

Les distances baryum—oxygène sont données dans le même tableau. C'est à notre connaissance le premier anion de ce type signalé dans le domaine de la cristallographie des arsénates.

Il est probable que la formulation chimique correcte de ce sel est Ba(OH)₆As₄O₈. Une étude est en cours

pour tenter de localiser les protons dans cet arrangement.

Référence

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α -Gallium Oxide Deuteriohydroxide: A Powder Neutron Diffraction Investigation

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Abstract. α -GaOOD, orthorhombic, space group *Pbnm*, $a = 4.516$ (5), $b = 9.779$ (7), $c = 2.966$ (3) Å (25°C). The structure has been determined by profile analysis of powder neutron diffraction data at both room temperature and 4.2 K. Asymmetric hydrogen bonds are present with the D atom displaced from the O—O direction by 12.5°. The O—D length is 0.995 Å.

Introduction. GaOOH exists as a stable phase in the Ga₂O₃—H₂O system in the domain $1 < p < 1500$ atm, $25^\circ\text{C} < t < 300^\circ\text{C}$ (Hill, Roy & Osborn, 1952). Powder X-ray diffraction data suggest that the compound is isostructural with diaspore (Böhm & Kahan, 1938), and this is supported by the formation of a

complete series of diaspore solid solutions extending from AlOOH to GaOOH (Hill, Roy & Osborn, 1952). Atom positions for 'diaspore' GaOOH have not previously been reported.

GaOOD was prepared from δ -Ga₂O₃ made by heating Ga(NO₃)₃·9H₂O (Koch Light Laboratories) at 250°C for 12 h. The oxide was characterized by its X-ray powder diffraction pattern (Roy, Hill & Osborn, 1952). A sample of GaOOD was prepared by reaction of the oxide with excess D₂O (99.8% isotopically pure, Nordsk Hydroelektrisch Co.) in an autoclave at 250°C and 32 atm for 96 h. The product was dried *in vacuo* and its composition confirmed by thermogravimetric dehydration. Infrared spectroscopy indicated isotopic

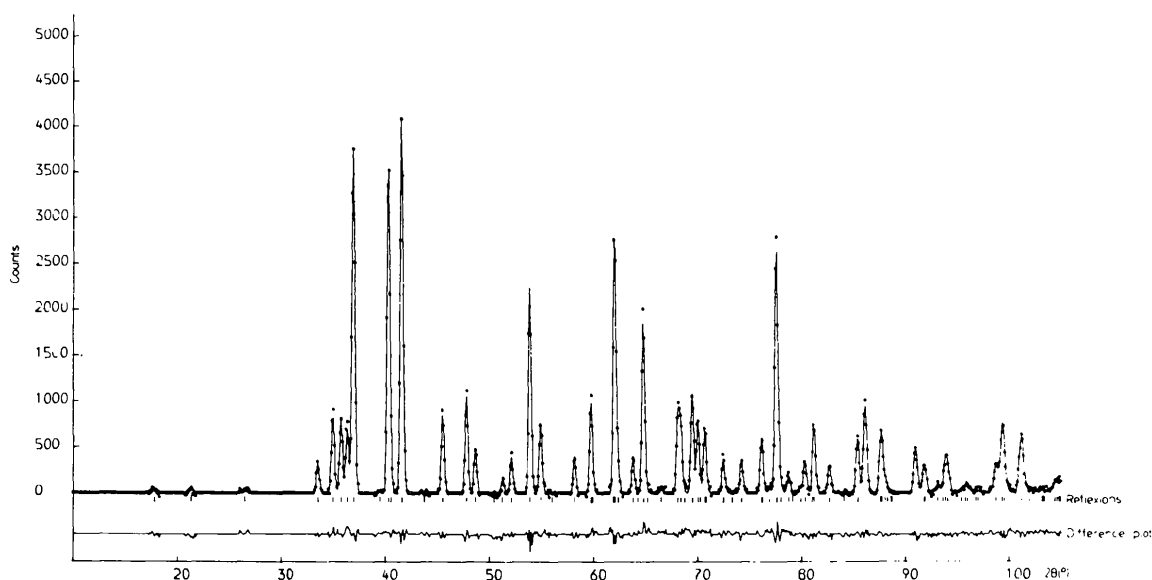


Fig. 1. Observed and calculated profiles for GaOOD (room-temperature run). • observed; — calculated.

purity. The Debye–Scherrer pattern confirmed the presence of a pure phase.

Neutron powder profiles were recorded on PANDA at AERE Harwell in the 2θ range 10 to 105° in steps of 0.1° . The sample (~ 5 g) was contained in a thin-walled V can sealed with an In gasket. A neutron wavelength of 1.542 \AA [obtained by reflexion from the (511) planes of a Ge monochromator at a take-off angle of 90°] was employed and the powder spectrum was recorded at room temperature, and at 4.2 K with a liquid He cryostat.

X-ray studies (Böhm & Kahan, 1938) have shown α -GaOOH to be isostructural with α -AlOOH (diaspore) and α -FeOOH (goethite), both of which have been the subjects of investigation by single-crystal neutron diffraction (Busing & Levy, 1958; Forsyth, Hedley & Johnson, 1968). In each case the space group was found to be $Pbnm$ with specific absences $h0l$, $h + l = 2n + 1$, and $0kl$, $k = 2n + 1$. The powder profiles observed were consistent with these absences and so the method of least-squares profile refinement (Rietveld, 1969) was applied in this space group. The program minimizes the function $\chi^2 = \sum_i w_i [y_i(\text{obs}) - (1/c)y_i(\text{calc})]^2$ where w_i is the weighting function, y_i the number of counts at the point $2\theta_i$ and c is the scale factor. The scattering lengths were $b_{\text{Ga}} = 0.72$, $b_{\text{O}} = 0.580$, $b_{\text{D}} = 0.667 \times 10^{-14} \text{ m}$ (Neutron Diffraction Commission, 1972). The refinement involved eight positional and four thermal parameters plus the lattice constants, three peak halfwidth parameters, the zero-point correction and scale factor.

$$R_{\text{profile}} = 100 \left\{ \frac{\sum_i w_i \left[y_i(\text{obs}) - \frac{1}{c} y_i(\text{calc}) \right]^2}{\sum_i w_i [y_i(\text{obs})]^2} \right\}^{1/2}$$

converged to 9.38 for the room-temperature and 10.22 for the 4.2 K data compared with 7.65 and 8.02

Table 1. Room-temperature and low-temperature atom parameters for α -GaOOD

Room-temperature parameters				
	x	y	z	$B (\text{\AA}^2)$
Ga	0.0512 (6)	−0.1447 (2)	0.25	0.38 (5)
O(1)	0.7020 (7)	0.1953 (3)	0.25	0.57 (7)
O(2)	0.1945 (8)	0.0546 (3)	0.25	0.41 (6)
D	0.4035 (7)	0.0869 (3)	0.25	1.50 (7)
Low-temperature parameters				
	x	y	z	$B (\text{\AA}^2)$
Ga	0.0515 (6)	−0.1443 (2)	0.25	0.07 (5)
O(1)	0.7006 (7)	0.1955 (3)	0.25	0.26 (8)
O(2)	0.1943 (8)	0.0551 (3)	0.25	0.23 (7)
D	0.4031 (7)	0.0883 (3)	0.25	1.22 (7)

respectively, expected from purely statistical errors. $R_f = 100 \sum |I_{\text{obs}} - (1/c)I_{\text{calc}}| / \sum I_{\text{obs}}$ was 5.16 and 4.69 respectively. Atom parameters and their estimated standard deviations are given in Table 1. The agreement between the observed and calculated profiles at room temperature is illustrated in Fig. 1. The profiles of the low- and room-temperature data were nearly identical, establishing that no structural change had occurred.

Discussion. Bond angles and distances are given in Table 2. A projection of the structure on (001) is shown in Fig. 2. The bond lengths at room temperature are derived from the X-ray lattice parameters. Estimates of the low-temperature lattice constants, made by scaling the X-ray parameters with the neutron diffraction data at room temperature and 4.2 K, are $a = 4.510$, $b = 9.766$, $c = 2.963 \text{ \AA}$.

The structural details of α -GaOOD and α -AlOOH are very similar, the bonds being somewhat longer in GaOOD (average Al–O = 1.916, average Ga–O = 1.991 \AA). This is consistent with the ionic radii of Ga^{3+}

Table 2. Interatomic distances and bond angles in α -GaOOD

	Room temperature	4.2 K
(a) Interatomic distances (\AA) (primed symbols represent atoms on adjacent plane)		
Ga–O(1)	1.938 (4)	1.934 (4)
Ga–O(1)′	1.920 (4)	1.922 (4)
Ga–O(2)	2.054 (5)	2.051 (5)
Ga–O(2)′	2.051 (5)	2.045 (5)
O(1)–O(2)	2.673 (5)	2.663 (5)
O(1)–D	1.715 (5)	1.702 (5)
O(2)–D	0.995 (5)	0.996 (5)
(b) Bond angles ($^\circ$). Typical e.s.d. for angles: 0.3° .		
Around Ga		
O(1)–Ga–O(1)′	97.7	97.6
O(1)′–Ga–O(1)′	101.1	100.8
O(1)–Ga–O(2)′	91.6	91.5
O(1)′–Ga–O(2)	93.5	93.7
O(2)–Ga–O(2)′	76.3	76.5
O(2)′–Ga–O(2)′	92.6	92.8
Around O(1)		
Ga–O(1)–Ga′	123.3	123.5
Ga′–O(1)–Ga′	101.4	100.8
Ga–O(1)–D	92.0	92.0
Ga′–O(1)–D	107.3	107.4
Around O(2)		
Ga–O(2)–Ga′	103.7	103.5
Ga′–O(2)–Ga′	92.6	92.8
Ga–O(2)–D	126.9	127.3
Ga′–O(2)–D	112.1	112.0
O(1)–O(2)–D	12.5	12.0

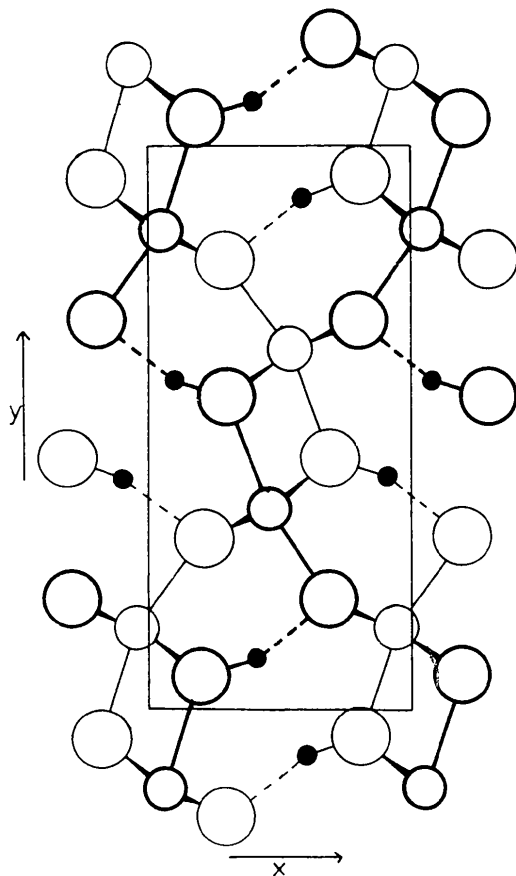


Fig. 2. A projection of the structure of GaOOD on to the (001) plane. Filled circles, D; large open circles, O; small circles, Ga. $-z = -0.25; -z = +0.25$.

and Al^{3+} (0.620 and 0.535 Å respectively, Shannon, 1976). The O—D...O distance of 2.673 in GaOOD is close to the 2.68 Å deduced from an infrared study (Cornelis-Benoit, 1965). It is between that found in diaspore (2.650 Å) and that in goethite (2.748 Å).

The bond lengths show that the D atom is associated with O(2) and is considerably displaced from the O—O line, the O(1)—O(2)—D bond angle being 12.5° . This value is similar to those found in α -AlOOH (12.1°) and α -FeOOH (11.6°).

Electrostatic-energy calculations, with a point-charge model, $M^{3+}(\text{O}^{2-})_2\text{H}^+$, for diaspore and goethite (Geise, Weller & Datta, 1971) predict a minimum in the total Madelung energy for off-line displacements of H in O—H...O of this order. A similar calculation for GaOOH with the computer program of van Gool & Piken (1969), the Ga and O coordinates reported here and a fixed OH length of 0.995 Å, led to a minimum in the total Madelung energy at $\angle \text{O—O—H} = 11.6^\circ$.

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