Acta Cryst. (1963). **16**, 376

Refinement of the Structure of Potassium Pentaborate Tetrahydrate

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(*Received* 18 *June* 1962)

Potassium pentaborate tetrahydrate is orthorhombic with four molecules in the unit cell of dimensions $a=11·062$, $b=11·175$, $c=9·041$ Å. The space group is *Aba*.

The structure has been determined with a precision corresponding to an R-factor of 0·030. The accuracy is ±0·1 Å for H–O bonds and ±0·005 Å for all other bonds.

The structure contains complex ions $[B_5O_6(OH)_4]^-$ constructed from one BO_4 tetrahedron and four triangular groups $BO_2(OH)$ by sharing of corners. The proper way of writing the chemical formula for the compound is $K[B_5O_6(OH)_4].2H_2O$.

The water molecules and the hydroxyl groups form hydrogen bonds. Each potassium atom is bonded to eight oxygen atoms.

Introduction

This paper gives the results of a reinvestigation of the crystal structure of potassium pentaborate tetrahydrate, $KB_5O_8.4H_2O$. An approximate structure for this compound was reported twenty-five years ago (Zachariasen, 1937).

Except for the much greater precision of the present work, the earlier results for the arrangement of potassium, boron and oxygen atoms have been confirmed. In the 1937 paper possible positions for the hydrogen atoms were suggested. These suggestions (in the terminology of the present paper) were: O_{VI}–$H_I\cdots O_I$, O_{VI}–$H_{II}\cdots O_{II}$, O_{VI}–$H_{III}\cdots O_{IV}$, O_{IV}–H_{IV}–O_V, corresponding to the formula $KH_2(H_3O)_2[B_5O_{10}]$. The positions of the hydrogen atoms were deduced directly from the diffraction intensities in the re-examination. The sites proposed for atoms H_I and H_{II} in the 1937 paper have been verified. However, for the H_{III} and H_{IV} atoms, the new results are $O_{VI}\cdots H_{III}$–O_{IV} and $O_{IV}\cdots H_{IV}$–O_V. Accordingly, the proper way of writing the chemical formula is $K[B_5O_6(OH)_4].2H_2O$ as proposed by Christ (1960).

Table 1. *Positional parameters*

	x	y	z
K	0	0	0
B_I	0	0	0·4041 ± 0·0011
B_{II}	0·1890 ± 0·0004	0·0943 ± 0·0005	0·3126 ± 0·0008
B_{III}	0·2042 ± 0·0004	0·9432 ± 0·0005	0·4952 ± 0·0011
O_I	0·0672 ± 0·0002	0·0843 ± 0·0003	0·3082 ± 0·0005
O_{II}	0·0832 ± 0·0002	0·9313 ± 0·0003	0·4991 ± 0·0006
O_{III}	0·2591 ± 0·0002	0·0254 ± 0·0003	0·4033 ± 0·0006
O_{IV}	0·2448 ± 0·0003	0·1753 ± 0·0003	0·2235 ± 0·0006
O_V	0·2816 ± 0·0002	0·8801 ± 0·0004	0·5802 ± 0·0006
O_{VI}	0·0151 ± 0·0003	0·1707 ± 0·0004	0·7588 ± 0·0005
H_I	0·978 ± 0·007	0·247 ± 0·007	0·804 ± 0·010
H_{II}	0·967 ± 0·006	0·111 ± 0·007	0·649 ± 0·011
H_{III}	0·161 ± 0·005	0·159 ± 0·007	0·741 ± 0·009
H_{IV}	0·251 ± 0·007	0·316 ± 0·007	0·193 ± 0·014

Experimental procedure

Crystals of potassium pentaborate tetrahydrate are orthorhombic with space group *Aba* and with four molecules in a unit cell of dimensions

$$a=11·062\pm0·003,\ b=11·175\pm0·003,$$
$$c=9·041\pm0·003\ \text{Å}\,.$$

The atomic positions are: $(000)(0\frac{1}{2}\frac{1}{2})+4K$ in $(000)(\frac{1}{2}\frac{1}{2}0)$, $4B_I$ in $(00z)(\frac{1}{2}\frac{1}{2}z)$, all other atoms in $(xyz)(\bar{x}\bar{y}z)(\frac{1}{2}-x,\frac{1}{2}+y,z)(\frac{1}{2}+x,\frac{1}{2}-y,z)$. Thus, there are 37 positional degrees of freedom.

All observations were made on a crystal ground into a nearly perfect sphere of radius 0·0190 ± 0·0001 cm. Cu $K\alpha$ radiation was used, and the intensities

Table 2. *Thermal parameters*

($\times 10^4$)

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
K	28·7 ± 0·7	74·0 ± 1·7	80·3 ± 2·1	4·5 ± 1·0	0	0
B_I	27·7 ± 3·7	42·0 ± 6·4	78·3 ± 11·9	0·6 ± 4·8	0	0
B_{II}	36·3 ± 2·9	49·9 ± 4·6	81·9 ± 7·5	−0·6 ± 3·8	4·6 ± 4·8	5·4 ± 6·1
B_{III}	39·4 ± 2·7	45·8 ± 4·4	83·9 ± 7·1	−7·7 ± 3·2	−3·7 ± 6·5	3·3 ± 7·4
O_I	30·6 ± 1·7	52·1 ± 3·0	83·3 ± 4·7	0·7 ± 2·3	0·5 ± 3·0	16·3 ± 3·9
O_{II}	33·2 ± 1·6	63·6 ± 3·1	79·7 ± 4·6	−7·5 ± 2·0	−2·0 ± 3·6	22·4 ± 4·6
O_{III}	28·4 ± 1·7	61·2 ± 3·0	111·1 ± 5·9	−5·2 ± 2·3	−2·9 ± 3·3	37·8 ± 4·0
O_{IV}	44·4 ± 1·9	69·0 ± 3·2	124·4 ± 8·6	−1·8 ± 3·2	−1·9 ± 3·7	45·1 ± 5·0
O_V	38·8 ± 2·2	84·2 ± 3·9	158·2 ± 7·6	−6·7 ± 2·5	−21·5 ± 4·1	63·9 ± 5·3
O_{VI}	46·5 ± 2·0	60·8 ± 3·7	107·9 ± 6·2	10·6 ± 2·5	−7·7 ± 3·6	−1·8 ± 4·4

were measured with a proportional counter. The experimental intensity data consisted of all reflections in the first two layer lines about the axes [010], [001] and [01$\bar{1}$].

Independent intensity measurements were made for the equivalent planes of each crystallographic form, and no intensity variation beyond statistical counter error was observed except for a very few of the very strongest reflections, such as (400), which are affected by secondary extinction.

In the final refinement stages a small extinction correction was applied according to the formula

$$I_{\text{corr.}} = I_{\text{obs.}}[1 - gI_{\text{obs.}}]^{-1} \qquad (5)$$

where the coefficient g was adjusted to give the best fit. The correction amounted to 10% in the extreme case of $|F_{400}|$, and was negligible for most reflections.

The high degree of internal consistency of the data indicates that the experimental structure factor values per unit cell are accurate to a probable error of $\pm 1{\cdot}0$ electron unit except for the very strongest reflections which may be affected by local variations of the secondary extinction.

The least-square refinements were carried out on the IBM-704 Computer of the Argonne National Laboratory using the Busing–Levi full matrix program. All observations were given the same weight, the McWeeny (1951) *f*-curves were assumed for hydrogen and boron and those of Berghuis *et al.* (1955) for potassium and oxygen.

The 1937 parameters served as starting coordinates for boron and oxygen atoms, the midpoints of the O–H · · · O vectors for hydrogen atoms. The ultimate

Table 3. *Structure factors*

H0L

HOL	F_{obs}	$1.042\lvert F_c\rvert$	A	B
200	11.0	10.6	-10.2	0
002	67.1	68.1	17.8	-62.9
202	38.9	38.9	11.6	-35.5
400	214.0	221.8	212.8	0
402	13.0	12.2	-6.5	-9.7
004	130.0	128.2	117.3	37.0
204	95.5	93.0	82.4	34.3
600	46.3	46.3	-44.5	0
404	43.6	42.7	35.3	-20.8
602	15.0	13.6	11.0	7.0
006	17.6	16.3	14.7	-5.2
206	65.3	65.3	51.5	-35.8
604	30.1	27.6	24.3	10.5
800	43.4	41.4	39.8	0
406	36.5	37.0	-30.3	18.4
802	12.6	11.5	10.6	3.1
804	46.3	47.5	13.1	-43.7
606	19.7	18.2	13.4	-11.3
008	29.5	30.2	28.6	4.7
208	32.3	32.2	26.4	16.2
10.0.0	32.4	32.4	31.1	0
10.0.2	45.2	45.7	43.5	5.0
408	26.1	25.6	24.2	3.8
806	38.0	37.2	-26.2	24.2
10.0.4	39.4	38.5	33.8	15.1
608	17.1	16.9	14.8	6.7
12.0.0	46.8	45.9	44.1	0
0.0.10	43.5	42.3	40.1	6.2
12.0.2	20.0	19.5	9.6	-16.1
2.0.10	7.0	7.3	5.2	-4.7
10.0.6	30.4	30.1	27.7	-8.3
808	28.1	28.1	26.6	4.2
4.0.10	16.4	15.3	14.7	1.0
12.0.4	25.8	25.6	21.5	-11.9
6.0.10	7.3	6.7	-2.8	-5.8
10.0.8	18.3	18.3	17.6	1.1
14.0.0	28.6	27.2	26.1	0
12.0.6	9.0	9.8	8.6	3.7
14.0.2	26.7	25.4	24.2	2.2

Table 4. *Structure factors*

HK0

HKO	F_{obs}	1.039 F	HKO	F_{obs}	1.039 F	HKO	F_{obs}	1.039 F
020	174.0	173.9	280	8.9	6.9	0.12.0	33.5	32.4
200	10.5	-10.6	820	9.1	8.1	1.12.0	22.8	-22.2
120	18.3	-19.2	660	46.0	46.4	980	28.6	-29.5
220	35.1	34.6	380	29.4	30.4	12.0.0	46.0	45.9
320	2.7	-3.5	480	24.2	22.8	2.12.0	28.1	28.3
040	22.7	-23.9	840	52.6	50.9	7.10.0	11.7	10.7
400	214.0	221.6	760	19.4	19.7	12.2.0	27.3	28.3
140	35.6	36.3	920	31.2	-31.7	3.12.0	5.3	5.9
240	49.0	48.3	580	22.0	-21.7	11.6.0	5.1	4.8
420	43.2	43.9	940	3.8	5.1	4.12.0	14.3	15.2
340	5.9	-4.7	0.10.0	23.5	22.2	12.4.0	25.4	25.4
520	36.7	-36.0	680	35.9	36.3	8.10.0	8.5	8.7
440	38.0	36.0	1.10.0	7.0	7.2	10.8.0	14.6	14.6
060	36.2	34.4	860	83.4	84.9	5.12.0	12.7	-12.6
600	46.4	-46.3	10.0.0	32.1	32.4	13.2.0	17.7	-16.3
160	35.3	-34.2	2.10.0	16.7	16.9	6.12.0	8.3	9.3
260	12.3	11.9	10.2.0	30.1	30.3	9.10.0	5.1	3.8
620	7.8	-6.9	3.10.0	0	2.0	12.6.0	24.7	24.5
540	18.9	19.7	780	26.0	25.5	11.8.0	3.0	1.7
360	50.8	50.4	4.10.0	15.8	15.8	13.4.0	10.3	9.7
460	98.2	98.6	10.4.0	10.6	10.3	7.12.0	0	1.9
640	38.7	36.1	960	29.4	-28.8	0.14.0	3.0	3.3
720	12.3	-11.9	5.10.0	8.0	8.5	1.14.0	18.1	-18.3
560	31.2	-30.9	11.2.0	18.6	18.8	14.0.0	27.4	27.2
080	14.9	-13.7	880	26.3	25.8	2.14.0	16.9	17.0
180	16.8	-17.9	6.10.0	14.9	14.9	10.10.0	7.9	8.6
800	43.5	41.4	10.6.0	5.2	5.3	14.2.0	23.7	23.6
740	11.6	-11.6	11.4.0	12.7	13.5	3.14.0	4.5	4.5

Table 5. *Structure factors*
HKK

HKK	F_{obs}	$1.063\lvert F_c\rvert$	A	B	HKK	F_{obs}	$1.063\lvert F_c\rvert$	A	B	HKK	F_{obs}	$1.063\lvert F_c\rvert$	A	B
111	36.2	37.3	-14.0	32.1	355	23.4	24.5	21.7	-8.0	10.4.4	21.0	21.0	18.8	-6.1
200	9.9	10.8	-10.2	0	733	45.7	46.6	43.4	5.5	955	17.9	18.5	16.6	-5.1
211	14.4	16.0	-2.6	-14.8	822	53.7	54.3	49.3	-13.3	11.3.3	19.0	19.5	17.0	6.9
022	198.0	194.6	164.9	-79.3	644	30.9	29.6	27.4	4.8	12.0.0	45.5	46.9	44.1	0
122	148.0	148.4	121.9	67.9	455	2.8	3.3	-2.9	-1.0	577	7.8	9.2	8.4	2.1
311	51.6	52.8	41.1	-27.8	911	44.9	45.6	41.0	-12.5	12.1.1	9.6	9.6	-4.1	8.0
222	53.0	53.3	34.0	36.9	833	28.5	30.1	23.6	-15.5	866	16.1	15.3	14.1	-3.0
400	236.0	226.3	212.8	0	555	30.8	30.6	28.2	-5.9	12.2.2	32.0	32.7	28.2	-12.3
411	24.4	25.5	-23.3	-5.8	744	14.0	14.3	-11.8	-6.4	677	5.8	6.9	4.7	4.5
322	16.2	16.4	12.0	-9.6	066	50.9	53.6	-33.3	37.8	088	5.8	5.0	-4.3	1.9
133	53.1	51.8	34.9	-33.9	166	40.0	40.8	37.5	-7.8	188	8.3	8.2	-7.5	2.0
422	105.0	107.0	92.3	-40.2	922	20.0	20.5	-15.3	-11.9	11.4.4	6.5	6.8	-1.4	6.2
233	80.6	81.2	-70.8	28.8	266	20.4	20.5	8.2	-17.5	10.5.5	9.5	9.2	6.9	-5.2
511	83.3	83.2	77.9	-6.7	655	8.9	8.8	4.4	-7.0	288	13.9	14.8	13.4	-3.8
333	60.3	59.9	55.6	-8.7	366	20.7	21.5	-18.0	9.1	12.3.3	7.2	7.4	0.5	-6.9
522	73.5	73.9	62.4	30.5	10.0.0	31.8	33.1	31.1	0	388	8.7	8.3	-7.5	2.1
600	47.5	47.3	-44.5	0	10.1.1	19.6	21.2	6.0	19.0	966	4.1	3.3	-3.1	0.3
433	29.8	29.3	-26.4	-7.9	933	27.7	28.0	22.7	-13.4	777	10.3	11.3	10.2	3.0
611	16.7	15.9	14.7	2.8	844	9.6	9.2	4.9	7.1	13.1.1	18.7	19.2	18.1	0.8
044	55.8	56.4	3.9	-52.9	466	13.3	14.5	1.7	13.5	488	7.9	8.3	6.3	4.6
144	57.6	58.2	51.3	-19.2	10.2.2	30.1	30.4	27.1	9.0	13.2.2	7.6	7.6	2.0	-6.9
244	34.0	32.9	26.0	16.6	755	5.9	5.8	-0.7	-5.4	11.5.5	23.4	23.7	22.3	-0.3
622	33.7	33.0	15.9	26.6	566	20.8	22.3	20.9	-1.4	588	4.9	5.7	-5.3	0.4
533	44.6	45.5	32.5	-27.9	944	13.3	13.7	1.4	12.8	12.4.4	2.6	2.7	2.5	0.3
344	16.8	15.7	-3.0	-14.4	10.3.3	23.0	22.6	20.9	3.5	877	5.9	6.1	-2.9	-5.0
711	61.1	61.0	44.5	-36.2	177	20.0	20.6	18.0	-7.1	10.6.6	7.5	8.1	5.2	-5.5
444	24.1	23.3	9.1	-20.0	11.1.1	9.7	7.7	-6.3	3.5	13.3.3	17.1	17.5	16.0	-4.2
633	41.2	41.6	-28.1	27.2	666	29.4	30.6	22.3	-18.3	688	10.3	11.5	10.8	-0.2
722	6.3	6.8	0.9	6.3	277	5.7	6.1	2.8	5.0	14.0.0	27.4	27.8	26.1	0
155	65.3	66.9	62.6	-6.8	855	5.2	5.2	4.3	-2.4	14.1.1	8.8	8.8	-3.3	7.6
800	42.9	42.3	39.8	0	377	13.4	13.9	13.0	-1.0	199	10.0	10.9	10.2	0.9
544	40.0	38.6	34.5	-11.2	11.2.2	0	0.4	-0.3	0.3	977	12.1	14.2	12.3	5.2
255	8.9	8.8	-6.8	-4.7	477	6.6	7.0	-2.2	-6.2					
811	11.9	12.1	-1.7	11.3	766	6.8	8.6	-8.1	0.3					

refinement provided for the simultaneous adjustment of 96 parameters (3 scale factors, 37 position coordinates, 56 thermal parameters). An isotropic temperature factor $B = 5{\cdot}9$ Å^2 was assumed for the hydrogen atoms. The final refinement yielded an R-factor of 0·030.

The results for positional and thermal parameters are listed in Tables 1 and 2. The agreement between observed and calculated structure factors is shown in Tables 3–5 for a minor fraction of the complete set of data.

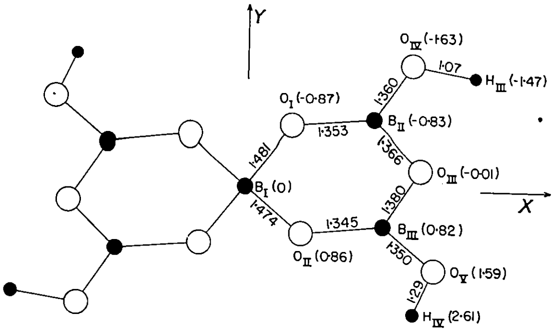

Fig. 1. Shows the configuration and bond distances of the group $[B_5O_6(OH)_4]^-$ as viewed along the Z-axis of the structure. The notation is the same as in Table 1. Numbers in parentheses give the height in Å above the plane $z = 0{\cdot}4041$ passing through the B_I atom. The numbers on the bonds denote the lengths in Å.

Description of the structure

The most interesting feature of the structure is the presence of the complexes $[B_5O_{10}]^{-5}$, or $[B_5O_6(OH)_4]^-$ with the hydroxyl hydrogen atoms included. The configuration of this polyion is shown in Fig. 1 (see also Fig. 3 of the 1937 paper). The complex consists of a central BO_4-tetrahedron with two opposite tetrahedral edges shared with $B_2O_3(OH)_2$-groups. The $B_2O_3(OH)_2$-group is very nearly planar.

The bond lengths within the polyion are:

$B_I - 2\,O_I = 1{\cdot}481 \pm 0{\cdot}007$ Å
$B_I - 2\,O_{II} = 1{\cdot}474 \pm 0{\cdot}003$

$B_{II}–O_I = 1{\cdot}353 \pm 0{\cdot}005$
$B_{II}–O_{III} = 1{\cdot}366 \pm 0{\cdot}007$
$B_{II}–O_{IV} = 1{\cdot}360 \pm 0{\cdot}007$

$B_{III}–O_{II} = 1{\cdot}345 \pm 0{\cdot}002$ Å
$B_{III}–O_{III} = 1{\cdot}380 \pm 0{\cdot}006$
$B_{III}–O_V = 1{\cdot}350 \pm 0{\cdot}007$

$H_{III}–O_{IV} = 1{\cdot}06 \pm 0{\cdot}08$
$H_{IV}–O_V = 1{\cdot}29 \pm 0{\cdot}09$

The polyions are held together in the structure by means of K–O bonds and O–H · · · O bindings between polyions and between a polyion and water molecules.

Each potassium atom is bonded to eight oxygen atoms at an average distance of 2·903 Å, the individual bond lengths being:

$K–2\,O_I = 3{\cdot}034 \pm 0{\cdot}004$ Å
$K–2\,O_V = 2{\cdot}856 \pm 0{\cdot}005$

$K–2\,O_{III} = 2{\cdot}819 \pm 0{\cdot}005$ Å
$K–2\,O_{VI} = 2{\cdot}903 \pm 0{\cdot}005$

The dimensions found for the four distinct O–H···O configurations are:

$O_{IV}\text{–}H_{III}\cdots O_{VI} = 2{\cdot}665 \pm 0{\cdot}006$ Å $\quad H_{III} - O_{IV} = 1{\cdot}06 \pm 0{\cdot}08$ Å
$H_{III}\cdots O_{VI} = 1{\cdot}63 \pm 0{\cdot}07$

$O_{V}\text{–}H_{IV}\cdots O_{IV} = 2{\cdot}662 \pm 0{\cdot}006 \quad H_{IV} - O_{V} = 1{\cdot}29 \pm 0{\cdot}09$
$H_{IV}\cdots O_{IV} = 1{\cdot}60 \pm 0{\cdot}08$

$O_{VI}\text{–}H_{I}\cdots O_{I} = 2{\cdot}920 \pm 0{\cdot}006 \quad H_{I} - O_{VI} = 1{\cdot}03 \pm 0{\cdot}07$
$H_{I}\cdots O_{I} = 1{\cdot}95 \pm 0{\cdot}08$

$O_{VI}\text{–}H_{II}\cdots O_{II} = 2{\cdot}828 \pm 0{\cdot}005 \quad H_{II} - O_{VI} = 1{\cdot}31 \pm 0{\cdot}07$
$H_{II}\cdots O_{II} = 1{\cdot}54 \pm 0{\cdot}07$

In recent years a number of borate structures have been determined with precision in this laboratory, and the results as to bond lengths for the whole group of compounds will be discussed in some detail in a forthcoming article.

Table 6. *Root mean square displacements*

Atom	Axis	Displacement	α	β	γ
K	1	0·131	0·99	−0·09	0
	2	0·182	0	0	1
	3	0·217	0·09	0·99	0
B_I	1	0·131	1·00	−0·03	0
	2	0·163	0·03	1·00	0
	3	0·180	0	0	1
B_{II}	1	0·147	0·95	0·15	−0·25
	2	0·173	−0·26	0·84	−0·46
	3	0·188	0·13	0·51	0·85
B_{III}	1	0·146	0·86	0·50	0·10
	2	0·175	−0·38	0·75	−0·53
	3	0·190	−0·32	0·43	0·84
O_I	1	0·138	1	0	0
	2	0·159	0	0·74	−0·67
	3	0·205	0·02	0·67	0·74
O_{II}	1	0·140	0·98	0·20	0
	2	0·158	0·11	−0·54	0·83
	3	0·221	−0·16	0·82	0·55
O_{III}	1	0·127	0·95	0·28	−0·16
	2	0·151	0·31	−0·66	0·69
	3	0·250	−0·07	0·70	0·71
O_{IV}	1	0·147	0·56	−0·59	0·59
	2	0·171	0·82	0·49	−0·29
	3	0·267	−0·12	0·64	0·75
O_V	1	0·141	0·82	−0·35	0·45
	2	0·170	0·56	0·65	−0·51
	3	0·306	−0·15	0·69	0·71
O_{VI}	1	0·157	0·89	−0·42	0·18
	2	0·202	0·29	0·82	0·50
	3	0·215	−0·33	−0·41	0·85

Table 6 shows the experimental anisotropic temperature factors converted to root mean square displacements along principal axes and the orientations of the principal axes expressed in terms of their direction cosines α, β, γ in a cartesian system with XYZ axes along the vectors **a**, **b**, **c** of the structure.

Although a detailed analysis of the thermal data has not been made, a cursory inspection indicates that the results are physically reasonable.

All but the potassium atoms and the O_{VI} atoms are constituents of the B_5O_{10}-group, the long axis of which has direction cosines $\alpha = 0{\cdot}995$, $\beta = 0{\cdot}10$, $\gamma = 0$. As is to be expected, the direction of minimum thermal displacement for all atoms in the structure is approximately parallel to the long axis of the polyion.

The atoms B_{II}, B_{III}, and O_I–O_V form nearly coplanar groups B_2O_5 with the normal to the plane having direction cosines $\alpha = -0{\cdot}07$, $\beta = 0{\cdot}69$, $\gamma = 0{\cdot}72$. It is seen that the direction of maximum thermal displacement for these atoms is nearly parallel to the normal of the B_2O_5 group.

The O_{IV} and O_V atoms, which form only one O–B bond each, show the largest heat motion and also the greatest anisotropy as one should expect.

We are grateful to the staff of the Applied Mathematics Division of Argonne National Laboratory for help with the least-square refinement program. The work was in part supported by the Advanced Research Projects Agencey.

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