

Hydrothermal Preparation of Zeolite Li–A(BW), $\text{LiAlSiO}_4 \cdot \text{H}_2\text{O}$, and Structure Determination from Powder Diffraction Data by Direct Methods

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The zeolite Li–A(BW), $\text{LiAlSiO}_4 \cdot \text{H}_2\text{O}$ was prepared hydrothermally and its structure solved from X-ray and neutron powder diffraction data by direct methods. The unit cell is $a = 10.313(1)$, $b = 8.194(1)$, $c = 4.993(1)$ Å, and the space group is $Pna2_1$, No. 33, $Z = 4$. The water molecule in the structure forms hydrogen bonds.

A large number of zeolites are ion exchange materials, and some of them may possibly have solid state ionic conducting properties also. This is of particular interest in the case of lithium ion-containing zeolites; batteries containing lithium metal-lithium electrolytes are of great technical interest. A previous investigation of the lithium zeolites $\text{Li}_8\text{Al}_6\text{Si}_6\text{O}_{24}\text{Cl}_2$ and $\text{Li}_8\text{Al}_6\text{Si}_6\text{O}_{24}\text{Br}_2$ showed solid state electrolytic properties for these compounds,¹ obtained in reactions of zeolite 13X ($\text{Na}_{86}\text{Al}_{86}\text{Si}_{106}\text{O}_{384} \cdot x\text{H}_2\text{O}$) with salt melts of LiCl and LiBr, respectively.¹ However, as the lithium zeolites could not be made as completely pure phases, it was decided to prepare the compounds by hydrothermal synthesis.

The sodium sodalite $\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}\text{Cl}_2$ was prepared hydrothermally from a gel in the temperature range 150–450 °C by Barrer and White² who assumed that zeolite 4A ($\text{Na}_{12}\text{Al}_{12}\text{Si}_{12}\text{O}_{48} \cdot 12\text{H}_2\text{O}$) was a precursor for the formation of the sodalite. Consequently, it was assumed in this work that the lithium sodalites could be made in hydrothermal reactions between zeolite 4A, or zeolite 13X, and aqueous solutions of lithium salts. In these reactions, two main products were obtained, the zeolite $\text{LiAlSiO}_4 \cdot \text{H}_2\text{O}$ and α -eucrypt-

tite (LiAlSiO_4), depending upon the experimental conditions (see below). The lithium sodalite was not obtained directly but could be made in a hydrothermal treatment of sodium sodalite with an aqueous solution of LiCl or LiBr.

The zeolite $\text{LiAlSiO}_4 \cdot \text{H}_2\text{O}$, abbreviated Li–A(BW) in the zeolite literature³, was first made by Barrer and White.⁴ Their preparations did not produce crystals large enough for a single-crystal X-ray diffraction structure determination, whereas in the present investigation, crystals of $\text{LiAlSiO}_4 \cdot \text{H}_2\text{O}$ were formed which were so used.⁵

A structure for $\text{LiAlSiO}_4 \cdot \text{H}_2\text{O}$ was determined by Kerr,⁶ by combining information from X-ray powder diffraction patterns and single-crystal electron diffraction patterns, from packing considerations, and from zeolite structure principles of known zeolite structures. The framework structure was refined by distance least-squares methods (see Ref. 6) in space group $Pna2_1$. Structure factors were then extracted from an X-ray powder diffraction pattern, and Fourier maps, phased on the framework structure yielded the position of the oxygen atom of the water molecule and two positions for the lithium atom with occupancy 0.64 and 0.27.⁶

Crystal structures of compounds with moderately large unit cells may be solved by direct

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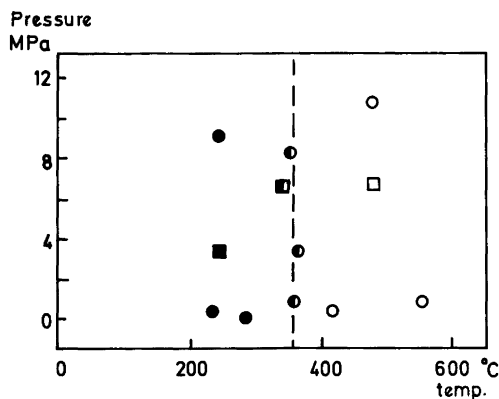


Fig. 1. P-T diagram showing the range for formation of LiAlSiO₄·H₂O (filled symbols) and the formation of α -LiAlSiO₄ (open symbols). A circle indicates a reaction of 4A with LiCl, a square indicates a reaction of 4A with LiBr solution. An external liquid water pressure at room temperature yields a hydrothermal pressure greater than that of the vapour pressure of water.

methods⁷ by combining information from X-ray and neutron powder diffraction patterns.^{8,9,10} Guinier photographs yield spectra with high resolution so that the patterns can be indexed and the space group determined. A large number of inorganic compounds can be regarded as heavy atom structures with respect to X-ray diffraction, and at least part of the structure can thus be found with structure factors determined from X-ray powder diffraction patterns using direct methods. Neutron powder diffraction patterns recorded with a spectrometer with high resolution and with 1.5 to 2.5 Å neutrons can yield structure factors by Gaussian fits to the diffraction peaks¹¹ that can be used in direct methods to solve the structure, or in Fourier calculations

phased on models derived from X-ray powder diffraction data. The procedure outlined above was applied in the present investigation to determine the crystal structure of LiAlSiO₄·D₂O; profile refinement¹² was used to refine the structure from neutron diffraction data.

Experimental

Chemistry. The materials used in the hydrothermal preparations were zeolite 4A and zeolite 13X (Union Carbide, Fluka), LiCl, LiBr, NaCl, NaBr, and NaI (Merck; analytical grade). In the synthesis of LiAlSiO₄·D₂O, D₂O of nominal purity (97 %) was used. The hydrothermal preparations were performed in a 250 ml gold-lined pressure vessel or in 2 ml gold ampoules sealed in 7 ml pressure vessels. Twelve experiments were made to determine the temperature/pressure ranges for the formation of the two compounds, zeolite Li-A(BW), and α -eucryptite (see Fig. 1). Table 1a lists selected experimental conditions for a few of the syntheses performed. The composition of the reaction products was determined by chemical analysis, giving the formulas listed in Table 1b. The compounds were decomposed with conc. HF.¹⁴ Lithium and sodium were determined by flame photometry; chloride, bromide, and iodide by potentiometric titration with silver nitrate.

X-Ray powder diffraction. The phases of the reaction products were identified from X-ray Guinier photographs recorded with a Guinier camera using CuK α ₁ radiation, $\lambda = 1.5405981$ Å and Si, $a = 5.43083$ Å, or quartz $a = 4.91309$, $c = 5.40462$ Å, as internal standards. The reciprocal lattice constants were adapted by the least-

Table 1a. Experimental conditions for hydrothermal preparation.

Exp.	Initial conditions	Temp/°C	Time/h	Result		
1	10 g 4A	10 g LiCl	150 ml H ₂ O	285	72	LiAlSiO ₄ ·H ₂ O
2	0.1 g 4A	0.4 g LiCl	1 ml H ₂ O	485	72	α -LiAlSiO ₄
3	10 g 4A	20 g NaCl	150 ml H ₂ O	200	72	NaCl-sodalite
4	5 g NaCl-sodalite	27 g LiCl	100 ml H ₂ O	200	72	LiCl-sodalite
5	10 g 4A	25 g NaBr	100 ml H ₂ O	250	144	NaBr-sodalite
6	7 g NaBr-sodalite	75 g LiCl	100 ml H ₂ O	180	122	LiBr-sodalite
7	20 g 4A	51 g NaI	100 ml H ₂ O	240	72	NaI-sodalite

Table 1b. Composition and unit cell parameters of compounds.

Compound	Analysis/weight %				Calculated formula	Unit cell/Å			Ref. 13 ^a
	Li	Na	X ⁻	H ₂ O		a	b	c	
LiAlSiO ₄ ·H ₂ O	4.84	0.06		13.6	Li _{1.02} Na _{0.004} AlSiO ₄ ·1·1H ₂ O	10.313	8.194	4.993	
NaCl-sodalite		18.8	6.7	0.8	Na _{8.0} Al ₆ Si ₆ O ₂₄ Cl _{1.8} ·0·4H ₂ O	8.876			8.878
LiCl-sodalite	6.11	1.08	7.8	1.5	Li _{7.6} Na _{0.4} Al ₆ Si ₆ O ₂₄ Cl _{1.9} ·0·7H ₂ O	8.469			8.447
NaBr-sodalite		16.9	13.9	0.7	Na _{7.7} Al ₆ Si ₆ O ₂₄ Br _{1.8} ·0·4H ₂ O	8.932			8.934
LiBr-sodalite	5.41	0.71	15.1	2.2	Li _{7.3} Na _{0.29} Al ₆ Si ₆ O ₂₄ Br _{1.8} ·1·1H ₂ O	8.511			
NaI-sodalite		16.0	19.4	0.9	Na _{7.8} Al ₆ Si ₆ O ₂₄ I _{1.7} ·0·6H ₂ O	9.010			9.008

^aLiCl-sodalite was prepared from natural sodalite and LiCl at 800 °C.¹³

squares method to the observed $\sin^2\theta$. The unit cell parameters determined from the Guinier photographs are listed in Table 1b. The intensities of the LiAlSiO₄·H₂O pattern were measured on a LS-18 film scanner.¹⁵

Infrared spectra. The infrared spectra of LiAlSiO₄·H₂O and LiAlSiO₄·D₂O were recorded on a Perkin-Elmer 180 spectrograph using pellets of KBr containing 1 % of the compounds. The spectra are displayed in Fig. 2 and show that LiAlSiO₄·D₂O also contains some H₂O. The spectrum of LiAlSiO₄·H₂O showed two absorption bands at 3620 and 3490 cm⁻¹ and that of LiAlSiO₄·D₂O two at 2675 and 2570 cm⁻¹, characteristic of weak hydrogen bonds of OH/OD groups.

Neutron powder diffraction. Two neutron powder diffraction patterns of LiAlSiO₄·D₂O were measured. One pattern was measured on the spectrometer D1A at Institut Laue-Langevin in Grenoble using 1.909 Å neutrons and recorded in the 2θ range 6–125°. The other pattern was measured on the spectrometer at channel 3T2 at the ORPHEE reactor in the Laboratoire Léon Brillouin, Saclay, in the 2θ range 7–109° using 1.226 Å neutrons. The diagram recorded on the D1A was used in the structure determination by direct methods; both diagrams were used in profile refinement of the structure.¹² In the structure factor calculations, the following scattering lengths (all in 10⁻¹² cm units) were used: Li, -0.194; Al, 0.345; Si, 0.415; O, 0.575; D, 0.667.¹⁶

Structure determination

When the structure of LiAlSiO₄·D₂O was solved from the neutron and X-ray powder diffraction data, only the structure proposed by Kerr⁶ was available and the positions of the deuterium atoms were not known. The structure arrived at by Krogh Andersen and Ploug-Sørensen⁵ is similar to that proposed previously⁶ except for the position of the lithium atom, and was used here for comparison (see Table 2). The coordinates found in the direct methods were transformed to the coordinate system used in Ref. 5.

The average scattering contribution per atom for the metal and oxygen atoms in LiAlSiO₄·H₂O was in the X-ray case: Li, 1%; Al, 19%; Si, 22%; and O, 7%. From a Guinier photograph or an X-ray powder diffraction pattern it would thus most likely be only the positions of Al and Si that could be found by using direct methods. In Ref. 6, *h k l* and *l* are listed for the powder pattern of

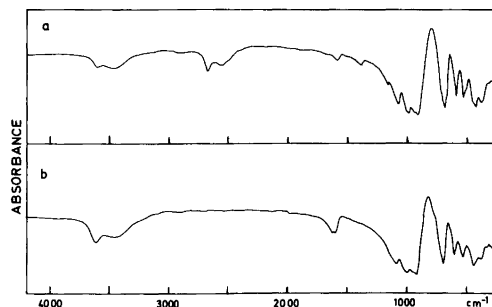


Fig. 2. Infrared spectra of (a) LiAlSiO₄·D₂O (with an impurity of H₂O) and of (b) LiAlSiO₄·H₂O.

Table 2. Atomic coordinates of LiAlSiO₄·D₂O and peak heights obtained from MULTAN. Coordinates in parentheses are atomic coordinates from Ref. 5.

$a = 10.313(1)$, $b = 8.194(1)$, $c = 4.993(1)$ Å; space group *Pna2*₁ (No. 33).

Structure solution Multan				Profile refinement ^b				
atom	x	y	z	peak ^a	x	y	z	B (Å ²)
Li	(0.3138	0.1849	0.7480)		0.3101(25)	0.1867(26)	0.7480(75)	2.3(5)
	0.320	0.120	0.750 ^c		0.3307(26)	0.1758(28)	0.7564(67)	1.0(4)
Al	(0.1593	0.0810	0.2500)		0.1589(15)	0.0780(15)	0.2500	2.2(3)
	0.166	0.100	0.265 ^c		0.1599(16)	0.0778(18)	0.2500	1.2(3)
	0.0950	0.1427	0.2693 ^d	2850 ^d				
	0.1361	0.0356	0.2500 ^e	1643 ^e				
Si	(0.3544	0.3757	0.2492)		0.3493(9)	0.3755(12)	0.2410(47)	0.6(2)
	0.3467	0.3884	0.2468	2150	0.3541(11)	0.3784(16)	0.2586(57)	1.1(3)
	0.3466	0.4096	0.2474 ^d	2180 ^d				
	0.3561	0.3934	0.2300 ^e	3269 ^e				
O 1	(0.0061	0.1584	0.1970)		0.0072(8)	0.1588(8)	0.1994(34)	1.3(1)
	0.0049	0.1658	0.2377	1590	0.0059(10)	0.1562(10)	0.1988(40)	0.8(1)
O 2	(0.2736	0.2198	0.1391)		0.2751(6)	0.2235(8)	0.1413(36)	1.1(2)
	0.2782	0.2141	0.1138	1540	0.2738(8)	0.2181(12)	0.1434(41)	1.2(2)
O 3	(0.1912	0.0399	0.5907)		0.1917(7)	0.0419(9)	0.5893(36)	1.5(2)
	0.1954	0.0456	0.5950	2300	0.1893(9)	0.0441(11)	0.5930(40)	1.1(2)
O 4	(0.1804	−.1008	0.0689)		0.1755(8)	0.8996(10)	0.0690(37)	2.7(2)
	0.1844	−.1273	0.0842	2550	0.1748(8)	0.8962(13)	0.0753(47)	1.8(2)
O 5	(0.4891	0.0903	0.7605)		0.4883(16)	0.0893(16)	0.7691(43)	3.6(2)
	0.4986	0.0835	0.7350	1535	0.4982(17)	0.0939(15)	0.7458(48)	3.1(2)
D 1					0.5489(28)	0.1619(39)	0.7979(70)	5.4(5)
	0.5749	0.1428	0.7306 ^c		0.5497(38)	0.1798(51)	0.8651(99)	4.0(9)
D 2	0.4965	0.0415	0.6236	1100	0.5111(26)	0.0451(20)	0.5898(50)	5.4(5)
	0.490	0.070	0.580 ^c		0.4965(69)	0.0587(56)	0.5773(95)	4.2(8)

^aRelative scale. ^bRefined atomic coordinates and temperature factor parameters. First lines are for data with $\lambda = 1.909$ Å, and second lines are for data with $\lambda = 1.226$ Å. ^cFrom difference Fourier calculations. ^dFrom X-ray powder diffraction data Ref. 6. ^eFrom Guinier photograph.

LiAlSiO₄·H₂O measured on a powder diffractometer. Structure factors to $\sin\theta/\lambda \leq 0.47\text{Å}^{-1}$ were derived from these data taking polarization factors and multiplicity in consideration. In the case of an intensity where more than one reflection contributed, the intensity was divided equally between the contributing reflections. The MULTAN programs⁷ determined 179 phase relations and gave a solution with the highest figure of merit of 2.56. The two highest peaks of the solution corresponded to the atomic positions of Al and Si (Table 2), with Si as the highest peak. Of the following four peaks (heights 1220–1030) of

the solution, two were spurious, and the other two corresponded to the position of the atoms O5 and O3 (see Fig. 3). This is not surprising, since the scattering contribution from an oxygen atom is rather small, and the structure factors are calculated rather uncertain from the intensities with more than one reflection contributing. In a similar way 39 structure factors were obtained from a Guinier photograph taken with CuK α_1 radiation, and these data gave with the MULTAN programs the positions of Si (as the highest peak) and Al (see Table 2).

Individual structure factors were extracted

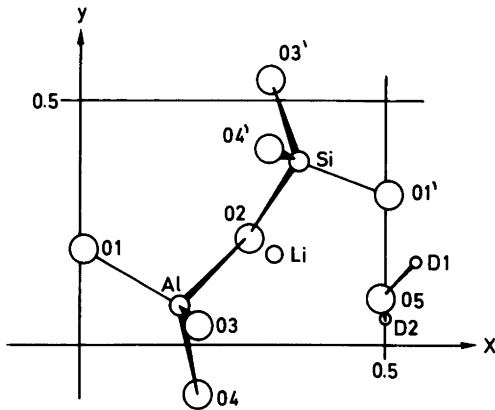


Fig. 3. Projection of a part of the unit cell along 001 showing the AlO_4 and SiO_4 tetrahedra and the water molecule.

from the neutron powder diffraction pattern measured with 1.909\AA neutrons using Gaussian fits.¹¹ Intensities of reflections with 2θ less than 124.5° ($\sin\theta/\lambda \leq 0.464\text{\AA}^{-1}$) were used in the structure determination. In the case of two completely overlapping reflections, these were excluded from the calculation to avoid the uncertainty referred to above. Intensities with $I > 2\sigma(I)$ were regarded as observed, thus giving 155 observed and 20 unobserved reflections that were used with the MULTAN programs.⁷ The total number of phase relationships was 127 and the coordinates of the 8 highest peaks of the solution with the greatest combined figure of merit of 2.95 are listed in Table 2. The coordinates x, y, z arrived at in the solution are transformed to $\bar{x}, \bar{y}-0.5, \bar{z}-0.07$. The shift in the z -coordinates was cho-

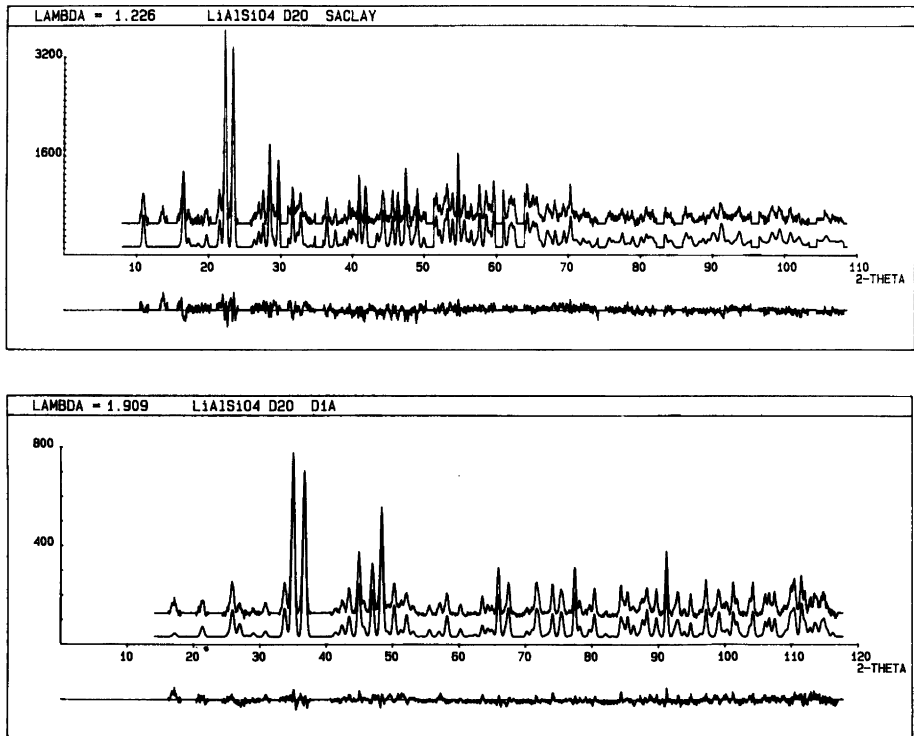


Fig. 4. Neutron powder diffraction diagrams of $\text{LiAlSiO}_4 \cdot \text{D}_2\text{O}$ taken with 1.226 and 1.909\AA neutrons. Upper curve is observed intensity and lower curve is calculated intensity. The curve below the abscissa is difference between observed and calculated intensities. The 1.226\AA spectrum contains an impurity of Al from the sample container, and these Bragg peaks are excluded from the spectrum. The R values for the two sets of data are:

$$R_{\text{Prof}} = \frac{\sum(y_{\text{obs}} - y_{\text{calc}})}{\sum y_{\text{obs}}}; \text{1.226 \AA data, 20 \% ; 1.909 data, 10 \% .}$$

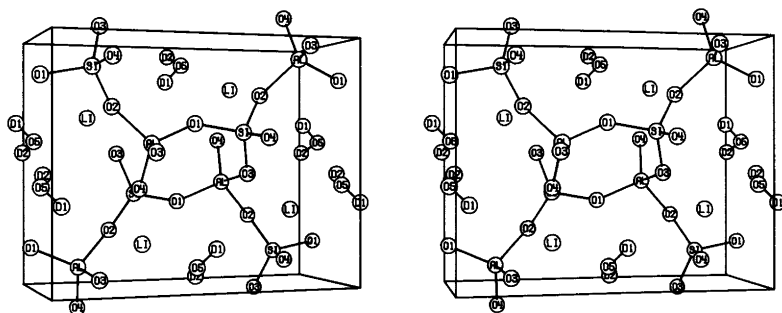


Fig. 5. Stereoscopic drawing of the structure of LiAlSiO₄·D₂O.

sen so that the coordinates could be compared with those of Ref. 5 and is allowed because the origin of the noncentrosymmetrical structure can be chosen arbitrarily on the z axis. The coordinates thus obtained were then transformed using the symmetry operations of the space group to yield the values listed in Table 2. The coordinates of 7 of the 8 peaks corresponded rather well with the atomic positions of the structure.⁵ A structure factor calculation was then made with the Hewat¹⁷ version of the Rietveld program with 5 oxygen atoms and the silicon atom inserted, followed by a difference Fourier map calculation phased on this model. This confirmed the position of the deuterium atom, D2. Successive repetitions of these calculations yielded the positions of all the atoms in the structure with 1 atom for each difference Fourier map in the following sequence: Li (as the largest negative peak), Al, and D1. The structure was then refined using the profile refinement method.¹⁷ The parameters refined were scale factor, overall temperature factor parameters, 3 profile parameters, asymmetry parameter, preferred orientation parameter, zero point, 3 unit cell parameters, and 29 positional parameters. In addition, the occupancy of lithium and deuterium was refined to account for impurities as partial substitution of H for D and Na⁺ for Li⁺. Fig. 4 shows observed and calculated intensities and their difference for the two sets of data. Fig. 5 is a stereoscopic drawing of the structure.

Discussion

It has recently been shown that crystal structures of compounds with moderately sized unit cells (up to 500Å³) can be solved by direct methods⁷ using powder X-ray diffraction^{10,18} or powder

neutron diffraction data.^{10,19} It is, however, an advantage to combine the scattering information obtained from powder X-ray and neutron diffraction of a compound. This investigation shows that the Al and Si atoms of the structure of LiAlSiO₄·H₂O can be found from a Guinier photograph or powder diffraction data using direct methods, and that the silicon, deuterium and oxygen atoms can be found from a neutron diffraction powder pattern. The complete structure was then derived by conventional difference Fourier calculations. The water molecule of the structure contained the atoms D1, D2, and O5. The Li atoms had a bond of 1.97Å to O5 and the water molecules were hydrogen-bonded to each other by D2 in a O5-D2-O5 bond of 2.91Å. A weak hydrogen bond was made by D1 with O1', the O5-D1-O1' distance being 3.00Å. The interatomic distances in the water molecule were O5-D1 0.97 and O5-D2 0.95Å. The structure of the water molecule and its hydrogen bonds were in acceptable agreement with the absorption band of the IR spectra of the compound. A more detailed discussion of the structure of LiAlSiO₄·H₂O will be given elsewhere.⁵

Detailed and precise information on a crystal structure is obtained from a single-crystal diffraction experiment rather than from a powder diffraction analysis. However, when single crystals are not available, powder diffraction is a realistic approach to the structure investigation. The present study demonstrates that the combination of X-ray and neutron diffraction data yields sufficient information for a crystal structure determination by the use of direct methods.

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