cooled. The space group, clearly centrosymmetric from the distribution of intensity statistics, was *Ccmb* (D_{2h}^{18}, No. 64) (precession photographs: *hkl* with $h + k = 2n$, $0kl$ for $l = 2n$, $hk0$ for $k = 2n$). The unit cell of Sm_5Ge_4 (Smith, Johnson & Tharp, 1967) is very similar to that found for Eu_5As_4 but the space groups differ, *viz Pnma* as against *Ccmb*; a careful check of precession photographs and powder patterns confirmed *Ccmb* for Eu_5As_4; the non-standard setting *Ccmb* is directly comparable to the *Pnma* setting of Sm_5Ge_4. The lattice parameters were obtained by centring 30 reflections with $2\theta \geq 50°$. Two equivalent sets of reflections, $hkl + \bar{h}k\bar{l}$, were collected using the θ–2θ scan technique with $2\theta \leq 70°$; background measurements were taken for half the total scan time at each end of the scan range which was varied as $(0{\cdot}7 + 0{\cdot}7\tan\theta + 0{\cdot}7)°$; 2342 measurements were made of which 80% were taken as significant ($I > 2\sigma$); these observed values were corrected for Lorentz, polarization and absorption (the transmission coefficients ranged from 0·15 to 0·35) and were then reduced to 942 independent observed values. The internal discrepancy factor between the symmetry-related sets ($= \sum \Delta I/\sum I$) was 5·9%. The positions of the two Eu atoms were derived from a Patterson map and a comparison with the known Sm_5Ge_4 results (Smith, Johnson & Tharp, 1967). The positions of the As atoms were derived from a Fourier map. These starting coordinates were refined firstly by isotropic, and then by anisotropic, full-matrix least squares. The final agreement indices are $R_1 = 6{\cdot}5\%$ and $R_2 = 6{\cdot}9\%$ for the isotropic refinement; for

Table 1. *Final positional* ($\times 10^4$) *and thermal parameters* ($\times 10^4$, *except* B_{iso})

The temperature factor is of the form $T = \exp[-(h^2\beta_{11} + \ldots + hk\beta_{12} + \ldots)]$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	B_{iso} (Å^2)
Eu(1)	803 (1)	1039 (1)	3352 (1)	40 (1)	8 (1)	26 (1)	4 (1)	17 (2)	−1 (1)	0·82 (1)
Eu(2)	2500	2500	0	36 (2)	7 (1)	28 (2)	0 (0)	2 (3)	0 (0)	0·79 (2)
As(1)	2500	514 (2)	0	32 (3)	7 (1)	26 (3)	0 (0)	18 (4)	0 (0)	0·67 (3)
As(2)	3618	2500	3889 (3)	33 (3)	10 (1)	20 (3)	0 (0)	0 (5)	0 (0)	0·70 (3)

---

* NRC No. 16621.

† To whom correspondence should be addressed.

Table 2. *Interatomic distances* (Å) *and coordination*

Eu(1) (CN = 10)	
Eu(1)–Eu(1)	3·559 (2)
–Eu(1)	3·803 (1)
–Eu(2)	3·805 (1)
–Eu(2)	3·757 (1)
–As(1)	3·136 (1)
–As(1)	3·078 (1)
–As(1)	3·105 (2)
–As(2)	3·258 (2)
–As(2)	3·239 (2)
–As(2)	3·415 (2)
Average Eu(1)–Eu	3·73
Average Eu(1)–As	3·21

As(1) (CN = 7)	
As(1)–2 × Eu(1)	3·136 (1)
–2 × Eu(1)	3·078 (1)
–2 × Eu(1)	3·105 (2)
– Eu(2)	3·138 (2)
Average As(1)–Eu	3·11

Eu(2) (CN = 14)	
Eu(2)–4 × Eu(1)	3·805 (1)
–4 × Eu(1)	3·757 (1)
–2 × As(1)	3·138 (2)
–2 × As(2)	3·259 (2)
–2 × As(2)	3·240 (2)
Average Eu(2)–Eu	3·78
Average Eu(2)–As	3·21

As(2) (CN = 9)	
As(2)–2 × Eu(1)	3·258 (2)
–2 × Eu(1)	3·239 (2)
–2 × Eu(1)	3·415 (2)
– Eu(2)	3·259 (2)
– Eu(2)	3·240 (2)
– As(2)	2·534 (4)
Average As(2)–Eu	3·29

the anisotropic refinement $R_1 = 4{\cdot}7\%$, $R_2 = 5{\cdot}6\%$, and the goodness of fit = 1·84 with NO = 942 and NV = 25 (for definitions see Wang, Gabe, Calvert & Taylor, 1976). The final difference Fourier map showed no significant ($>3\sigma$) detail. The coordinates and thermal parameters are given in Table 1 and the interatomic distances in Table 2.* An indexed powder pattern with observed and calculated intensities is given elsewhere (Taylor, Calvert & Wang, 1977).

Discussion. The structure comprises layers perpendicular to the *b* axis with $y = \pm(0{\cdot}05,\ 0{\cdot}10,\ 0{\cdot}25,\ 0{\cdot}40,\ 0{\cdot}45)$. Because of symmetry it is sufficient to consider two basic layers with *y* between 0 and $\frac{1}{4}$ (Fig. 1), one buckled (*A*) and one planar (*B*). Using Schlafli symbols to specify the networks (Pearson, 1972), net *A* is composed of two As(1) atoms forming a 4^4 network at $y = 0{\cdot}05$ plus four Eu(1) atoms at $y = 0{\cdot}10$ forming a 3^2434 network which, when combined, form a puckered $3^4 + 3^7$ (1:2) net in which the As atoms centre the squares in the Eu net. Net *B* is composed of four As(2) plus two Eu(2) atoms which form a pentagonal $5^3 + 5^4$ (2:1) net lying in the mirror plane at $y = \frac{1}{4}$. These are repeated by symmetry to give the overall stacking sequence $AB\underline{A}A'B'\underline{A}'$ (underlined symbols indicating a mirror image and primed symbols a shifted net). The As(2) atoms of the *B* network (Fig. 1) occur in pairs (As–As = 2·54 Å) and each of these As atoms is the centre of a trigonal prism of Eu(1) atoms in the $A + \underline{A}$ nets (Fig. 2). In addition each As(2) is bonded to two Eu(2) atoms in the *B* net; thus the As(2) coordination is a tricapped trigonal prism sharing one face with another prism centred by the other As atom of the pair. Alternatively the As(2) pair can be considered to centre a 12-vertex polyhedron of Eu atoms. The As(1) atoms (Fig. 2) centre a trigonal prism of Eu(1) atoms in the $A' + \underline{A}$ nets. The pair of Eu(1) atoms in the A' net is a shared edge of the pairs of As(2) trigonal prisms in adjacent half-cells above and below. In addition the As(1) atoms are bonded to Eu(2) atoms in the *B* nets; thus the As(1) coordination is that of a monocapped skew-trigonal prism. The resulting stacking motif is illustrated in Fig. 2. From a detailed

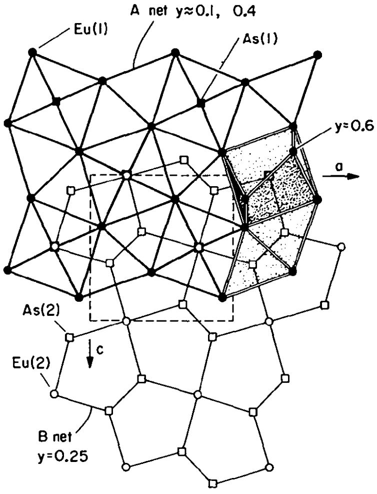

Fig. 1. A projection of the Eu_5As_4 structure between $0 < y < \frac{1}{2}$ onto (010). The individual nets *A* and *B* are shown overlapped in the central portion. In addition two Eu(1) atoms at $y = 0{\cdot}6$ which cap the As(1) trigonal prisms are added on the right-hand side of the figure where the stacking unit of Fig. 2 is emphasized by shading and double lines. See text for details; circles represent Eu atoms, squares As atoms.

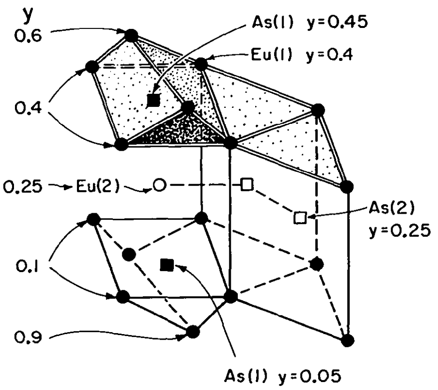

Fig. 2. A perspective view of the stacking motif emphasized in Fig. 1; see text for details.

---

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33357 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

comparison of Figs. 1 and 2 it can be seen that the coordination of the Eu(2) atoms is that of a hexacapped square prism formed of eight Eu(1) atoms capped by four As(2) plus two As(1) atoms. The coordination of the Eu(1) atoms is an irregular 10-vertex polyhedron (Table 2). The occurrence of 10-fold coordination, of varying regularity, for rare-earth elements has been discussed by Bandurkin & Dzhurinskii (1973); it also occurs, for example, in $LaSb_2$ (Wang, Bodnar & Steinfink, 1966). The occurrence of As(2) pairs (As—As = 2·54 Å) allows one to consider Eu_5As_4 as a polyanionic compound (Hulliger & Mooser, 1965) containing As_2^{4-} ions and application of the general valence rule (Pearson, 1972) shows that Eu_5As_4 is not a valence compound, in agreement with the observed continuous network of Eu—Eu bonds with distances consistent with metallic radii. Here Eu can be taken as Eu^{3+} = 3·60 Å, and Eu^{2+} = 4·08 Å, whereas the observed value for Eu^{2+} is 4·2 Å in Eu_3As_4 (Smart, Calvert & Taylor, 1978) and in Eu_2As_2 (Wang, Gabe, Calvert & Taylor, 1977).

Details of two other structure types related to the structure of Eu_5As_4 are given in Table 3. The common factor is the occurrence of the same tiling units stacked so as to produce the structural entity illustrated in Fig. 2. This is similar to the situation of Y_5Bi_3 in *Pnma* (Wang, Gabe, Calvert & Taylor, 1976) which has the same tiling unit and structural motif as Rh_5Ge_3 (Geller, 1955) and Yb_5Sb_3 (Brunton & Steinfink, 1971) although these occur with a different space group requiring a different distribution of site-sets. In Sm_5Ge_4 (Smith, Johnson & Tharp, 1967) one finds that net *A* is equivalent to the combination of layers *G* plus *S* of Sm_5Ge_4 and that net *B* is equivalent to layer *C* of Sm_5Ge_4. (The pentagonal description of net *B* is more directly related to contact distances and is simpler for illustrations than the square–triangle net illustrated for Sm_5Ge_4.) The symmetry of *Pnma* requires six site-sets rather than the four required in *Ccmb* (Table 3). Other compounds reported to have the Sm_5Ge_4 structure are Nd_5Ge_4, Gd_5Ge_4, Tb_5Ge_4, Er_5Ge_4, Y_5Ge_4, Tb_5Si_4, Er_5Si_4 and Y_5Si_4 (Smith, Tharp & Johnson, 1966), La_5Pb_4 (Merlo & Fornasini, 1969), Yb_5Au_4 (Iandelli & Palenzona, 1969) and Gd_5Pb_4 (Demel & Gschneidner, 1969). Smith, Johnson & Tharp (1967) do not specify the coordination of Ge(3) in Sm_5Ge_4 to be trigonal prismatic but the trigonal-prismatic description given here is preferred because it is consistent with observations on other rare-earth pnictides, *viz* Eu_3As_4 (Smart, Calvert & Taylor, 1978), Eu_5As_3 (Wang, Gabe, Calvert & Taylor, 1978) and Y_5Bi_3 (Wang, Gabe, Calvert & Taylor, 1976). Another structure type with the structural motif of Fig. 2 is that of Gd_5Si_4 (Iglesias & Steinfink, 1972) which is a (less symmetrical) version of the Sm_5Ge_4 type. Fig. 3 gives the tiling units, which are not given in the original. There is one significant difference – Gd_5Si_4 has an Si—Si bond arising from a close approach of the trigonal prisms

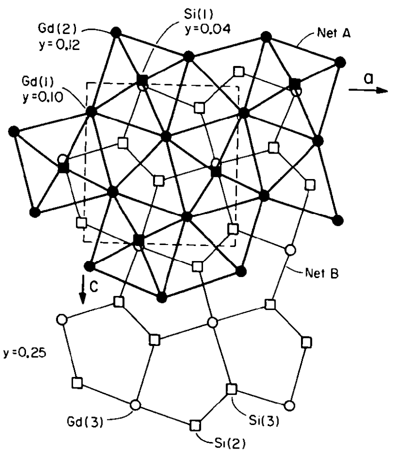

Fig. 3. The Gd_5Si_4 structure drawn to show the nets similar to those of Eu_5As_4. The atoms with $0 < y < \frac{1}{4}$ are shown; circles represent Gd atoms and squares Si atoms.

Table 3. *Details of the structure types* Eu_5As_4, Sm_5Ge_4 *and* Gd_5Si_4

		Eu_5As_4				Sm_5Ge_4				Gd_5Si_4	
Space group		*Ccmb*				*Pnma*				*Pnma*	
a (Å)		8·021				7·75				7·4738	
b (Å)		15·802				14·94				14·724	
c (Å)		8·058				7·84				7·7362	
	x	*y*	*z**		*x*	*y*	*z*		*x*	*y*	*z*
Eu(1)	8	10	34	Sm(1)	12	12	34	Gd(2)†	6	12	34
	92	10	84	Sm(2)	97	10	82	Gd(1)	91	10	84
Eu(2)	25	25	0	Sm(3)	29	25	0	Gd(3)	24	25	1
As(1)	25	5	0	Ge(3)	28	5	97	Si(1)	24	4	5
As(2)	36	25	39	Ge(1)	41	25	39	Si(3)	36	25	42
	14	25	61	Ge(2)	18	25	63	Si(2)	12	25	65

* Fractional coordinates × 10^2.

† The origin has been shifted by subtracting 0·62, 0, 0·48 from the published values.

centred by Si(1) atoms. It seems possible that β-Yb_5Sb_4 (Bodnar & Steinfink, 1967) is a stacking variant of the Eu_5As_4 structure. Very recently Cromer (1977) has reported the structure of Pu_5Rh_4 and Beznosikova, Chebotarev, Luk'yanov, Shapovalov & Timofeeva (1976) those of Pu_5Rh_4 and Pu_5Ir_4; these also have tiling units similar to those in Sm_5Ge_4 and details are given by Cromer (1977).

References

Bandurkin, G. A. & Dzhurinskii, B. F. (1973). *J. Struct. Chem. (USSR)*, **14**, 271–276.

Beznosikova, A. V., Chebotarev, N. T., Luk'yanov, A. S., Shapovalov, M. P. & Timofeeva, L. F. (1976). *Sov. At. Energy*, **40**, 495–498.

Bodnar, R. E. & Steinfink, H. (1967). *Inorg. Chem.* **6**, 327–330.

Brunton, G. & Steinfink, H. (1971). *Inorg. Chem.* **10**, 2301–2303.

Cromer, D. T. (1977). *Acta Cryst.* B**33**, 1993–1995.

Demel, J. T. & Gschneidner, K. A. (1969). *Mater. Nucl. Pays-Bas*, **29**, 111–120.

Geller, S. (1955). *Acta Cryst.* **8**, 15–21.

Hulliger, F. & Mooser, E. (1965). *Prog. Solid State Chem.* **2**, 300–377.

Iandelli, A. & Palenzona, A. (1969). *J. Less-Common Met.* **18**, 221–227.

Iglesias, J. & Steinfink, H. (1972). *J. Less-Common Met.* **26**, 45–52.

Merlo, F. & Fornasini, M. L. (1969). *Atti Accad. Naz. Lincei Cl. Sci. Fis. Mat. Nat. Rend.* **46**, 265–269.

Ono, S., Hui, F. L., Despault, J. G., Calvert, L. D. & Taylor, J. B. (1971). *J. Less-Common Met.* **25**, 287–294.

Pearson, W. B. (1972). *The Crystal Chemistry and Physics of Metals and Alloys*, pp. 3, 202, 605, 628. Toronto: John Wiley.

Smart, M., Calvert, L. D. & Taylor, J. B. (1978). To be published.

Smith, G. S., Johnson, Q. & Tharp, A. G. (1967). *Acta Cryst.* **22**, 269–272.

Smith, G. S., Tharp, A. G. & Johnson, Q. (1966). *Nature (London)*, **210**, 1148–1149.

Taylor, J. B., Calvert, L. D., Utsunomiya, T., Wang, Y. & Despault, J. G. (1978). *J. Less-Common Met.* **57**, 39–51.

Taylor, J. B., Calvert, L. D. & Wang, Y. (1977). *J. Appl. Cryst.* **10**, 492–494.

Wang, Y., Bodnar, R. E. & Steinfink, H. (1966). *Inorg. Chem.* **5**, 1468–1470.

Wang, Y., Gabe, E. J., Calvert, L. D. & Taylor, J. B. (1976). *Acta Cryst.* B**32**, 1440–1445.

Wang, Y., Gabe, E. J., Calvert, L. D. & Taylor, J. B. (1977). *Acta Cryst.* B**33**, 131–133.

Wang, Y., Gabe, E. J., Calvert, L. D. & Taylor, J. B. (1978). To be published.

Acta Cryst. (1978). B**34**, 1965–1968

Structural Studies of Precursor and Partially Oxidized Conducting Complexes. XIV. An X-ray Diffraction Investigation of One-Dimensional Potassium Tetracyanoplatinate Bifluoride Trihydrate*

By Richard K. Brown, Paul L. Johnson, Thomas J. Lynch†
and Jack M. Williams‡

Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439, *USA*

(*Received* 29 *August* 1977; *accepted* 1 *February* 1978)

Abstract. $K_2[Pt(CN)_4](FHF)_{0.3}.3H_2O$, KCP(FHF) hereafter, tetragonal, $P4mm$ (C_{4v}^1), $a = 9.850$ (2), $c = 5.846$ (1) Å, $Z = 2$, $D_m = 2.61$, $D_x = 2.67$ g cm^{-3}. A room-temperature single-crystal X-ray diffraction study was performed. The structural solution was obtained by assuming KCP(FHF) to be isostructural with $K_2[Pt(CN)_4]Br_{0.3}.3H_2O$, KCP(Br), and by using difference Fourier mapping. The absolute configuration was determined by comparison of solutions utilizing xyz *versus* $xy\bar{z}$ coordinates and application of Hamilton's R-factor significance test. Refinement using full-matrix least-squares techniques led to $R(F_o^2) = 0.036$ for 876 independent data and to $R(F_o^2) = 0.035$ for the 740 data with $F_o^2 > 1\sigma(F_o^2)$. The main structural feature is that the $[Pt(CN)_4]^{1.7-}$ groups stack to form Pt–Pt chains, with differing intrachain separations [Pt–Pt = 2.928 (1) and 2.918 (1) Å], which are parallel to **c**, as is the disordered $(F-H-F)^-$ anion array.

---

* Work performed under the auspices of the Division of Basic Energy Sciences of the US Department of Energy.

† Research participant sponsored by the Argonne Center for Educational Affairs; from Marist College, Poughkeepsie, New York.

‡ Author to whom correspondence should be addressed.