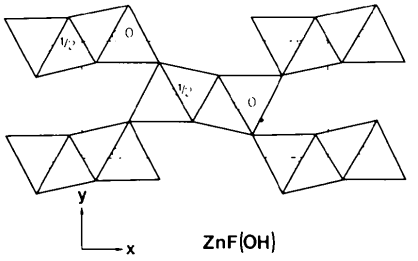

Fig. 3. The structure of ZnF(OH) projected along **c**. The *z* coordinates of the Zn atoms are given. The unit cell is indicated with dashed lines.

hydrogen bonds O···F in CdF(OH) (2·81 Å) are weaker than those in HgF(OH) (2·52 Å) and in InO(OH) (O···O 2·54 Å).

CdF(OH) differs from both CdF_2, with the fluorite (CaF_2) structure, and the layer structures CdCl(OH) (Hoard & Grenko, 1934) and $Cd(OH)_2$ (Natta, 1928). ZnF_2 has the rutile structure, but ZnF(OH) (Volkova, Samarets, Polishchuk & Laptash, 1978), shown in Fig. 3, has the diaspore [AlO(OH)] structure (Busing & Levy, 1958), which is of the rutile type, but with the columns of octahedra doubled.

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The Structure of Trieuropium Tetraarsenide*

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Abstract. Eu_3As_4, orthorhombic, *Fdd*2, a = 14·6419 (7), b = 17·6357 (5), c = 5·8866 (2) Å, U = 1520 Å^3, FW = 755·6, D_m = 6·42, Z = 8, D_x = 6·60 Mg m^{-3}, μ(Mo $K\alpha$) = 42·7 mm^{-1}, F(000) = 2568. Diffractometer data gave R = 3·8% for 1800 independent observed *hkl*, for the model described below, when refined by full-matrix least-squares procedures. The structure consists of a continuous network of [Eu_6] trigonal prisms. Two-thirds of the prisms contain As atoms which form As_4 chains (As–As = 2·47, 2·56 Å, As–As–As = 115·9°) and thus the structure can be considered to be polyanionic. Both Eu atoms are 16-coordinated (to 8 Eu and 8 As) with average distances Eu–Eu = 4·19 and Eu–As = 3·19 Å, consistent with metallic Eu^{2+}.

Introduction. This study was undertaken to characterize a new phase in the Eu–As system (Ono, Hui, Despault, Calvert & Taylor, 1971; Taylor, Calvert, Utsunomiya, Wang & Despault, 1978) which had a composition in the range 43–45 at.% Eu. Intensity data were collected on a four-circle computer-controlled diffractometer with graphite-monochromated Mo $K\alpha$ radiation (λ = 0·70926 Å) using local programs (for details see Wang, Gabe, Calvert & Taylor, 1976; Larson & Gabe, 1978). The crystal used was a fragment 0·1 × 0·04 × 0·04 mm from an Eu–As alloy

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of composition ~50 at.% Eu which had been melted at 1373 K and slowly cooled to allow the peritectic formation of crystals. The space group was determined from precession photographs (hkl with $h + k$, $k + l = 2n$; $0kl$ with $k + l = 4n$; $h0l$ with $l + h = 4n$). The lattice parameters were obtained by centring 54 reflections with 2θ in the range 57–75°. Three sets of reflections hkl, $\bar{h}\bar{k}l$ and $\bar{h}k\bar{l}$ (with $2\theta \leq 80°$) were collected with a $\theta/2\theta$ scan using the profile-analysis technique (Grant & Gabe, 1978). The scan range was varied as a function of θ (range = 1·4° + 0·7° tan θ) to account for wavelength dispersion; 3810 measurements were made equivalent to 2376 independent reflections, of which 1800 were taken as observed ($I \geq 2\sigma I$); these were corrected for Lorentz, polarization and absorption effects (Gabe & O'Byrne, 1970). Transmission coefficients ranged from 0·22 to 0·33. Equivalent sets of reflections were averaged ($\langle \Delta I \rangle / \langle I \rangle = 2\%$). The structure was refined, with allowance for anomalous dispersion and extinction ($g = 2{\cdot}97 \times 10^{-7}$), by anisotropic full-matrix least squares to $R_1 = 0{\cdot}038$ and $R_2 = 0{\cdot}042$, where $R_1 = (\sum \Delta F / \sum F_o)$ and $R_2 = (\sum w|\Delta F|^2 / \sum wF_o^2)^{1/2}$, starting from Eu coordinates derived from a Patterson map. The enantiomorphic form was tested by reversing the f'' contribution; the result showed no significant difference.

The final difference Fourier map contained no significant detail. A microprobe analysis of the crystal used (Owens, 1978) gave Eu = 60·36 (30), As = 39·64 (20) weight % (calc. for Eu_3As_4, 60·33 and 39·67%). The final parameters are given in Table 1 and interatomic distances in Table 2.* An indexed powder pattern is given by Ono, Hui, Despault, Calvert & Taylor (1971).

Discussion. The structure (Fig. 1) consists of a space-filling network of triangular prisms of Eu atoms, in which two-thirds of the prisms contain As atoms close to their centres. The prisms share rectangular faces in two distinct ways, in which the 'trigonal axes' of adjacent prisms are either parallel or perpendicular (Fig. 2), thus forming enantiomorphic polyhedra. The detailed arrangement can be visualized from Fig. 2 where it can be seen that the twofold axes, which are perpendicular to the As(2)–As(2) bonds, lie along the face diagonals of the central pair of prisms forming the enantiomorphic unit, whence it follows that c = 5·89 Å ~ $\sqrt{2}$ × the average Eu–Eu distance = 1·414 × 4·19 = 5·93 Å. The details of face and edge sharing between prisms can be deduced from a comparison of Figs. 1 and 2.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34449 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional parameters* (×10⁴)

	x	y	z
Eu(1)	0	0	0
Eu(2)	9979 (1)	1666 (1)	−4732 (2)
As(1)	847 (1)	1697 (1)	240 (9)
As(2)	4127 (1)	−31 (1)	−19 (6)

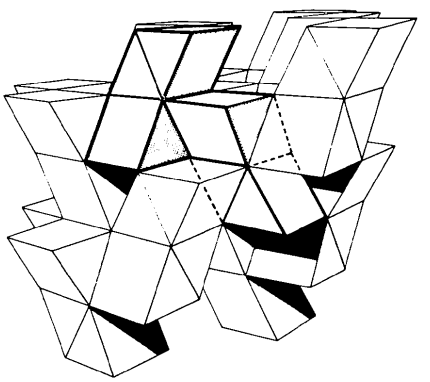

Fig. 1. A model of the Eu_3As_4 structure viewed from a point close to the c axis in the bc plane; the a axis is approximately vertical. Columns parallel to c are joined to form sheets which share triangular faces leaving empty prisms between sheets. The mode of sharing is emphasized by drawing in the hidden lines in two polyhedra (outlined by heavy lines), one left-handed and one right-handed.

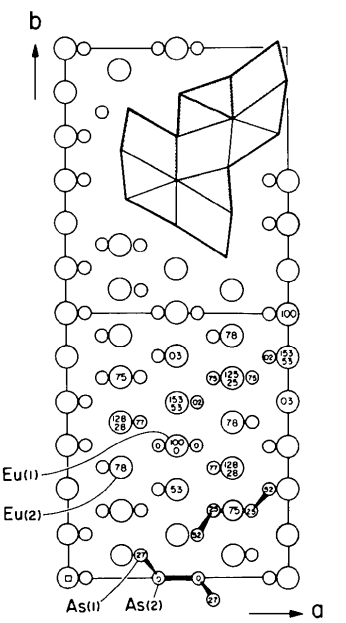

Fig. 2. A projection of the Eu_3As_4 structure onto (001). Two unit cells are outlined: in the lower cell z coordinates (× 100) of the atoms comprising two complete enantiomorphic polyhedra are given, two As_4 chains are outlined and representative atoms are labelled. A perspective view of two polyhedra is superimposed on the upper cell (from which some atoms are omitted). (Note that the angles and distances in the perspective view are not directly comparable to those in the projection.)

Table 2. *Interatomic distances* (Å)

Eu(1)–2As(1)	3·104 (3)	As(1)–As(2)	2·471 (4)
2As(1)	3·243 (2)	Eu(1)	3·104 (3)
2As(2)	3·199 (4)	Eu(1)	3·243 (2)
2As(2)	3·220 (3)	Eu(2)	3·130 (2)
2Eu(2)	4·049 (2)	Eu(2)	3·185 (3)
2Eu(2)	4·131 (1)	Eu(2)	3·191 (5)
2Eu(2)	4·272 (1)	Eu(2)	3·222 (5)
2Eu(2)	4·295 (1)		
Eu(2)–As(1)	3·130 (2)	As(2)–As(1)	2·471 (5)
As(1)	3·185 (3)	As(2)	2·559 (3)
As(1)	3·191 (5)	Eu(1)	3·199 (3)
As(1)	3·222 (5)	Eu(1)	3·220 (3)
As(2)	3·138 (2)	Eu(2)	3·138 (2)
As(2)	3·171 (2)	Eu(2)	3·171 (2)
As(2)	3·198 (2)	Eu(2)	3·198 (2)
As(2)	3·247 (2)	Eu(2)	3·247 (2)
Eu(1)	4·049 (2)		
Eu(1)	4·131 (1)		
Eu(1)	4·272 (1)		
Eu(1)	4·295 (1)		
2Eu(2)	4·162 (2)		
2Eu(2)	4·209 (1)		

The As atoms have seven and eight neighbours, respectively (Table 2) while the Eu atoms are 16-coordinated. The As–As distances of 2·47 and 2·56 Å are comparable with those in metallic arsenic (2·516 Å).

The As atoms within a polyhedron form a 'discrete' four-membered chain, with As–As–As angles of 115·9 (1)°. This structural grouping appeared to be unique for arsenic when first reported (Smart & Calvert, 1972). Discrete four-membered chains had been earlier predicted for polyanions with an average anion coordination of $\frac{3}{2}$ [*i.e.* $m = 4$, $C_a = \frac{3}{2}$ (Hulliger & Mooser, 1965, Table 10)], though not then observed. The isostructural Sr_3As_4 has As–As = 2·48, 2·55 Å and As–As–As = 116° (Deller & Eisenmann, 1977). $NdAs_2$ (Wang, Heyding, Gabe, Calvert & Taylor, 1978) has As_4 chains with As–As = 2·48, 2·50 Å and As–As–As = 104·3°. A mixture of four- and eight-membered chains is known for Ca_2As_3 (Deller & Eisenmann, 1976) where the four-membered chains have As–As distances of 2·53 and 2·49 Å, and As–As–As = 110·2°.

Application of the general valence rule of Pearson (1972) based on the presence of an As_4 polyanion shows that the rule is obeyed but the structure has a continuous network of Eu–Eu bonds with typical metallic values. The average observed Eu–Eu distance in Eu_3As_4 (4·19 Å) indicates the presence of Eu^{2+} [predicted for Eu^{3+} 3·65, for Eu^{2+} 4·09 Å; observed at 4·2 Å in Eu_2As_2 (Wang, Gabe, Calvert & Taylor, 1977) where Eu^{2+} is known to be present from magnetic data]. Although there are 48 essentially similar-sized triangular prisms in the unit cell, only 32 of these contain As atoms, and there is no apparent disordering of the As atoms among the available sites. If the 16 prisms were each to contain a complete *B* or *C* atom, this would give a structure of composition AB_2 or $A_3B_4C_2$ with 72 atoms per unit cell. Apparently no structure of this type is known at present.

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