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Structure of Sodium Tetradeuteroborate, $NaBD_4$

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The structure of $NaBD_4$ was determined from powder neutron data and refined using Rietveld's method. The compound has a sodium chloride-type structure, in space group $F\bar{4}3m$, $a = 6.137(7)$ Å, B–D, 1.160(7); angle D–B–D, 109.5(2)° at 295 K, with D atoms tetrahedrally oriented about *B* (at 1/2,0,0, etc.), and along all cube diagonals. This gives a random distribution of BD_4^- tetrahedra in two different configurations. © 1985 Academic Press, Inc.

Introduction

Recent structural work in this laboratory has been on Cu(I)–BH_4 complexes. In reviewing BH_4 compounds the somewhat anomalous structure of $NaBH_4$ was found where the tetrahedral BH_4 anion crystallized at a site with octahedral symmetry. Consequently, it was decided to check this structure using neutron diffraction.

In 1947, Soldate (*1*) analyzed X-ray powder data for sodium tetrahydrogen borate, $NaBH_4$, at room temperature. The compound crystallized in a face-centered cubic cell, $a = 6.151(9)$ kX, $Z = 4$. Intensity calculations involving only sodium and boron atoms favored a sodium chloride structure with BH_4 octahedral sites (*oct*); over a zinc blende one with BH_4 in tetrahedral holes (*tet*). For model *oct*, two possible arrangements were proposed for the BH_4 tetrahedra which were centered at 1/2,0,0; 0,1/2,0; 0,0,1/2; 1/2,1/2,1/2. They were the disordered model (*dis*) with the hydrogens on all eight cube diagonals which gave two randomly tetrahedral distributed BH_4^- groups and an ordered model (*ord*), where there was no disorder with only one set of tetrahedra, and the hydrogens on four of the cube diagonals. In his work, Soldate did not reach any conclusions about the location of the hydrogens. Abrahams and Kalnajs (*2*) confirmed the cell, $a = 6.1635(5)$ Å at 298 K, and found a phase change at 190 K. The new phase at 78 K had a body-centered tetragonal cell, $a = 4.354(5)$ Å, $c = 5.907(5)$ Å. The λ or transition point was, according to Stockmayer and Stephenson (*3*), the result of an order–disorder transition involving different orientations of BH_4^-.

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However, Abrahams and Kalnajs (*2*) found the predicted low-temperature structure to be correct.

Peterson (*4*) collected single-crystal neutron data on potassium tetrahydrogen borate. His solution was based on a sodium chloride-type (*oct*) structure in $Fm3m$, with half hydrogen atoms (*dis*) along cube diagonals. This is analogous to Soldate's *oct dis* model, except a more symmetrical space group was being selected. B–H, 1.260 Å, and H–B–H, 109.50° were found.

This current work clarifies the situation using neutron powder data collected on isostructural $NaBD_4$. The deuteride was selected in order to avoid the large background that is produced by the large spin incoherent neutron scattering of ^1H. Naturally occurring boron containing ^{10}B was used. To reduce the effect of absorption, the material was packed lightly into a small radius (R_s) tube (μR_s = 0.56 measured). This gave limited intensities, and, because of high thermal parameters, little significant data at larger 2θ angles.

$NaBD_4$ [Batch No. 1468431 from E. Merck, Darmstadt, West Germany; fine powder, guaranteed deuteration at 98%] (0.5 g) was tampered under dry helium into a 5-mm-diameter vanadium can, and enclosed with an indium O-ring seal. The can was rotated at the center of a horizontal

TABLE I

REFINEMENT OF VARIOUS MODELS FOR $NaBD_4$

Model		R_p	R_w	R_B	G_0F	Reason for rejection
oct dis $F\bar{4}3m$		2.6	3.4	1.5	1.8	Accepted
oct dis $F\bar{4}3m$	Isotope	2.6	3.3	1.8	1.7	Refined H and D occupation; found H insignificant
oct ord $F\bar{4}3m$		3.2	4.3	1.5	2.9	Temp. factor for D too high [17(1) Å^2]
oct dis $Fm3m$		Same as *oct dis* $F\bar{4}3m$				
oct dis $F23$		Same as *oct dis* $F\bar{4}3m$				
oct anion $Fm3m$		3.3	4.4	1.6	3.1	Temp. factors too high [31(2) Å^2]
tet dis $F\bar{4}3m$		3.3	4.5	4.5	3.1	Refinement did not converge, temp. factors too high [18(4) Å^2]
tet ord $F\bar{4}3m$		3.2	4.2	4.4	2.8	Refinement did not converge, temp. factors too high [50(5) Å^2]

R_p, the pattern R factor $= 100[\Sigma|y_i - y_{ci}|/\Sigma y_i]$

R_{wp}, weighted pattern R factor $= 100[\Sigma w(y_i - y_{ci})^2/\Sigma w y_i^2]^{1/2}$

R_{Bragg}, Bragg R factor $= 100\Sigma|I_{o_{hkl}} - I_{c_{hkl}}|/\Sigma I_{o_{hkl}}$

y_i, observed intensity at a 2θ value, y_{ci}, calculated intensity at same value

I_{hkl}, intensity for a reflection hkl

R_w, for integrated intensity $= 100[\Sigma w_i(I_{o_i} - I_{c_i})/\Sigma w i I_{oi}]$

Note. Weight used in Rietveld refinement $= \dfrac{1}{\sigma^2(y_i)}$ if background refined.

neutron diffractometer ($\lambda = 1.0887(5)$ Å, copper monochromator about 111) with a ^{3}He gas proportional counter, attached to hole 4H1 on the Australian Atomic Energy Commission's HIFAR (DIDO Type) 10-MW reactor (flux at specimen 6.7×10^9 neutrons m^{-2} sec^{-1}). Data were obtained using a digital electronic data acquisition over the complete spectrum.

Attempts were made to fit the data to the various models already proposed. A further arrangement, model *anion*, was considered with the BD_4^- group taken as a complete scattering entity and refined as such. Calculations on the various models are summarized in Table I. The Rietveld method (*5*) was used for refinement with scattering lengths for BD_4^- group, D, B, Na, and H at 32.04, 6.672, 5.35, 3.63, and −3.741 fm^{-1}, respectively. Initially, Soldate's original model was refined. These refined parameters were then used to test all other models. Refinement was continued for up to 15 cycles after which no significant further refinement was possible. Data had been collected from 5.0 to 110.0° in 2θ, but the only significant intensities were from 15.10 to 21.70° and 27.20 to 52.90°. In profile refinement, absorption correction was incorporated into the Wiles and Young program (*5*) using the algorithm of Rouse *et al.* (*6*). Background was interpolated between 12 fixed points (F_B) or refined (R_B) using a three-parameter algorithm $[b_0 + b_1(2\theta) + b_{-1}(2\theta)^{-1}]$.

In the Wiles and Young program, the positions used were Na(0,0,0); B(either *oct* 1/2,1/2,1/2 or *tet* 1/4,1/4,1/4), and D(x,x,x and/not $-x,-x,-x$) with relative occupancy factor to give total atom ratios of 1 : 1 : 4. All x parameters were constrained to move together. In the case of two related D atoms, their temperature factors were also constrained to move together. Refinement for the model [*oct dis* $F23$] in noncentrosymmetric space group $F23$, gave a simi-

TABLE II

Data for *oct dis* $F\bar{4}3m$ Model

(*hkl*)	2θ	Integrated observed intensity	Mult	Integrated calculated intensity[a]
111	17.683(3)	38,991 ± 259	8	38,700
002	20.456(4)	23,823 ± 230	6	22,939
022	29.093(19)	9,115 ± 160	12	10,819
113	34.21(1)	4,198 ± 150	24	3,951
222	35.78(1)	3,504 ± 174	8	3,845
004	41.55(3)	2,260 ± 128	6	2,447
133	45.44(4)	1,726 ± 170	24	1,436
024	46.73(3)	1,915 ± 150	24	2,194
224	51.524(13)	5,268 ± 160	24	3,868

$\lambda = 1.0887(5)$ Å; $\mu R_s = 0.56$; $a = 6.137(7)$ Å includes error in λ

Atomic parameters

Atom	x/a	y/b	z/c	Å^2
Na	0.0	0.0	0.0	1.8(2)
B	0.5	0.5	0.5	1.8(2)
D(1)[b]	0.3901(6)	0.3901(6)	0.3901(6)	4.1(3)
D(2)[b]	0.6099(6)	0.6099(6)	0.6099(6)	4.1(3)

[a] Estimated using F_{obs} and F_{calc} in LINUS refinement.

[b] Half weight.

lar result to *oct dis* $F\bar{4}3m$. This had deuterium atoms tetrahedrally orientated about B, and along the eight cube diagonals, to produce a random distribution of tetrahedra in two different static configurations, $F\bar{4}3m$. For all models, the halfwidth parameters were determined independently from single Gaussian fits and then fixed. In order to verify the results for the original model, the integrated intensities were refined using the full matrix least-squares program LINUS (7). The calculations were in excellent agreement with the fixed background results, $R = 0.083$, $R_w = 0.075$, $N_o = 9$, $N_v = 2$.

Tables I and II show that model *oct dis* $F\bar{4}3m$ fits the data. Other unrelated models did not successfully refine.

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