the variation in Se—O distances is small and SeO$_4$ groups are quite regular (Table 4). The average Se—O distance is 1·626 Å [Se(1)—O 1·627, Se(2)—O 1·627, Se(3)—O 1·624 Å], which is in good agreement with other selenate structures (Valkonen et al., 1975).

As shown in Fig. 2, one unit cell is made up of 8 ScO$_6$ octahedra and 12 SeO$_4$ tetrahedra. These groups are linked through shared O atoms and together form a three-dimensional network.

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Neodymium Diarsenide: A Single-Crystal Structure Refinement*

By Yu Wang, R. D. Heyding,† E. J. Gabe, L. D. Calvert‡ and J. B. Taylor

Division of Chemistry, National Research Council of Canada, Ottawa K1A 0R9, Canada

Abstract. NdAs$_2$, monoclinic, $P2_1/c$, $a = 4·1081$ (2), $b = 6·8201$ (2), $c = 10·4431$ (3) Å, $\beta = 106·718$ (3)°, $Z = 4$, $U = 280·22$ Å^3, FW 294·1, $D_x = 6·97$ g cm^{-3}, μ(Mo $K\alpha$) $= 429$ cm^{-1}, $F(000) = 504$. The model below was refined by full-matrix least squares with allowance for anomalous dispersion and extinction to $R_2 = 0·054$ for 928 observed diffractometer data. The structure is of a new distinctive type. The Nd atoms form buckled 6^3 nets which are stacked along the short a axis giving a continuous three-dimensional Nd network with open hexagonal channels. Adjoining pairs of hexagons outline skew prisms which are centred by almost planar As$_4$ zigzag chains. These polyanions are centrosymmetric, with terminal and bridge As—As distances of 2·477 and 2·497 Å respectively; the As—As—As angle is 104·3°. The overall coordination numbers are 14, 16 and 12 for Nd, As(1) and As(2), respectively, with average As—As, Nd—As and Nd—Nd distances of 2·49, 3·18 and 4·09 Å respectively.

Introduction. Intensity data were collected on a computer-controlled Picker diffractometer using local programs [for details not given here see Wang, Gabe, Calvert & Taylor (1976)]. NdAs$_2$ crystals were grown on polycrystalline NdAs$_2$ (0·05 g) at 600°C in a tube of 7 ml volume containing iodine (0·03 g) and arsenic (0·05 g). Two fragments were studied, both protected by sealed capillaries. The larger, a lath-shaped fragment (0·04 × 0·06 × 0·2 mm) mounted along its length, was used to collect 2044 reflections with $2\theta < 65°$ by the θ–2θ scan technique (Mo $K\alpha$ radiation, graphite monochromator) with a scan range which was varied as (0·6 × 0·7 tan θ + 0·6)°; 91% of the reflections were taken as observed ($I > 2\sigma$; where σ is the standard deviation of the net count). The lattice parameters were derived from 68 reflections with $2\theta > 60°$ and agree well with those reported earlier (Ono, Despault, Calvert & Taylor, 1970). Two symmetry-equivalent sets ($hk\bar{l}$ + hkl, $\bar{h}k\bar{l}$ + $\bar{h}kl$) were collected, corrected for absorption (Wang, Gabe, Calvert & Taylor, 1976), Lorentz and polarization factors and then averaged to give 932 independent observed hkl; the discrepancy between the two sets ($\sum \Delta I/\sum I$) was 0·022 and transmission factors ranged from 0·09 to 0·21. The space group had been determined (Ono, Despault, Calvert & Taylor, 1970) as $P2_1/c$ and this was confirmed by precession photographs ($h0l$ observed for $l = 2n$ and $0k0$ for $k = 2n$). A trial structure was obtained by direct methods and these coordinates were refined by full-matrix least squares with allowance for anomalous dispersion and isotropic extinction correction (Larson, 1970) using the laboratory PDP-8 computer and local programs; the final values for R_1 and R_2 are 0·049 and 0·054 with

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* NRCC No. 16657.

† Visiting scientist from Chemistry Department, Queen's University, Kingston, Ontario.

‡ To whom correspondence should be addressed.

goodness of fit 0·893 (NO = 928, NV = 29), where R_1 = $(\sum |F_o - F_c|/\sum F_o)$, $R_2 = [\sum w(F_o - F_c)^2/\sum wF_o^2]^{1/2}$ and goodness of fit = $[\sum w(F_o - F_c)^2/(NO-NV)]^{1/2}$ and $w = 1/\sqrt{[\sigma^2(F_o) + 0·0002F_o^2]}$. The observed structure factors corrected for extinction and those calculated from the final coordinates are given in Table 1.* There was no significant detail on the electron density difference map based on the final parameters of Table 2. The coordination distances (Frank & Kasper, 1958) are given in Table 3. Only the results of the refinement for the larger crystal are quoted. The results from the smaller crystal (which was studied first) were thought to require confirmation because the final R_2 value (0·111) was high and absorption problems were severe as the rod-shaped crystal was mounted perpendicular to its long axis. Results are given in Table 4. Only the thermal parameters differ markedly; a half-normal probability plot of the positional parameters (Abrahams & Keve, 1971) was linear with intercept 0·018 and slope 1·12.

Discussion. $NdAs_2$ is of an unknown structural type and is isostructural with $PrAs_2$, $CeAs_2$ and $LaAs_2$ (below 750°C) (Ono, Despault, Calvert & Taylor, 1970). These phases are of interest for their electrical properties and crystal chemistry. Untwinned crystals were obtained only for $NdAs_2$. The (100) projection of $NdAs_2$ (Fig. 1) provides a convenient geometrical description for what appears to be a novel and distinctive structure type. The Nd atoms lie on puckered 6^3 nets which form open channels. The hexagons adopt the chair configuration. The skew prisms formed by adjacent Nd hexagons ($\pm a = 4·11$ Å apart) are centred by As_4 chains (Fig. 2). These four-membered chains are the most distinctive feature and can be considered as discrete polyanions as defined by Busmann (1961) and Hulliger & Mooser (1965). The chains are centrosymmetric with As—As distances of 2·477 and 2·497 Å, respectively, for terminal and bridge pairs; the As—As—As angle is 104·8°. These distances are comparable with those in metallic arsenic (2·516 Å)

and also the four-membered chains which occur in Ca_2As_3 (Deller & Eisenmann, 1976) with terminal and bridge distances of 2·490 and 2·529 Å, respectively, and the bridge distance of 2·550 Å in Eu_3As_4 (Smart, Calvert & Taylor, 1978), and the terminal As—As distance (2·475 Å) of Eu_3As_4. The terminal atom in the As_4 chain, As(1), has seven near neighbours (five Nd and two As), plus nine next-nearest nieghbours for a total coordination of 16. The bridge atom, As(2), has eight near neighbours (four Nd and four As), with four next-nearest neighbours to give a total coordination of 12. The Nd atom has nine near neighbours (all As), plus five Nd as next-nearest neighbours with a total coordination of 14. Thus, while the near-neighbour distances are evidence of strong, directed bonds, the overall coordination remains high. $NdAs_2$ can be

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* Table 1 has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33429 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. *Coordination distances* (Å)

Nearest neighbours		Next-nearest neighbours	
Nd–As(1)	2·9876 (1)	Nd–Nd	4·1081 (2) × 2
	2·9965 (1)		4·0563 (1) × 2
	3·0528 (1)		4·1043 (1)
	3·1409 (1)		
	3·1819 (1)		
–As(2)	3·0820 (1)		
	3·0864 (1)		
	3·1393 (1)		
	3·1801 (1)		
As(1)–As(2)	2·4773 (1)	As(1)–As(1)	3·7636 (1) × 2
	3·3225 (1)		4·1081 (2) × 2
–Nd	2·9876 (1)		4·1616 (1)
	2·9965 (1)	–As(2)	3·7023 (1)
	3·0528 (1)		3·7934 (1)
	3·1409 (1)		4·1628 (2)
	3·1819 (1)		4·1852 (1)
As(2)–As(1)	2·4773 (1)	As(2)–As(1)	3·7023 (1)
	3·3225 (1)		3·7934 (1)
–As(2)	2·4970 (1)		4·1628 (2)
	3·1974 (1)		4·1852 (1)
–Nd	3·0820 (1)		
	3·0864 (1)		
	3·1801 (1)		
	3·1393 (1)		
Average values			
As–As*	2·49	As–Nd	3·18
		Nd–Nd	4·09

* Average of two short distances.

Table 2. *Fractional positional coordinates and thermal parameters* ($Å^2 \times 10^4$)

The temperature factor is of the form $\exp[-2\pi^2(U_{11}a^{*2} + ... + 2U_{12}a^*b^* + ...)]$.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Nd	0·9124 (1)	0·3126 (1)	0·1402 (1)	75 (3)	75 (3)	45 (3)	2 (2)	28 (2)	−1 (1)
As(1)	0·4610 (3)	0·6436 (1)	0·1708 (1)	90 (4)	87 (4)	64 (4)	−4 (3)	33 (3)	−2 (3)
As(2)	0·2727 (3)	0·3777 (1)	0·4503 (1)	103 (5)	83 (5)	50 (4)	−4 (3)	35 (3)	2 (3)

Table 4. *Refinement results for the two crystals*

|	Small crystal	Large crystal
2θ maximum (°)	65	65
Size (mm)	0·02 × 0·03 × 0·1	0·04 × 0·06 × 0·2
Number of measurements	1022	2044
Number of sets	1	2
Number of hkl (obs.)	727	928
$\Delta I/\sum I$	–	0·022
R_1	0·094	0·049
R_2	0·111	0·054
Nd x	0·9125 (7)	0·9124 (1)
y	0·3119 (4)	0·3126 (1)
z	0·1404 (4)	0·1402 (1)
B_{iso} (Å²)*	0·33 (7)	0·04 (2)
As(1) x	0·4633 (13)	0·4610 (3)
y	0·6437 (8)	0·6436 (1)
z	0·1717 (6)	0·1708 (1)
B_{iso} (Å²)*	0·56 (18)	0·23 (3)
As (2) x	0·2737 (13)	0·2727 (3)
y	0·3783 (8)	0·3777 (1)
z	0·4496 (6)	0·4503 (1)
B_{iso} (Å²)*	0·51 (18)	0·23 (4)
Goodness of fit	6·08 (726,28)	0·893 (928,29)
Transmission factor	0·10–0·36	0·09–0·21
Extinction coefficient	–	1·26 (6) × 10⁻⁵

* Equivalent B_{iso}.
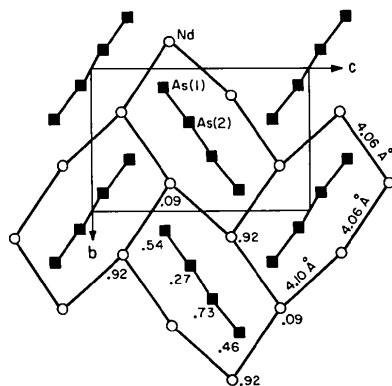
Fig. 1. The (100) projection. Nd atoms are marked by open circles, As atoms by solid squares. Representative atoms are labelled and z coordinates given. The distances in the Nd hexagons are also indicated. The unit cell is marked by fine lines and the As₄ chains and Nd hexagons by heavy lines.

written as $Nd_2^{6+}As_4^{6-}$ and conforms to the general valence rule of Pearson (1964) and is thus a possible semiconductor. Considering the average principal quantum number ($\bar{n}$ = 4·7) and the electronegativity difference (Δx = 0·8) (Mooser & Pearson, 1959) the values lie in a borderline region between expected semiconductor and metallic behaviour. The average Nd—As
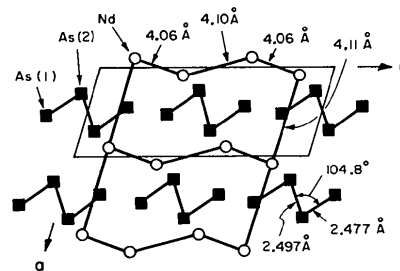

Fig. 2. The (010) projection showing two skew hexagonal prisms, outlined by heavy lines. Other details as in Fig. 1.

distance (3·18 Å) is comparable to that expected for metallic coordination (3·21 Å for CN = 12) and although the Nd network is continuous the average value of the Nd—Nd distances (4·09 Å) would be, at most, a very weak interaction (bond order $\simeq$ 0·05; r = 1·642 Å) (Pauling, 1947) so that direct experimental evidence would be required to characterize $NdAs_2$. It may be noted in this connection, that the structure of the high-temperature form of $LaAs_2$ is now known from that of the isotype LaP_2 (von Schnering, Wichelhaus & Nahrup, 1975). This is a valence compound with discrete P_3 and P_5 chains and contains a continuous network of metal—metal coordination distances with an average La—La distance of 3·96 Å (expected for CN = 12: 3·76 Å).

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