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High-temperature $LaAs_2$

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High-temperature (>1023 K) lanthanum diarsenide crystallizes in the monoclinic space group *Cc* and adopts the LaP_2 structure type, previously reported in the alternate setting *Ia* [von Schnering, Wichelhaus & Schulze Nahrup (1975). *Z. Anorg. Allg. Chem.* **412**, 193–201]. HT-$LaAs_2$ is a Zintl compound consisting of As_3^{5-} and As_5^{7-} chains [As—As 2.460 (3)–2.569 (3) Å] coordinating onto La^{3+} ions [La—As 3.049 (2)–3.295 (2) Å] in tricapped trigonal prismatic geometry.

Comment

$LaAs_2$ was reported to transform reversibly at 1023 K from its low-temperature $NdAs_2$-type structure ($P2_1/c$; Wang *et al.*, 1978) to a unique high-temperature structure (Ono *et al.*, 1970). Precession photography on HT-$LaAs_2$ originally suggested the monoclinic space group *B*2/*b* (an alternate setting of *C*2/*c*) with $a = 12.891$, $b = 9.140$, $c = 14.450$ Å, and $\gamma = 135.16°$. A misleading tetragonal or orthorhombic indexing ($a \sim b = 9.07$, $c = 14.31$ Å) was also proposed for HT-$LaAs_2$, and subsequently for LaP_2 and HT-CeP_2 (Hayakawa *et al.*, 1976). An independent single-crystal structure determination on LaP_2 confirmed its monoclinic symmetry, but in the non-centrosymmetric space group *Ia* (an alternate setting of *Cc*). By extension, the powder pattern of HT-$LaAs_2$ calculated based on the LaP_2 structure was found to match the observed pattern, with monoclinic cell parameters $a = 9.140$, $b = 14.450$, $c = 9.090$ Å, and $\beta = 90.0°$ (von Schnering *et al.*, 1975). Because no single-crystal structure determination on HT-$LaAs_2$ has been forthcoming since that time (Ono *et al.*, 1970), a detailed study seemed warranted.

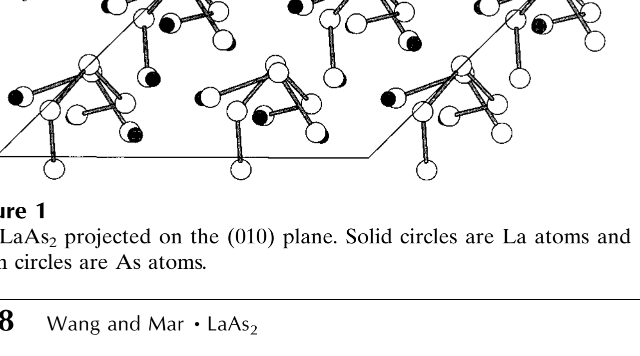

Figure 1
HT-$LaAs_2$ projected on the (010) plane. Solid circles are La atoms and open circles are As atoms.

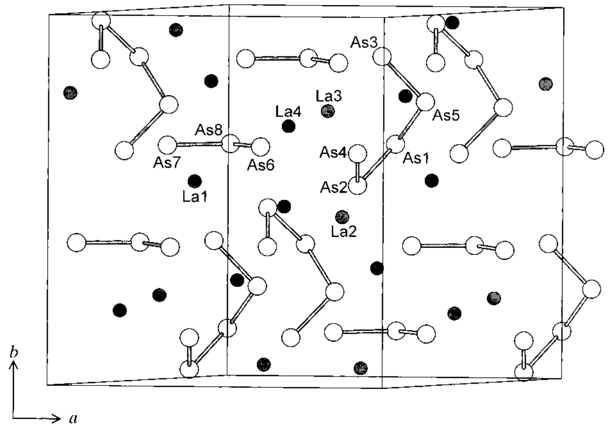

Figure 2
HT-$LaAs_2$ projected approximately on the (001) plane, showing the labeling of atoms. Only As—As bonds are drawn.

The structure of HT-$LaAs_2$ was determined here in standard setting *Cc*. It contains two kinds of discrete chain polyarsenide anions, As_3^{5-} and As_5^{7-}. They pack in an alternating fashion along the *b* direction, with their mean planes roughly perpendicular to each other (Figs. 1 and 2). The bond angles in the As_3^{5-} (V-shaped) and As_5^{7-} (fragment of a boat conformation of a six-membered ring) ions are smaller [99.43 (9)–108.98 (10)°] than those of the corresponding polyphosphide ions in LaP_2 (102.6–113.6°) (von Schnering *et al.*, 1975), reflecting the greater *p* character in the As—As bonds. The order of short–long–long–short bond lengths in the As_5^{7-} ion also contrasts with short–long–short–short in the P_5^{7-} ion in LaP_2. The four inequivalent types of La^{3+} ions intervene between the polyarsenide ions, and are each coordinated by nine As atoms in a distorted tricapped trigonal prism.

Consistent with the Zintl concept, assignment of formal charges of 1− for the bridging and 2− for the terminal As atoms leads to the formulation $La^{3+}As^{1-}As^{2-}$, with the expectation of semiconducting or possibly semimetallic properties. HT-$LaAs_2$ does not appear to bear a simple structural relationship to LT-$LaAs_2$, which possesses As_4^{6-} fragments instead (Wang *et al.*, 1978).

A similarity to the $ThSi_2$-type structure ($I4_1/amd$), which contains Si-centred Th_6 trigonal prisms (Pearson, 1972), was suggested previously (Ono *et al.*, 1970), but the relationship is remote. (A portion of the HT-$LaAs_2$ structure, which can be described as $As_5La_4\square_6$, bears an antitype relationship to $ThSi_2$, but the pattern of vacancies removes the fourfold symmetry. Then, additional As atoms are inserted into this highly distorted framework to yield the $LaAs_2$ structure.)

Experimental

HT-$LaAs_2$ was obtained as a by-product from a reaction of powders of elemental lanthanum, tin and arsenic in the ratio 2:1:5, heated in an evacuated fused-silica tube at 1223 K for 4 d, and followed by cooling to room temperature over 1 d. Powder X-ray diffraction analysis revealed the major phase to be HT-$LaAs_2$, along with LaAs and SnAs. The needle-shaped crystals were verified to contain La and As in the ratio 1:2 according to an EDX (energy-dispersive X-ray) analysis on a Hitachi F2700 scanning electron microscope.

Crystal data

$LaAs_2$
$M_r = 288.75$
Monoclinic, *Cc*
$a = 12.864$ (3) Å
$b = 14.422$ (3) Å
$c = 9.0830$ (18) Å
$\beta = 134.83$ (3)°
$V = 1195.2$ (4) Å^3
$Z = 16$

$D_x = 6.419$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 24 reflections
$\theta = 11.12$–15.06°
$\mu = 35.931$ mm^{-1}
$T = 295$ (2) K
Needle, black
0.20 × 0.03 × 0.02 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
θ–2θ scans
Absorption correction: numerical (*SHELXTL*; Sheldrick, 1997)
$T_{min} = 0.052$, $T_{max} = 0.534$
6855 measured reflections
1751 independent reflections (plus 1743 Friedel-related reflections)

2990 reflections with $F^2 > 2\sigma(F^2)$
$R_{int} = 0.077$
$\theta_{max} = 29.97°$
$h = -18 \rightarrow 18$
$k = -20 \rightarrow 20$
$l = -12 \rightarrow 12$
3 standard reflections
frequency: 250 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.104$
$S = 1.010$
3494 reflections
110 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0331P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 2.496$ e Å^{-3}
$\Delta\rho_{min} = -2.230$ e Å^{-3}
Extinction correction: *SHELXTL* (Sheldrick, 1997)
Extinction coefficient: 0.00045 (3)
Absolute structure: Flack (1983)
Flack parameter = 0.03 (4)

Crystal integrity was verified by Weissenberg photographs, which show monoclinic symmetry and systematic absences consistent with the space groups *C*2/*c* or *Cc*. After the structure was successfully solved and refined in *Cc*, it was standardized with the program *STRUCTURE TIDY* (Gelato & Parthé, 1987). While analysis of the final refined structure by *ADDSYM* (Le Page, 1988) in the *PLATON* suite of programs (Spek, 1997) indicated the presence of a fourfold screw axis and an inversion centre as pseudosymmetry elements, the deviation of two of the atoms, As2 and As5 (0.243 Å), is large and close to the generous default limit (0.25 Å) for positional errors set by the program. These distortions of the As2 and As5 positions result in the formation of the asymmetric As_5^{7-} anionic units and are largely responsible for the lowering to monoclinic symmetry and the choice of a non-centrosymmetric space group.

Data collection: *CAD*-4/*PC* (Enraf–Nonius, 1992); cell refinement: *CAD*-4/*PC*; data reduction: *XCAD*4 (Harms & Wocadlo, 1996); program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *ATOMS* (Dowty, 1997); software used to prepare material for publication: *SHELXTL*.

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Table 1
Selected geometric parameters (Å, °).

La1—As6^{i}	3.049 (2)	La3—As3^{iii}	3.105 (2)
La1—As7^{ii}	3.121 (3)	La3—As5	3.115 (3)
La1—As6	3.152 (2)	La3—As2^{iii}	3.122 (2)
La1—As3	3.152 (2)	La3—As3	3.150 (3)
La1—As1^{iii}	3.172 (3)	La3—As4^{iii}	3.190 (3)
La1—As3^{i}	3.173 (2)	La3—As8^{ix}	3.253 (2)
La1—As8^{iv}	3.200 (2)	La4—As8	3.057 (2)
La1—As2^{v}	3.245 (2)	La4—As7^{iii}	3.122 (3)
La1—As5	3.295 (2)	La4—As4^{x}	3.132 (2)
La2—As2	3.057 (2)	La4—As6^{i}	3.159 (3)
La2—As3^{iii}	3.067 (3)	La4—As7	3.167 (2)
La2—As4^{vi}	3.107 (2)	La4—As5^{iii}	3.173 (2)
La2—As7^{vii}	3.117 (2)	La4—As1^{iii}	3.173 (2)
La2—As7	3.139 (2)	La4—As6^{xi}	3.223 (2)
La2—As8^{vii}	3.147 (2)	La4—As2^{v}	3.293 (2)
La2—As1	3.176 (3)	As1—As5	2.537 (3)
La2—As5	3.200 (2)	As1—As2	2.569 (3)
La2—As4	3.214 (2)	As2—As4	2.460 (3)
La3—As6^{viii}	3.071 (2)	As3—As5	2.463 (3)
La3—As4	3.081 (2)	As6—As8^{iv}	2.468 (3)
La3—As1^{iii}	3.092 (2)	As7—As8	2.505 (3)
As5—As1—As2	108.98 (10)	As3—As5—As1	105.12 (10)
As4—As2—As1	99.43 (9)	As6^{xi}—As8—As7	101.91 (10)

Symmetry codes: (i) $x, 1-y, z-\frac{1}{2}$; (ii) $x-\frac{1}{2}, \frac{1}{2}-y, z-\frac{1}{2}$; (iii) $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$; (iv) $x-\frac{1}{2}, \frac{1}{2}+y, z$; (v) $\frac{1}{2}+x, \frac{1}{2}+y, z$; (vi) $x, -y, z-\frac{1}{2}$; (vii) $x, -y, \frac{1}{2}+z$; (viii) $x, 1-y, \frac{1}{2}+z$; (ix) $x, y, 1+z$; (x) $\frac{1}{2}+x, \frac{1}{2}-y, z-\frac{1}{2}$; (xi) $\frac{1}{2}+x, y-\frac{1}{2}, z$.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1274). Services for accessing these data are described at the back of the journal.

References

Dowty, E. (1997). *ATOMS*. Shape Software, Kingsport, Tennessee, USA.
Enraf–Nonius (1992). *CAD*-4/*PC*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Gelato, L. M. & Parthé, E. (1987). *J. Appl. Cryst.* **20**, 139–143.
Harms, K. & Wocadlo, S. (1996). *XCAD*4. University of Marburg, Germany.
Hayakawa, H., Nomura, K. & Ono, S. (1976). *J. Less Common Met.* **44**, 327–330.
Le Page, Y. (1988). *J. Appl. Cryst.* **21**, 983–984.
Ono, S., Despault, J. G., Calvert, L. D. & Taylor, J. B. (1970). *J. Less Common Met.* **22**, 51–59.
Pearson, W. B. (1972). In *The Crystal Chemistry and Physics of Metals and Alloys*. New York: Wiley Interscience.
Schnering, H. G. von, Wichelhaus, W. & Schulze Nahrup, M. (1975). *Z. Anorg. Allg. Chem.* **412**, 193–201.
Sheldrick, G. M. (1997). *SHELXTL*. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.
Spek, A. L. (1997). *PLATON*. Version 281097. Utrecht University, The Netherlands.
Wang, Y., Heyding, R. D., Gabe, E. J., Calvert, L. D. & Taylor, J. B. (1978). *Acta Cryst.* B**34**, 1959–1961.