

iances. For example, the goodnesses-of-fit for x', y', z' , and β'_{22} are 0.41, 0.48, 0.39, and 0.32, each for 22 degrees of freedom, the polar-axis problem being ignored, the coordinate e.s.d.'s of atom B(1) taken equal to their B(2) counterparts [coordinates of B(1) were held fixed in MD], and a $\cos\beta$ estimate of the x - z covariance (Templeton, 1959) inserted in evaluating the e.s.d.'s for z' . We note that these values are close to the reciprocal of the goodness-of-fit value of 2.08 reported by MD, suggesting that the e.s.d.'s given by MD are considerably greater than required by the random errors in the data and probably reflect errors in the model that are independent of the choice of Laue group.

The glide plane in Cc should result in the systematic absence of reflections $h'0l'$ with l' odd – or, relative to the original $P1$ description, of $h, k, -h - 2k$ with h odd. Of the 65 such reflections in the range of the supplementary tables, five are omitted (presumably because the net count was negative or zero), 52 are starred [presumably because I was less than $3\sigma(I)$], and eight are unstarred. No $\sigma(F_o)$ values are given. We cannot assert that these reflections are really absent; but it is certain that the triclinic structure fails to account for them, as the average value of F_c/F_o for the 60 reflections listed is 0.18 (0.06 for the eight unstarred), and it seems extremely unlikely that any (necessarily) quite different structure could ever be found to agree so well ($R = 0.035$, $R_w = 0.045$) with all the data. Instead, we believe that either the observed 60 are somehow in error or they represent some slight imperfection of the crystal. In any case, they are so weak (the largest F_o among them is only about a fortieth of the largest of all the F_o 's) as to be almost certainly undetectable on any photograph.

The Laue symmetry of Cc , $2/m$, requires equivalence of reflections hkl and $h, -h - k - l, l$ in the triclinic indexing. Lack of e.s.d.'s for the reported F_o 's precludes a definitive test of the equivalence, and we have carried out only a partial

study. For the 84 pairs in the supplementary tables with l equal to 0 or 1 and with one or both F_o 's greater than 1000 (for example), the average $|\Delta F_o|/\langle F_o \rangle$ is 0.030, only 50% greater than would correspond to the lack-of-confidence term $(0.04I)^2$ used by MD in assigning observational errors. (Again the triclinic structure fails to account for any apparent deviations from monoclinic symmetry, as the average $|\Delta F_c|/\langle |F_c| \rangle$ for these same 84 pairs is only 0.010.) We gain the impression that the deviations from monoclinic symmetry are at worst no greater than would be expected from the weights (or σ 's) assigned by MD, confirming our earlier conclusion that the parameter e.s.d.'s reported are considerably greater than required by the random errors in the data.

The refinement by MD in $P1$ should have led to no problems of singularity or abnormally large covariances other than those due to the polar axes (Schomaker & Marsh, 1979), but we cannot test this point precisely. Altogether, the main advantage in describing this structure in Cc lies in imposing exact, rather than approximate, symmetry relationships between different ions and, in so doing, increasing the accuracy of the determination. Of course, Cc also provides the natural explanation of the near identity of the two molecules in the unit cell (noted but not explained by MD) and the monoclinic metrical symmetry of the lattice, which is pretty well hidden by the triclinic indexing but should have been suggested by the original (MD) pseudotetragonal indexing.

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Acta Cryst. (1980). **B36**, 220–221

Is there an oxygen atom in La_2Sb^* ? By Y. WANG,[†] L. D. CALVERT[‡] and J. B. TAYLOR, *Chemistry Division, National Research Council of Canada, Ottawa, Canada K1A 0R9*

(Received 20 August 1979; accepted 25 September 1979)

Abstract

La_2Sb has space group $I4/mmm$, $a = 4.629$ (2), $c = 18.098$ (6) Å, $Z = 4$, $D_x = 6.84$ Mg m⁻³ with La(1) in 4(c) $0, \frac{1}{2}, 0$, La(2) in 4(e) $0, 0, z$ [$z = 0.3203$ (1)] and Sb in 4(e) [$z = 0.1377$ (2)] and equivalent isotropic B 's of 1.12 (8), 0.70 (6) and 0.74 (7) Å² respectively. Interatomic distances are La–La 3.273 (1), 3.992 (2), 4.146 (3) and La–Sb 3.306 (4), 3.360 (2), 3.400 (2) Å. No significant electron density was found at the sites 2(a) or 2(b), contrary to the

case of $\text{Eu}_4\text{As}_2\text{O}$, an apparently isostructural compound. The structure was refined by full-matrix least squares using 455 observed diffractometer data.

The structure of La_2Sb was first reported by Stassen, Sato & Calvert (1970) based on photographic data. In 1977, during a diffractometer study of 'Eu₂As', thought to be isostructural with La_2Sb , it was found that the formula was really $\text{Eu}_4\text{As}_2\text{O}$ (Wang, Calvert, Gabe & Taylor, 1977). It was therefore suggested that other structures assigned to the La_2Sb type might also contain an extra atom. This has been confirmed for $\text{Ba}_4\text{As}_2\text{O}$ (von Schnering & Schmettow, 1979). A re-examination of La_2Sb was therefore undertaken. A

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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 [$I > 2\sigma(I)$, $2\theta_{\max} = 90^\circ$, 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.

Acta Cryst. (1980). **B36**, 221–222

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*

(Received 4 September 1979; accepted 24 September 1979)

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), $B(\text{As}) = 0.81$ (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 Ln^{3+} 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^\dagger	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}
$2\theta_{\max}$ (°)	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, $U_{11} \neq U_{22}$ and $U_{12} \neq U_{13} = U_{23} = 0$.

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

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