

search for a crystal of La_2Sb (the original crystal had decomposed) eventually yielded a workable crystal. Full-matrix least-squares refinement of 455 reflections [$I > 2\sigma(I)$, $2\theta_{\text{max}} = 90^\circ$, monochromatized $\text{Mo } K\alpha$ radiation, diffractometer data with anisotropic temperature factors and allowance for anomalous dispersion] gave $R = 0.086$.* (This relatively high value of R reflects the poor quality of the crystal, the best found in an extensive search.) A difference Fourier synthesis showed no residual electron density at the $2(a)$ or $2(b)$ sites although there were small ripples close to atom sites. Full details of the structure are given by Stassen, Sato & Calvert (1970).

* Full atomic parameters and a list of structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34791 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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The structures of Eu_4As_3 and La_4Sb_3 .* By Y. WANG,† L. D. CALVERT‡ and J. B. TAYLOR, *Chemistry Division, National Research Council of Canada, Ottawa, Canada K1A 0R9*

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Abstract

Ln_4X_3 (Ln = rare earth, X = P, As, Sb, Bi) compounds have the anti- Th_3P_4 structure with space group $I\bar{4}3d$ (No. 220), $Z = 4$ and Ln atoms in $16(c) x, x, x$ and X atoms in $12(a) \frac{3}{8}, 0, \frac{1}{4}$. Eu_4As_3 has $a = 9.214$ (1) Å, $x(\text{Eu}) = 0.06798$ (3), $B(\text{Eu}) = 1.19$ (1), $B(\text{As}) = 1.33$ (6) Å², $D_x = 7.07$ Mg m⁻³, $\text{Eu}-(3 + 3)\text{As}$, $\text{As}-(4 + 4)\text{Eu} = 3.042$ (1), 3.348 (1), $\text{Eu}-3\text{Eu} = 3.581$ (1) Å. La_4Sb_3 has $a = 9.649$ (1) Å, $x(\text{La}) = 0.07063$ (2), $B(\text{La}) = 0.83$ (1), $B(\text{Sb}) = 0.81$ (2) Å², $D_x = 6.81$ Mg m⁻³, $\text{La}-(3 + 3)\text{Sb}$, $\text{Sb}-(4 + 4)\text{La} = 3.211$ (1), 3.476 (1), $\text{La}-3\text{La} = 3.720$ (1) Å. The Ln–X distances are normal. The Ln atoms form two distinct enantiomorphic three-dimensional networks composed of three-connected ten-membered rings. These Ln–3Ln distances correspond to the values expected for Ln³⁺ metallic bonds.

Introduction

Detailed structures of the lanthanon pnictides (Ln_4X_3 ; Ln = rare-earth element, X = Group V element) with the anti- Th_3P_4 -type structure are of considerable interest in connection with their physical properties, e.g. ferromagnetism and superconductivity (Hulliger & Vogt, 1970; Hulliger & Ott, 1977). A study of the Eu–As system (Taylor, Calvert, Utsunomiya, Wang & Despault, 1978) found that the powder intensities were not sensitive to the As vacancy concentration. Accordingly, single-crystal structure studies

We conclude that La_2Sb contains no interstitial atom; moreover, it is known to be metallic (Hulliger & Ott, 1977). Thus compounds with this structure fall into two classes with La_2Sb representing one class and $\text{Eu}_4\text{As}_2\text{O}$ and $\text{Ba}_4\text{As}_2\text{O}$ another; both Eu and Ba are divalent whereas La is trivalent.

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were undertaken to define the composition more precisely. Crystals were extracted from the available specimens and tested by Laue photographs. After many tests, one reasonable crystal was found in a specimen of composition Eu_4As_3 , melted and annealed in Ta at 1923 K and then rapidly cooled. Subsequently a second structure was determined for a La_4Sb_3 crystal from a specimen of composition La_4Sb_3 melted and annealed in Ta at 2173 K and then slow cooled. Intensity data were collected using the profile-analysis technique (Grant & Gabe, 1978) on a four-circle computer-controlled diffractometer with graphite-monochromated $\text{Mo } K\alpha$ radiation ($\lambda = 0.70932$ Å) with local programs (for details see Gabe & O'Byrne, 1970; Grant & Gabe, 1974;

Table 1. Ln_4X_3 ($I\bar{4}3d$)

	Eu_4As_3	La_4Sb_3
a (Å)	9.214 (1)	9.649 (1)
V (Å ³)	782.4	898.3
x for Ln	0.06798 (3)	0.07063 (2)
U_{11}, U_{33} for Ln*	0.0151 (1), 0.0004 (1)	0.0105 (1), -0.0004 (1)
U_{11}, U_{33} for X†	0.0151 (4), 0.0204 (8)	0.0095 (1), 0.0119 (2)
R_1, R_2^\ddagger	0.028, 0.021	0.021, 0.016
Total independent reflections	416	404
Observed $ I > 2\sigma(I)$	362	388
$\Sigma(\Delta I)/\Sigma(I)$ (%)	2	3
Extinction coefficient	—	8.97×10^{-6}
$2\theta_{\text{max}}$ (°)	80	75
Scan range (2θ) (°)	$1.6 + 0.7 \tan\theta$	$1.4 + 0.7 \tan\theta$
Crystal size (mm)	$0.12 \times 0.04 \times 0.02$	$0.14 \times 0.07 \times 0.04$
μ (mm ⁻¹)	45.02	22.76
Transmission coefficient	0.26–0.39	0.18–0.33
$F(000)$	1404	1524
D_x (Mg m ⁻³)	7.07	6.81

* For Ln, $U_{11} = U_{22} = U_{33}$ and $U_{13} = U_{23} = U_{12}$.

† For X, U_{11}, U_{22}, U_{33} and $U_{12} = U_{13} = U_{23} = 0$.

‡ $R_1 = \Sigma|\Delta F|/\Sigma F_o$; $R_2 = (\Sigma w|\Delta F|^2/\Sigma wF_o^2)^{1/2}$; $w = 1/(\sigma^2(F_o)_{\text{counts}})$.

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Wang, Gabe, Calvert & Taylor, 1976; Larson & Gabe, 1978). The space group was determined from precession photographs (hkl : $h + k + l = 2n$; hhl : $2h + l = 4n$) and intensity statistics to be $I\bar{4}3d$. The systematic absences were also measured to check the possibility that the crystal had lower symmetry due to ordering (Carter, 1972). In addition, the La_4Sb_3 data were refined in $I2_13$ to a result not significantly different from $I\bar{4}3d$. Details for each crystal are given in Table 1. Two complete unique sets, each containing hkl and $\bar{h}\bar{k}\bar{l}$, were measured and averaged. All calculations were carried out on the laboratory computer using the NRC-PDP-8 system of programs (Larson & Gabe, 1978). The structure was refined using the observed reflections with allowance for anomalous dispersion and isotropic extinction (Larson, 1969). For Eu_4As_3 extinction was negligible and not refined. Refinement was by anisotropic full-matrix least squares with starting coordinates from Hulliger & Vogt (1970).*

For both structures the final difference maps contained no significant details. (A refinement with variable As occupancy did not give significantly different results.) A microprobe analysis (Owens, 1978) of the Eu-As crystal gave $\text{Eu}_{4.01(3)}\text{As}_{2.99(3)}$. The stoichiometric formula was therefore accepted for our crystal.

For comparison, La_4Sb_3 , known to be stoichiometric (Gambino, 1967), was also studied.

Discussion

The Th_3P_4 structure (Meisel, 1939) has been described in detail elsewhere (Heim & Bärnighausen, 1978, and references therein). The anti version of this structure is observed for pnictides of the rare earths, Ln_4X_3 (Hohnke & Parthé, 1966; Bodnar & Steinfink, 1966; Gambino, 1967; Hulliger & Ott, 1977), but to date no diffractometer single-crystal study is known to us. Structural details are of interest in discussing the superconductivity of Ln_4X_3 compounds which are an order of magnitude different from the analogous Ln_3Y_4 ($Y = \text{S}, \text{Se}, \text{Te}$) compounds with the normal Th_3P_4 structure. The interatomic distances are given in the *Abstract* and the average Ln-X values, *viz* $\text{Eu-As} = 3.20 \text{ \AA}$ and $\text{La-Sb} = 3.34 \text{ \AA}$, are equivalent to those expected for Ln^{3+} metallic phases. Each Ln atom is connected to three other Ln atoms (Maas, 1970), forming two distinct enantiomorphic sets of three-connected ten-membered rings (Heim & Bärnighausen, 1978) in which the bonding is comparable to that for the Ln^{3+} metal. For La these are the face-centred

cubic and double hexagonal close-packed forms of the element (3.75 and 3.77 Å respectively) and for Eu^{3+} the 12-coordination value is 3.60 Å. Similar geometrically distinguishable Ln sublattices are observed in other lanthanon pnictides, even anion-rich ones, *e.g.* the high- and low-temperature forms of LaAs_2 , and in NdAs_2 (Wang, Heyding, Gabe, Calvert & Taylor, 1978). The lattice parameter and stoichiometry found for La_4Sb_3 are in excellent agreement with those of Hulliger & Ott (1977), 9.6485 (8) Å and $\text{La}_4\text{Sb}_{2.94-3.02}$, and consistent with those of Hohnke & Parthé (1966), 9.648 Å, and Gambino (1967), 9.63 Å. For Eu_4As_3 both lattice parameter and stoichiometry differ from those given by Hulliger & Vogt (1970) and we conclude that our single crystal is stoichiometric Eu_4As_3 .

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*Lists of structure factors for both compounds have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34788 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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