

SHORT STRUCTURAL PAPERS

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Acta Cryst. (1978). B34, 2281–2284

Structure of Two Forms of Europium Arsenide Eu_5As_3 *

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(Received 21 February 1978; accepted 23 March 1978)

Abstract. Eu_5As_3 crystallizes in two forms. The low-temperature form has the Mn_5Si_3 structure, space group $P6_3/mcm$ (No. 193), $a = 8.8646$ (9), $c = 7.0811$ (4) Å, $c/a = 0.7988$, $D_m = 6.57$, $Z = 2$, $D_x = 6.85$ g cm⁻³, with Eu(1) in 4(*d*), Eu(2) in 6(*g*) [0.74473 (9), 0.74473 (9), $\frac{1}{4}$], As in 6(*g*) [0.39050 (15), 0.39050 (15), $\frac{1}{4}$]; the high-temperature form is a disordered variant of the Ca_5Pb_3 structure, space group $P6_3mc$ (No. 186), $a = 15.2430$ (15), $c = 7.2517$ (2) Å, $c/a = 0.4757$, $Z = 6$, $D_x = 6.72$ g cm⁻³. The disorder in the high-temperature form is related to anisotropic thermal motion of Eu(2) parallel to *c* in the low-temperature form. Diffractometer data (Mo *K* α radiation) yielded $R = 0.038$ for 349 reflections for the low-temperature form and $R = 0.059$ for 898 reflections for the high-temperature form, after refinement by full-matrix least squares. Average interatomic distances in the two forms (high-temperature form in parentheses) are Eu–As 3.31 (3.33), and Eu–Eu 3.73 and 3.98 Å (3.78 and 4.00 Å). Comparison with related structures indicates that Eu is close to divalent in both forms.

Introduction. In the Eu–As system two phases have been observed in the region close to 62.5 at.% Eu (Taylor, Calvert, Utsunomiya, Wang & Despault, 1977). The form later identified as having the Ca_5Pb_3 structure was obtained from melts of the composition 62.5 at.% Eu while from melts with compositions >62.5 at.% Eu, the Mn_5Si_3 type was obtained. This crystal-structure study was undertaken to clarify the relationship between these two forms.

Crystals of the Mn_5Si_3 form were obtained from an ingot of overall composition 70 at.% Eu by slow cooling from 1700 K (which is above the liquidus) and mounted in sealed glass capillaries. Sample handling was in an argon-atmosphere dry box with O_2 and H_2O

<1 part per million (Yoshihara, Taylor, Calvert & Despault, 1975). The two forms were characterized by Guinier powder photographs and precession photographs. Reflection conditions for the low-temperature (LT) form were $h\bar{h}0l$: $l = 2n$, and for the high-temperature (HT) form $hh2hl$: $l = 2n$. Intensity data were measured on a four-circle diffractometer using monochromatized Mo *K* α radiation (Table 1). Details of the data treatment and the absorption calculation have been reported elsewhere (Wang, Gabe, Calvert & Taylor, 1976). Crystals of the Ca_5Pb_3 form (later identified as the HT form) were obtained by slowly cooling a melt of composition 62.5 at.% Eu, melting point ~1550 K; experimental details and material analyses are given in Taylor *et al.* (1977). At the conclusion of the structure refinement, the crystals, polished sections of the source ingots, and standards of known Eu–As composition were analysed by an electron microprobe in the laboratories of the Department of Energy, Mines and Resources (Owens, 1976).

Table 1. *Crystal data*

	LT form	HT form
Reflections used for cell parameters	52 with $2\theta > 50^\circ$	30 with $2\theta > 56^\circ$
Structure type	Mn_5Si_3	Ca_5Pb_3 variant
Cell contents	$Z = 2$	$Z = 6$
Volume (Å ³)	481.9	1459.2
Formula weight	984.7	984.7
$F(000)$	828	2484
Linear absorption coefficient (cm ⁻¹)	434	429
Transmission factors	0.14–0.22	0.10–0.18
Scan range (°)	$0.7 + 0.7 \tan \theta$ + 0.7	$0.6 + 0.7 \tan \theta$ + 0.8
$2\theta_{\text{max}}$ (°)	70	60
Number of unique reflections	475	898
Microprobe analyses		
Crystal	$\text{Eu}_{5.00(1)}\text{As}_{3.00(5)}$	*
Grains from ingot	$\text{Eu}_{5.00(1)}\text{As}_{3.00(5)}$	$\text{Eu}_{5.00(1)}\text{As}_{3.00(1)}$

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* Crystal lost in polishing.

The structure of the LT form was refined by full-matrix least squares, using the Mn_2Si_3 parameters as a starting set (Lander & Brown, 1967). The refinement was based on the average of four equivalent sets of θ - 2θ scan data. The values of R_1 ($\sum \Delta F / \sum F_o$) and R_2 [$(\sum w|\Delta F|^2 / \sum wF_o^2)^{1/2}$] were 0.22 and 0.16 with isotropic and 0.038 and 0.041 with anisotropic temperature factors, and $\sum \Delta w|\Delta F|^2 / (\text{NO}-\text{NV}) = 0.80$ for NO = 349 and NV = 11. The atomic and thermal parameters are given in Table 2.*

Refinement of the HT structure was more difficult. Initial attempts, using the parameters of Ca_5Pb_3 (Helleis, Kandler, Leicht, Quiring & Wolfel, 1963), indicated disorder across the mirror planes at $z = \frac{1}{4}$ and $\frac{3}{4}$. Using the fact that the $hk0$ data from the LT and HT forms are superimposable, good x and y values were obtained from refinement of the $hk0$ data alone starting from the parameters of the LT form. Next, each Eu atom at x, \bar{x}, z was split into three with $z = \frac{1}{4}, \frac{1}{4} - z$ and $\frac{1}{4} + z$ and an occupancy of $\frac{1}{3}$. The As atoms were split into two in a similar way and refinement was started with $B = 1.0 \text{ \AA}^2$. Gradually, split atoms were eliminated and restrictions removed from refinable parameters. The final results are given in Table 2, where it can be seen that Eu(1) is disordered in the

threefold manner described above, Eu(2) and Eu(3) have reduced to two positions and all other atoms have single positions. The agreement factors are $R_1 = 0.059$ and $R_2 = 0.045$, and $\sum \Delta w|\Delta F|^2 / (\text{NO}-\text{NV}) = 1.98$ for NO = 898 and NV = 34. The final difference map does not show any significant feature, but the temperature and occupancy factors show a rather wide spread. This is perhaps not too surprising in view of the amount of disorder and the large absorption corrections applied.

The LT form has the Mn_2Si_3 structure which has been discussed extensively and thus needs no detailed description (Hohnke & Parthé, 1969; Pearson, 1972; Martínez-Ripoll & Brauer, 1973; Wang *et al.*, 1976; Raman & Ghassem, 1973). The interatomic distances are listed in Table 3. The layer structure can be described in Schläfli symbols (Pearson, 1972) as a 6^3 net [Eu(1)] at $z = 0, \frac{1}{2}$ plus a $6^2 3^3 + 6^2 3$ [1 : 1, Eu(2) and As] net at $z = \frac{1}{4}, \frac{3}{4}$. The most significant feature is the anisotropic motion of the Eu(2) atom parallel to c . The structure of the HT form is a disordered variant of the Ca_5Pb_3 structure, lacking the mirror planes of the LT form and with a distinctly longer c axis (Table 1). The Eu(1) atom of the LT form becomes the Eu(4) atom of the HT form, retaining the same 6^3 net (medium lines, Fig. 1). The nets of the LT form at $z = \frac{1}{4}, \frac{3}{4}$ are now buckled. The net at $z \sim \frac{1}{4}$ (dotted lines, Fig. 1) is composed of three different groups, centred on the points $0, 0, \frac{1}{4}$; $\frac{1}{3}, \frac{2}{3}, \frac{1}{4}$; and $\frac{2}{3}, \frac{1}{3}, \frac{1}{4}$. The group at $0, 0, \frac{1}{4}$ is composed of Eu(2) + As(1) atoms, that at $\frac{1}{3}, \frac{2}{3}, \frac{1}{4}$ of Eu(3) + As(3) atoms and that at $\frac{2}{3}, \frac{1}{3}, \frac{1}{4}$ of Eu(1) +

Table 2. Atomic parameters for Eu_5As_3

Low-temperature form

	x	y	z	$\beta_{11}=\beta_{22}$	β_{33}	β_{12}	$B(\text{\AA}^2)$
Eu(1) 4(<i>d</i>)	$\frac{1}{2}$	$\frac{2}{3}$	0	63 (1)	48 (1)	$\beta_{11}/2$	1.1 (1)
Eu(2) 6(<i>g</i>)	0.74473 (9)	x	$\frac{1}{4}$	36 (1)	305 (3)	49 (2)	1.3 (1)
As 6(<i>g</i>)	0.39050 (15)	x	$\frac{1}{4}$	27 (1)	85 (3)	32 (3)	0.8 (2)

High-temperature form

	x	y	z	Occupancy	$B(\text{\AA}^2)$	$\langle x \rangle \ddagger$	$\langle z \rangle \ddagger$
Eu(1)	0.4166 (4)	$-x$	0.1783 (16)	0.44 (2)	0.8 (2)	0.4170	0.2428
Eu(1)'	0.4167 (5)	$-x$	0.2551 (14)	0.39 (2)	0.5 (2)		
Eu(1)''	0.4183 (8)	$-x$	0.3410 (27)	0.24 (1)	1.5 (3)		
Eu(2)	0.9134 (3)	$-x$	0.6878 (12)	0.71 (2)	0.8 (1)	0.9145	0.7079
Eu(2)'	0.9177 (7)	$-x$	0.7701 (23)	0.23 (2)	0.5 (3)		
Eu(3)	0.2497 (4)	$-x$	0.7909 (14)	0.58 (3)	0.6 (1)	0.2497	0.8165
Eu(3)'	0.2498 (4)	$-x$	0.8462 (15)	0.50 (3)	1.5 (2)		
Eu(4)	0.3435 (2)	0.0163 (1)	0*	1.0†	1.24 (3)		
As(1)	0.1306 (6)	$-x$	0.7500 (12)	0.98 (3)	0.7 (2)		
As(2)	0.2022 (4)	$-x$	0.2177 (13)	0.88 (3)	0.4 (2)		
As(3)	0.4635 (6)	$-x$	0.7511 (11)	1.10 (3)	0.9 (2)		

* Fixed to establish origin.

† Held constant.

‡ Weighted average values.

Table 3. *Interatomic distances (Å) for Eu₅As₃*

Low-temperature form

Eu(1)—2 Eu(1)	3.5406 (2)	Eu(2)—4 Eu(1)	3.7932 (5)
—6 Eu(2)	3.7932 (5)	—2 Eu(2)	3.9195 (4)
—6 As	3.2595 (5)	—4 Eu(2)	4.2019 (6)
		—2 As	3.0447 (11)
As—2 Eu(2)	3.0447 (11)	—1 As	3.1401 (16)
—1 Eu(2)	3.1401 (16)	—2 As	3.7380 (5)
—4 Eu(1)	3.2595 (5)		
—2 Eu(2)	3.7380 (5)		
—1 As	4.038 (1)		

High-temperature form (σ 's all <0.003)

Eu(1)—2 Eu(4)	3.699	Eu(2)—2 Eu(4)	3.748
—2 Eu(3)	3.799	—2 Eu(2)	3.910
—2 Eu(1)	3.826	—2 Eu(4)	3.910
—2 Eu(4)	3.898	—4 Eu(2)	4.271
—2 Eu(3)	4.710	—2 As(1)	3.049
—2 As(2)	3.042	—1 As(2)	3.082
—1 As(3)	3.156	—1 As(1)	3.528
—1 As(3)	3.771	—1 As(1)	4.108
—1 As(3)	3.885		

Eu(3)—2 Eu(1)	3.800	Eu(4)—2 Eu(4)	3.651
—2 Eu(4)	3.802	—1 Eu(1)	3.699
—2 Eu(3)	3.825	—1 Eu(2)	3.748
—2 Eu(4)	3.888	—1 Eu(3)	3.802
—2 Eu(1)	4.710	—1 Eu(3)	3.888
—2 As(3)	3.153	—1 Eu(1)	3.898
—1 As(2)	3.168	—1 Eu(2)	3.910
—1 As(1)	3.181	—1 As(1)	3.175
—1 As(2)	4.520	—1 As(3)	3.190
		—1 As(2)	3.233
		—1 As(3)	3.309
		—1 As(2)	3.324
		—1 As(1)	3.401

As(1)—2 Eu(2)	3.049	As(2)—2 Eu(1)	3.042
—1 Eu(3)	3.181	—1 Eu(2)	3.082
—2 Eu(4)	3.175	—1 Eu(3)	3.168
—1 Eu(2)	3.528	—2 Eu(4)	3.233
—2 Eu(4)	3.401	—2 Eu(4)	3.324
—1 Eu(2)	4.108	—1 Eu(3)	4.520
—1 As(2)	3.883	—1 As(1)	3.883
—1 As(2)	4.298	—1 As(1)	4.298

As(3)—2 Eu(3)	3.053
—1 Eu(1)	3.156
—2 Eu(4)	3.190
—2 Eu(4)	3.309
—1 Eu(1)	3.771
—1 Eu(1)	3.885
—2 As(3)	4.106

As(2). Table 3 lists the interatomic distances for the HT phase, based on the weighted average coordinates of the full disordered structure (Table 2). The separation of the sites Eu(1) and Eu(1)' is 1.18 Å, that for Eu(2) and Eu(2)' is 0.61 Å and that for Eu(3) and Eu(3)' is 0.40 Å. Mean values of Eu—Eu and Eu—As distances are listed in Table 4. Values for the full disordered structure were calculated and compared with those of Table 3, but as no significant differences were noted they are not given. The detailed coordinations are essentially those of the Mn₅Si₃ type.

Discussion. Taking the structural results and the microprobe results together with the phase-analytical results (Taylor *et al.*, 1977) it was concluded that the two phases were HT and LT forms of essentially stoichiometric Eu₅As₃. Values of Eu—Eu and Eu—As distances (Table 4) are not greatly changed between the two forms. The LT form has two distinct average Eu—Eu distances, 3.73 and 3.97 Å, centred on Eu(1) and Eu(2) respectively, and this feature is clearly retained in the HT form with an average distance of 3.78 Å centred on Eu(4), as compared with 3.99, 4.01 and 4.02 Å centred on Eu(1), Eu(2) and Eu(3) respectively. The type structure, Mn₅Si₃, also has two different types of Mn atoms (Lander & Brown, 1967),

Table 4. *Average interatomic distances (Å)*

	CN	Eu—Eu	Eu—As	Domain volume*
Low-temperature form				
Eu(1)	14	3.730	3.260	28.4
Eu(2)	15	3.982	3.341	34.0
As	9 + 2	—	3.305	28.0
High-temperature form				
Eu(1)	15	3.986	3.379	34.1
Eu(2)	15	4.022	3.363	34.5
Eu(3)	15	4.005	3.395	33.9
Eu(4)	14	3.781	3.272	29.3
As(1)	9 + 2	—	3.341	28.3
As(2)	9 + 2	—	3.330	28.3
As(3)	9 + 2	—	3.324	28.4

* Frank & Kasper (1958).

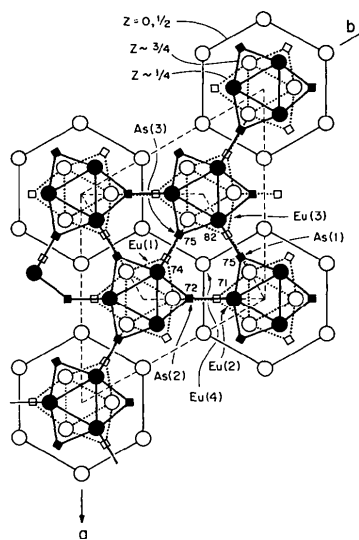


Fig. 1. The HT Eu₅As₃ structure projected on to (0001). The Eu(4) atoms are plotted at averaged x,y coordinates. The z coordinates of one set of atoms are marked. Dashed lines outline the unit cells of the HT and LT forms.

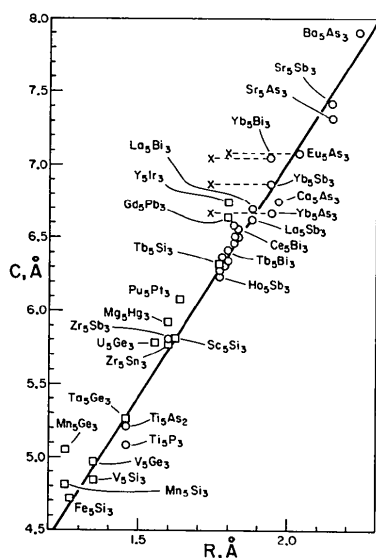


Fig. 2. The c axes of A_5B_3 compounds plotted against the CN 12 metallic radius of the A atoms. The straight line ($c = 0.56 + 3.23R_A$) is a least-squares fit for compounds with $B = P, As, Sb, Bi$ (open circles). Squares mark representative examples of other A_5B_3 phases. In the central region only a few points are labelled.

the electron density of the Mn(1) atom in 4(d) being found to be spherical and that of Mn(2) nonspherical, as is also its spin density. Observed values for $Eu^{2+}-Eu^{2+}$ distances in similar compounds are 4.19 Å in Eu_3As_4 (Smart, Calvert & Taylor, 1978), 4.20 Å in Eu_2As_2 (Wang, Gabe, Calvert & Taylor, 1977), 3.93 Å in Eu_4As_2O (Wang, Calvert, Gabe & Taylor, 1977), and for $Eu^{3+}-Eu^{3+}$ 3.76 Å in Eu_5As_4 (Wang, Calvert, Gabe & Taylor, 1978). It has been argued (Taylor *et al.*, 1977), on the basis of cell-volume plots and near-neighbour diagrams, that Eu_5As_3 contains divalent Eu in conformity with Ca_5As_3 , Sr_5As_3 and Ba_5As_3 . The LT and HT forms of Eu_5As_3 contain $AsEu_6$ trigonal prisms with virtually the same average As-Eu and Eu-Eu distances. The most significant difference is the short Eu-Eu distance ($= c/2$) changing from 3.54 to 3.65 Å with some distortion of the prisms. This change appears to be directly associated with the high thermal motion of Eu(2) in the LT form, becoming disorder in Eu(1), Eu(2) and Eu(3) in the HT form.

A_5B_3 structures ($B = P, As, Sb$ or Bi), with the Mn_5Si_3 structure, show a nearly linear relation between

the c axis and the radius of the A atom (Fig. 2), which extends from Ti_5P_3 ($c = 5.09$ Å) to Ba_5As_3 ($c = 7.90$ Å); c/a values are from 0.69 (Zr_5Sb_3) to 0.83 (Ba_5As_3) and radius ratios R_B/R_A are from 0.68 (Eu_5As_3) to 0.99 (Zr_5Sb_3). The elements Eu and Yb when plotted with their divalent radius give a better fit. Thus the A atom radius is a significant factor, and in the near-neighbour diagram for Mn_5Si_3 structures [p. 66 of Pearson (1972) and Fig. 3 of Taylor *et al.* (1977)] the structures occur in a band parallel to the $A-A$ contacts, with a nearly constant $A-A$ compression, down to values approximately equivalent to the single-bond radius (Hohnke & Parthé, 1969). Where a structure requires that the $A-A$ distance ($= c/2$) be much too compressed, the Mn_5Si_3 structure is replaced by the Y_5Bi_3 structure (Wang *et al.*, 1976).

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