JOURNAL OF SOLID STATE CHEMISTRY 73, 80–91 (1988)

Neutron Diffraction and ^{1}H Rigid Lattice Wide-Line NMR Studies of Powder (K, Bi^{III}, Bi^{V}) Pyrochlores

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Received January 5, 1987; in revised form June 26, 1987

The structure of an *A* cation-deficient pyrochlore $(K, Bi)_{\simeq 1.5}Bi_2O_{\sim 6}(H_2O)_{\sim 1}$ has been investigated by powder neutron diffraction using a deuterated sample. Main results of previous X-ray work are confirmed: 25% of *A* sites are empty; only a small amount of oxygen is found in 8(b) positions, a greater proportion being located in 32(e) positions which are displaced toward the *A* vacancy. The latter oxygen atoms belongs to a heavy water molecule, the deuterium atoms of which are distributed near 96(g) positions. Proton wide-line nuclear magnetic resonance experiments were performed at 4 K using an undeuterated sample. The experimental NMR spectrum has been simulated using three distinct models, all of them giving an acceptable chemical composition. Only one of these models gives the number of water molecules located in 32(e) sites in agreement with the neutron diffraction results. This same model reveals two other protonated species: water molecules, with short H–H distance, and OH groups belonging to the octahedral network. © 1988 Academic Press, Inc.

Introduction

The low-temperature synthesis of a nonstoichiometric compound containing tri- and pentavalent bismuth, potassium, oxygen, and hydrogen has been previously described (*1*). From analytical and structural investigations (*2*) it was concluded that this phase belongs to the well-known $A_2B_2X_6X'$ pyrochlore family with

A = K and Bi(III) (K/Bi $\simeq$ 3);
B = Bi(III) and Bi(V) (Bi(III)/Bi(V) $\simeq$ 0.10–0.15);
X, X' = O, OH, and/or H_2O.

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0022-4596/88 $3.00

In addition to the general characteristics of compounds of this family, it displays some special features:

—Bi(III) ions are one part of the cations belonging to the octahedral subarray. Although this is rather surprising in view of their dissymmetric electronic structure ($6s^2$ lone pair), other examples are known, such as $BaBiO_3$ (*3*) or $Bi_2(Ru_{2-x}Bi_x)O_{7-y}$ (*4*).

—About 25% of *A* sites are empty; it was suggested (*2*) that this situation allowed the seventh *X'* atom to be displaced toward the *A* vacancy.

Little information was known about protons in this phase. It was therefore decided to undertake low temperature proton wide-line nuclear magnetic resonance (NMR) experiments and powder neutron diffraction investigations (ND) which were performed on a deuterated sample.

Sample Synthesis and Analyses

Two different samples were used for NMR and neutron experiments.

Phase I (*NMR*). Phase I was synthesized according to the previously described procedure (*1*, *2*).

Phase II (*neutron*). It was believed that interaction between the solid and heavy water could yield incomplete exchange and lead to difficulties when dealing with the neutron diffraction data. Phase II was therefore synthesized using deuterated reagents.

First, 25 g of metallic potassium was reacted with heavy water (from Commissariat à l'Energie Atomique, 99.8% purity) in a polytetrafluorethylene vessel in a stream of dry nitrogen. Solid bismuth trichloride (10 g; RP Prolabo) and dried bromine (7 ml; Merck suprapur) were then added to 100 ml of the resulting KOD solution (4.8 *M*). The oxidation reaction was carried out at a temperature of 110°C for 2 hr.

The separation of the solid phase from the mother solution was achieved by centrifugation. The same procedure was repeated seven times after every washing operation using 30 ml of D_2O. The residual potassium concentration of the last washing solution was less than 250 ppm.

The solid phase was then kept in an atmosphere which was dried using phosphoric oxide. The chemical analysis and the deuterium content determination were performed after the neutron diffraction experiments, the second one by means of a mass spectrum analysis using a Riber 10-10 spectrometer. As contact between ambient atmosphere and sample cannot be avoided during the introduction of the latter, repetition of analyses clearly showed an increase of hydrogen content, resulting probably in an exchange between heavy and atmosphere waters. Deuterated species concentrations (Table I) must therefore be considered as lower limits. With the hypothesis that the mass 18 in Table I corresponds only to OD species, i.e., only HOD and no H_2O has been formed from D_2O during the contact with ambient atmosphere, the same exchange rate per D atom number would result from the analysis ($\simeq 0.1$) whatever the nature of OD or D_2O of the initial species.

Analytical data for phases I and II were collected using procedures described in Ref. (2). They are given in Table II. A fairly good agreement was found between cation contents, weight losses (taking into account replacement of hydrogen by deuterium), and cell parameters. However, there was

TABLE I

RESULTS OF THE FIRST MASS SPECTRUM ANALYSIS OF PHASE II

Mass	Nature	Weight (%)
20	D_2O	49.1
19	DOH	25.6
18	H_2O + OD	23.1
17	OH	2.2

TABLE II

ANALYTICAL DATA

	Bi[a]	Bi^{V}	*K*	Weight[b] loss (%)	Balance	Density (g · cm^{-3})	*a* (Å)[c]
Phase I	3.64	2.65	1.75	6.91	99.9	6.58	10.965
Phase II	3.56	2.74	1.78	7.78	99.1	5.96	10.966

Note. Concentrations are in 10^{-3} mole · g^{-1}.

[a] Total bismuth content.

[b] After pyrolysis at 850 K.

[c] Cell parameter at 290 K computed from X-ray powder data.

some discrepancy between experimental densities: the density of phase I was in agreement with previous results (*2*) while the density of phase II was too low. The density was measured after all other experiments and it was believed that some contamination (carbonation for example) occurred during the handling of the sample. This contamination appeared after elemental analyses which were performed just after the preparation and is then assumed to be correct. If all protons belong to water molecules, data for phase I lead to the formula,

$$K_{1.14}Bi^{III}_{0.65}Bi^{V}_{1.73}O_{5.85}[H_2O]_{0.97},$$

which can also be written

$$[K_{1.14}Bi^{III}_{0.37}\square_{0.49}][Bi^{III}_{0.27}Bi^{V}_{1.73}]O_{5.85}[H_2O]_{0.97},$$

where □ represents a vacancy in *A* sites. Since the sum of cations is close to 3.50, this formulation is in agreement with previous results (*2*).

Using the experimental value of density led to the following formula for phase II

$$K_{1.06}Bi^{III}_{0.49}Bi^{V}_{1.63}O_{5.35}[D_2O]_{1.01},$$

where the sum of cations is only 3.18. To overcome this difficulty, it was assumed that the cation distribution in phase II was not different from that of other samples (sum of cations = 3.5). The coefficients in the above formula were accordingly adjusted to match this requirement. This leads to the formula

$$[K_{1.17}Bi^{III}_{0.33}\square_{0.5}][Bi^{III}_{0.21}Bi^{V}_{1.79}]O_{5.87}[D_2O]_{1.11}.$$

It will be seen in the next section that neutron diffraction results agree with this assumption.

Neutron Diffraction Study

Experimental

The powder diffraction patterns were collected on the D1A high-resolution diffractometer of the ILL with λ = 1.3885(3) Å, the wavelength being calibrated with a Ni powder standard (*a* = 3.5238 Å). The powdered sample was inserted in a cylindrical vanadium container (Ø = 15 mm) held in a vanadium-tailed liquid helium cryostat. Data were collected from $2\theta = 10$ to 160° in steps of 0.05°. Measurement time was about 30 sec per step. The raw data from the 10 counters were summed using a conventional ILL program (*5*). Integrated intensities and standard deviations were determined by fitting the shape of Bragg peaks to Gaussians and the background to a first-order polynomial (*6*). The cell parameters were obtained by least-squares refinement of the diffraction angles for the strongest peaks, the zero-point correction of the instrument being included in the refinement.

Because the symmetry is high (space group $Fd\bar{3}m$) there are few peak overlappings for *hkl* planes with different θ angles (but many for *hkl*'s with the same θ angles). Therefore the Rietveld method was not necessary and the structure was refined by a conventional program using 49 integrated intensities. The following scattering lengths (all in fm) were used (*7*): 6.674 (D), 5.805 (O), 3.67 (K), 8.526 (Bi).

In spite of the presence of lone pair cations in *A* and *B* sites, careful examination of reflection profiles in the 5 and 298 K spectra did not reveal any loss of symmetry compared to the room temperature X-ray study (*2*). The structure was therefore refined in the cubic $Fd\bar{3}m$ space group, characteristic of most of the pyrochlore-type compounds

$A_2B_2X_6X'$. This structure is usually described as resulting from the interpretation of two three-dimensional networks: a B_2X_6 network composed of corner-linked BX_6 octahedra and a A_2X' network with corner-linked A_4X' tetrahedra (for further details see, for instance, Refs. (*8*) and (*9*)).

The low-temperature data were first analyzed. It was assumed that the octahedral network (Bi at 16(c) and O at 48(f)) did not contain any vacancy. After subtraction of the contribution of these ions from the intensities, a difference Fourier map was computed: it revealed maxima located at 16(d) positions. Taking them into account (9.36 K and 2.64 Bi) and computing a new difference map disclosed three atomic locations: 8(b) ($\frac{3}{8}$, $\frac{3}{8}$, $\frac{3}{8}$), 32(e) (x, x, x; $x \simeq 0.45$), and 96(g) (x, x, z; $x \simeq 0.4$; $z \simeq 0.5$).

Since the distance between 32(e) and 96(g) positions was about 1 Å, it was assumed that the oxygen atom of a heavy water molecule lay in the former position, with the deuterium atoms in the latter. It was also assumed that an oxygen atom rather than a deuterium atom was located at 8(b) position, in agreement with potential energy calculations (*9*). The situation of both oxygen atoms inside two (K, Bi)$_3$□ tetrahedra sharing a vacancy is shown in Fig. 1.

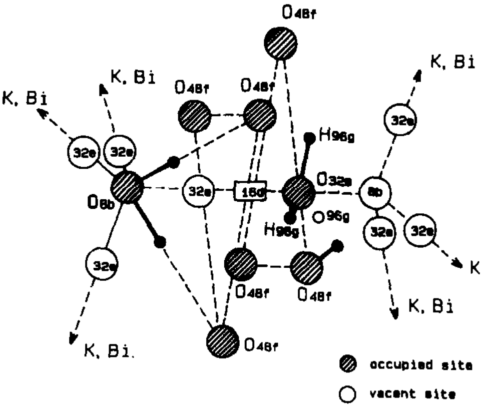

FIG. 1. Partial view of the pyrochlore structure around a 16(d) position.

Refinement of coordinates of 48(f), 32(e), and 96(g) positions, together with isotropic thermal coefficients of 16(c), 16(d), and 48(f) atoms (other coefficients were arbitrarily set to 2 Å^2) and occupancy factors of 16(d), 32(e), and 96(g) sites, led to an R value ($R = \Sigma|(I_{\text{obs}} - I_{\text{cal}}|/\Sigma I_{\text{obs}}$) of 0.068.

Results are given in Table III. Refinement using data collected at 290 K did not lead to significant differences. Observed and computed values of intensities of the 5 K spectrum are compared in Table IV. The most significant interatomic distances are listed in Table V.

Discussion

Results of neutron diffraction (ND) experiments are in good agreement with previously published X-ray data (*2*). Refine-

TABLE III

ATOMIC PARAMETERS OF PHASE II AT 5 K (a = 10.943(1) Å)

Wyckoff positions	Nature of atoms	Relative occupation	x	y	z	B (Å^2)^a
16(c)	Bi$^{\text{III}}$, Bi$^{\text{V}}$	1	0	0	0	0.66(6)
48(f)	O	1	0.3238(4)	0.125	0.125	1.08(6)
16(d)	K, Bi$^{\text{III}}$	0.76(1)	0.5	0.5	0.5	2.0(2)
32(e)	O	0.11(3)	0.450(3)	0.450	0.450	2
8(b)	O	0.15(5)	0.375	0.375	0.375	2
96(g)	D	0.08(1)	0.410(3)	0.410	0.519(4)	2

^{a} The thermal parameter is in the form: $\exp(-B\ \sin^2\theta/\lambda^2)$.

TABLE IV

COMPUTED AND OBSERVED INTENSITY DATA FOR 5 K SPECTRUM

h k l	Mul	I_{cal}	I_{obs}	h k l	Mul	I_{cal}	I_{obs}
1 1 1	8	3.67	0.77	11 3 1	48	7.29	
3 1 1	24	8.26		9 7 1	48	6.48	
2 2 2	8	40.52		9 5 5	24	71.97	
		48.77	53.74			85.79	83.59
3 3 1	24	6.49	9.61	8 6 6	24	0.59	
4 2 2	24	45.26	42.83	10 6 0	24	70.12	
3 3 3	8	24.49				70.71	64.98
5 1 1	24	8.50		11 3 3	24	36.94	
		33.00	33.00	9 7 3	48	75.31	
4 4 0	12	137.56	135.49	10 6 2	48	108.95	
5 3 1	48	34.83	30.68			221.21	228.64
6 2 0	24	8.10	10.17	8 8 4	24	155.90	
5 3 3	24	20.34		12 0 0	6	2.64	
6 2 2	24	74.43				158.54	166.31
		94.77	97.24	11 5 1	48	85.45	
4 4 4	8	12.03	11.01	7 7 7	8	3.71	
5 5 1	24	74.21				89.16	93.93
7 1 1	24	2.73		12 2 2	24	60.21	
		76.94	71.45	10 6 4	48	66.90	
5 5 3	24	1.61				127.11	129.68
7 3 1	48	93.22		12 4 0	24	84.01	73.41
		94.84	103.52	10 8 2	48	8.54	5.93
8 0 0	6	46.11	44.09	9 9 3	24	5.69	
7 3 3	24	28.84	26.35	11 7 1	48	10.18	
8 2 2	24	96.70		13 1 1	24	9.09	
6 6 0	12	35.56		11 5 5	24	6.88	
		132.26	125.07			31.84	39.16
5 5 5	8	18.99		10 6 6	24	44.13	39.69
7 5 1	48	2.74		12 4 4	24	49.37	57.02
6 6 2	24	79.42		11 7 3	48	0.57	
		101.15	97.96	9 7 7	24	1.27	
8 4 0	24	36.50	39.87	13 3 1	48	4.36	
9 1 1	24	25.12				6.20	6.20
7 5 3	48	0.08		12 6 2	48	34.89	35.44
		25.20	22.35	9 9 5	24	0.54	
6 6 4	24	17.03	19.49	13 3 3	24	71.57	
9 3 1	48	17.97	6.83			72.11	65.99
8 4 4	24	58.22	58.02	10 8 6	48	6.19	
9 3 3	24	3.71		14 2 0	24	3.30	
7 5 5	24	23.56		10 10 0	12	51.23	
7 7 1	24	32.40	35.66			60.72	62.17
10 2 0	24	17.71		13 5 3	48	34.03	
8 6 2	48	39.31		11 9 1	48	0.00	
		57.02	56.62	10 10 2	24	54.16	
7 7 3	24	77.34		14 2 2	24	42.32	
9 5 1	48	5.84				130.51	128.16
		83.17	87.65	12 8 0	24	75.40	72.46
10 2 2	24	64.41		11 9 3	48	3.01	
6 6 6	8	28.53		9 9 7	24	3.50	
		92.94	88.62			6.50	10.88
9 5 3	48	16.93	18.70	10 10 4	24	51.88	
10 4 2	48	8.32	6.32	12 6 6	24	0.05	
11 1 1	24	0.64		14 4 2	48	0.20	
7 7 5	24	10.14				52.05	53.61
		10.78	16.76	13 7 1	48	41.03	
8 8 0	12	16.69	12.78	13 5 5	24	0.06	
				11 7 7	24	24.70	
						65.79	55.89

TABLE V

MOST SIGNIFICANT INTERATOMIC DISTANCES (Å)

Bi 16(c)–O 48(f)	2.10
(K, Bi)–O 48(f)	2.73
(K, Bi)–O 32(e)	3.14
(K, Bi)–O 8(b)	2.37
O 48(f)–O 48(f)	2.85
O 48(f)–O 32(e)	2.73
O 32(e)–O 8(b)	3.32
O 32(e)–D 96(g)	0.98
D 96(g)–D 96(g)	1.69

Note. Estimated standard deviation is 0.03 Å.

ment of the occupation factor of 16(d) sites (Table III) confirms that 25% of these sites are empty. The major part of the X' anions are found to be localized in 32(e) positions rather than in 8(b) sites. However, the positional parameter of the former, $x = 0.45$ (Table III), is somewhat larger than the X-ray value ($x = 0.41$).

This situation results in a (K, Bi) 16(d)–0 32(e) distance of 3.14 Å which looks excessively large unless one notes that the 32(e) oxygen atom belongs to a heavy water molecule, as previously assumed, since the value of the ratio of occupation rates of 32(e) and 96(g) sites (3.65/7.7 = 0.47) is not far from the theoretical value.

The geometrical characteristics of the so-defined heavy water molecule are the following: O–D and D–D distances of 0.98 and 1.69 Å, respectively and D–O–D angle of 119°. While the first value agrees with the distance usually ascribed to an O–H bond, the last two values are too large to lie within the range defined by Ferraris *et al.* (*10, 11*) in their surveys of water molecule geometry in crystalline hydrates. According to these authors, the maximum H–O–H angle value would be 114°, for water molecules giving rise to hydrogen bonds with oxygen atoms as acceptors. However, this value would be easily reached by displacing

D atoms only 0.05 Å out of their 96(g) location in the DOD plane. This situation would remain in agreement with ND results (Table III). Using this assumption leads to a D–D intramolecular distance of 1.65 Å, which is equal to the maximum value listed by Ferraris *et al.*

Furthermore, the existence of hydrogen bonds can be inferred from the shortest O 32(e)–O 48(f) distances (2.74 Å). These hydrogen bonds are nearly linear as the expected D–O–D angle value is 114° compared with the O 48(f)–O 32(e)–O 48(f) angle value of 117°. The location of D atoms exactly in 96(g) sites would lead to bifurcated H bonds with a 158° angle.

The (K, Bi)$_3$□ tetrahedron which shares a vacancy with another one containing a 32(e) water molecule cannot itself be occupied by a 32(e) water molecule because the resulting O 32(e)–O 32(e) distance would be only 1.90 Å (Fig. 1). However, it may be occupied by an oxygen atom located in its center in a 8(b) position (O 8(b)–O 32(e) = 3.32 Å) or by some undetected oxygen atoms distributed over another 32(e) position with an x parameter smaller than 0.45 (for instance, $x = 0.40$ would lead to an acceptable O–O distance of 2.85 Å), or even on positions of higher multiplicity as supposed later in this discussion.

The question arises as to why ND failed to detect more D atoms, especially around O 8(b) atoms. Several reasons can be put forward:

—O 8(b) is not bound to any D atom.

—D atoms are distributed over 96(g) and 192(h) positions, resulting in a very low density per position.

—Oxygen atoms are bound to H atoms, as a result of isotopic exchange during preparation and handling of the sample.

We will come back to the question of the distribution of hydrogen in the next section.

It is reasonable to assume that each kind of X' species (O, OD, or OD$_2$) has to be associated with one kind of tetrahedra. For instance, in view of the 8(b)–16(d) distance of 2.37 Å, it may be suggested that O 8(b) are located preferably in Bi$_3$□ tetrahedra, giving rise to Bi^{3+}–O distances which are in agreement with the sum of ionic radii of both ions. In the same way, K$_3$□ tetrahedra can be occupied by the water molecules which were detected by ND: large K–O distances of 3.14 Å agree with this situation.

For tetrahedra which are composed of both K and Bi atoms, i.e., KBi$_2$□ and K$_2$Bi□, the situation should be more complex and optimization of K–O and Bi–O distances in each case would need more than one set of positions for oxygen atoms.

Proton Magnetic Resonance Study

Method

In the rigid lattice regime, i.e., at low enough temperature to avoid motion narrowing of the resonance line, proton NMR is a useful tool to study the nature of the chemical species, OH, H$_2$O, H$_3$O$^+$, in the structure of compounds, because these different species give different dipolar spectra. The dipole–dipole interactions between nuclear spins are then responsible for the width and the shape of the spectrum. The elementary interaction between two spins r apart is proportional to r^{-3} and depends on the relative orientation of the direction joining the spins and the main magnetic field.

The nearest-neighbor protons must be considered all together, characterized by their number and geometrical arrangement, constituting a magnetic configuration of spins.

Interconfiguration magnetic interactions of spins are taken into account by convolution of the shape function of each used configuration by a Gaussian function of parameter β.

Writing $\beta = 1.5\ \mu X^{-3}$, where μ is the magnetic moment of the proton, X represents a distance close to the shortest distance between protons belonging to two different configurations (identical or not).

This convolution corresponds to an a priori isotropic distribution of spins outside a given configuration.

To summarize, the shape of a spectrum depends on the number and geometrical arrangement of the spins of the configuration and also on the parameter β of the Gaussian enlargement. The shape of the spectrum for one configuration of spins varies continuously with the influential parameters which are actually subject to strong constraints, for example, by the likelihood of the distances; it is not possible to modify only a part of the calculated spectrum without reconsidering the whole calculation. This remark will find an application in the results section where a defect in the simulation of the experimental spectrum is attributed to an actually marked nonisotropic distribution of spins outside a configuration.

The most appropriate manner to acquire a spectrum with a view toward interpretation is to record the centrosymmetrical derivative of the absorption spectrum. We will now call this derivative "the spectrum." The spectra of some simple configurations have been calculated, considering the isotropic orientation of the groups inside a powder sample.

Spectra of pairs of spins $\frac{1}{2}$ as for H_2O were first calculated and observed by Pake (*12*) (configuration D); the parameter r represents the distance between the spins; the typical spectrum exhibits two main peaks separated by 1 to 1.6×10^{-3} T and, depending on β, two secondary ones 2 to 3×10^{-3} T distant.

Spectra for three spins $\frac{1}{2}$ located at the corners of an equilateral triangle configuration of sidelength r, as for H_3O^+ ions, have been calculated by Andrew and Bersohn (*13*), Richards and Smith (*14*), and obtained by Richards and Smith (*15, 16*) and Kakiuchi *et al.* (*17*). They exhibit a narrow component flanked by two peaks distant by about 1.9×10^{-3} T.

The spectra of compounds with H_2O and OH groups can be simulated by adding two D configurations (model D + D) as proposed by Porte *et al.* (*18, 19*) as long as the direct interaction between a H from OH (H_{OH}) and a H from H_2O (H_{H_2O}) is small enough compared to the H–H interaction between the two protons, at a distance r of each other, of the H_2O molecule (H_{OH}–$H_{H_2O} > 1.6\,r$). In the other case the experimental spectra can be simulated using a three-spin isosceles triangle magnetic configuration (T) at the base corners of which are located the two H_{H_2O}; the H_{OH} is assumed to be located at the third corner (*20–28*); the base is of length r and the other sides are of length r'. H_2O or OH hydrogen atoms not belonging to triangle configuration are taken into account using a D configuration (model T + D).

Along the results section, we use ($T + D_1 + D_2$) models of which the nine independent parameters are: W_T and W_{D_1} weighting parameters ($W_T + W_{D_1} + W_{D_2} = 1$) r_T, r'_T, and X_T; r_{D_1} and X_{D_1}; r_{D_2} and X_{D_2}.

We also use a ($D_1 + D_2 + D_3$) model with eight independent parameters. For consistency we must have r and r' smaller than X.

The experimental spectrum has been recorded at liquid helium temperature using a bridge spectrometer based on rf hybrid junction; the resonance frequency was 16 MHz (*28*).

Results

A look at the experimental spectrum (Fig. 2) suggests the existence of two types of molecular water from the two well-separated double-extrema of the derivative absorption curve, at 1.2 and $1.4–1.6 \times 10^{-3}$ T peak to peak. The first maximum would be a priori attributed to molecular water with a normal r value (1.58–1.65 Å) that we shall call n-H_2O; the second extrema would cor-

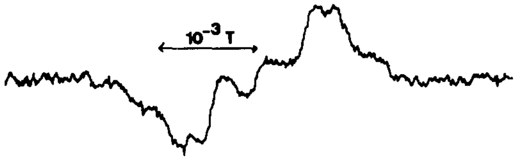

FIG. 2. Experimental ^{1}H rigid lattice wide-line NMR absorption-derivative spectrum of phase I.

respond to a very short r distance (1.40–1.44 Å) (s-H_2O). Moreover, a double-extrema of the curve at about 0.28 × 10^{-3} T suggests the presence of OH groups. The existence of H_3O^+ ions in the compound, which would be chemically improbable, has been completely ruled out by simulation trials as expected from Method.

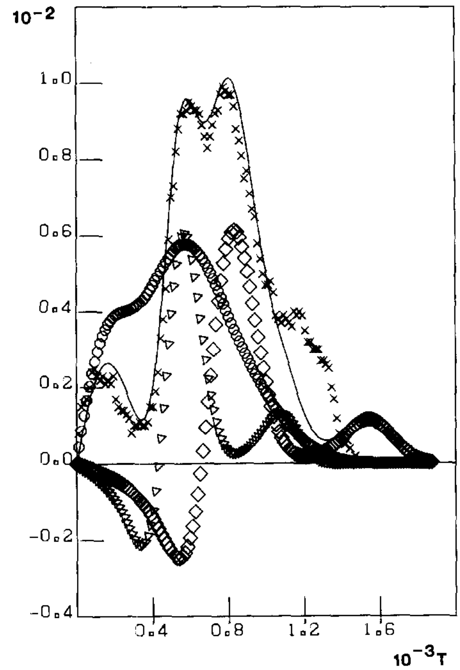

FIG. 3. Simulation of the experimental NMR spectrum of phase I using model T + D_1 + D_2 number 1: X, experimental spectrum; —, computed curve; ○, weighted computed contribution of configuration T; ◇, weighted computed contribution of configuration D_1; ▷, weighted computed contribution of configuration D_2.

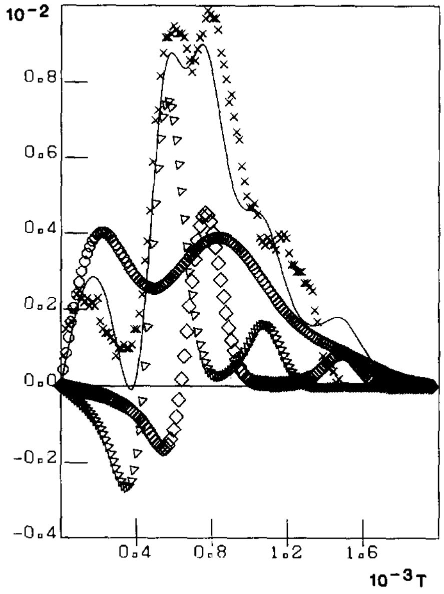

FIG. 4. Simulation of the experimental NMR spectrum of phase I using model T + D_1 + D_2 number 2: X, experimental spectrum; —, computed curve; ○, weighted computed contribution of configuration T; ◇, weighted computed contribution of configuration D_1; ▷, weighted computed contribution of configuration D_2.

Three different calculated spectra have been found to describe the experimental one (Figs. 3–5, half derivative of the absorption spectra). Getting three acceptable calculated spectra is not surprising due to the large number of independent parameters necessary for models using three magnetic configurations.

All the calculated spectra show a common defect, compared to the experimental spectrum: the outer maximum does not appear at a correct abscissa. The corresponding experimental maximum abscissa (1.17 × 10^{-3} T from the center) is too large to be ascribed to a main maximum, characteristic of a known magnetic configuration of spins. It is only a secondary maximum as happens on a well-resolved Pake spectrum (*12*) for a two-spin configuration. Then we propose to explain this defect by anisotropic interconfiguration interactions (see Method).

Two of the proposed models use a T configuration to include OH groups into the

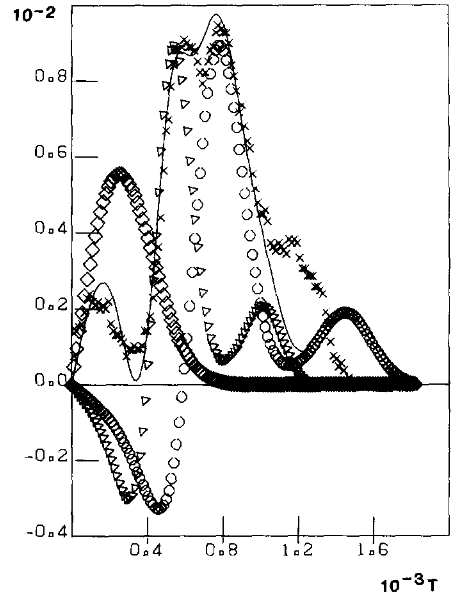

FIG. 5. Simulation of the experimental NMR spectrum of phase I using model $D_1 + D_2 + D_3$ number 3: X, experimental spectrum; —, computed curve; ○, weighted computed contribution of configuration D_1; ▷, weighted computed contribution of configuration D_2; ◇, weighted computed contribution of configuration D_3.

calculation so as to avoid possible quantitative errors as explained under Method. The first one associates a proton of an OH group to two protons of a *n*-H_2O molecule to form the T configuration (Table VI, Fig. 4). The water molecules *s*-H_2O are assumed to be independent of the OH groups and are described by a D_1 configuration. As *n*-water molecules are found more numerous than OH groups, those not described by the T configuration need a D_2 one. Values of the parameters for this ($T + D_1 + D_2$) model 1 are given in Table VI.

The second model using a T configuration of spins associates the proton of an OH group to the two protons of a *s*-water molecule; D_1 and D_2 configurations describe respectively excess *s*- and *n*-water molecules (Table VI, Fig. 4).

Last, the $D_1 + D_2 + D_3$ model is obtained by adding independent contributions of protons of *s*- and *n*-water molecules and of OH groups (Table VI, Fig. 5).

The quantitative distribution of protons among the different species found using each model and assuming 1.94 H atoms per phase I formula unit is reported in Table VII. With the previous assumption that all 48(f)-type sites of the formulation $A_2B_2X_6X'$ are occupied by O atoms and postulating that these O atoms are either bridged ones or OH group ones, the chemistry formula (I) with the proposed localization may be written as

$$\underset{16(d)}{(\mathrm{K}_{1.14}\mathrm{Bi}^{\mathrm{III}}_{0.37}\square_{0.49})}\underset{16(c)}{(\mathrm{Bi}^{\mathrm{III}}_{0.27}\mathrm{Bi}^{\mathrm{V}}_{1.73})}\underset{48(f)}{\mathrm{O}_{5.70}(\mathrm{OH})_{0.30}}(\mathrm{H_2O})_{0.82}.$$

Model 1 results in this actual formula and model 3 is also compatible, containing $O_{5.73}(OH)_{0.27}(H_2O)_{0.83}$ per formula group. However, model 2 leads to $O_{5.66}(OH)_{0.39}(H_2O)_{0.77}$ corresponding to 6.05 O atoms in 48(f) sites instead of 6.00, the discrepancy between

TABLE VI

MODELS AND PARAMETERS OF THE SIMULATED SPECTRA OF (K, Bi^{III}, Bi^{V}) PYROCHLORE (PHASE I)

Models		T configuration					D_1 configuration			D_2 configuration			D_3 configuration		
Number	Nature	*w*	*r* (Å)	*r'* (Å)	*r'*/*r*	*X* (Å)	*w*	*r* (Å)	*X* (Å)	*w*	*r* (Å)	*X* (Å)	*w*	*r* (Å)	*X* (Å)
1	$T + D_1 + D_2$	0.47(1)	1.65(2)	2.29(4)	1.39	2.25(5)	0.33(1)	1.40(2)	2.55(5)	0.20(1)	1.58(2)	2.80(5)			
2	$T + D_1 + D_2$	0.60(1)	1.44(2)	2.16(4)	1.5	2.15(5)	0.17(1)	1.42(2)	2.85(5)	0.23(1)	1.58(2)	2.85(5)			
3	$D_1 + D_2 + D_3$						0.55(1)	1.43(2)	2.48(5)	0.31(1)	1.61(2)	2.75(5)	0.14(1)	2.30(5)	2.30(5)

Note. Estimated deviations for the parameters are in parentheses.

TABLE VII

NUMBER OF DIFFERENT SPECIES CONTAINING THE PROTONS, PER FORMULA UNIT OF PHASE I (1.94 H), FROM NMR RESULTS

Model	OH groups	Total H_2O	Short r H_2O (s-H_2O)	Medium to large (n-H_2O)
1	0.30	0.82	0.32	0.50
2	0.39	0.77	0.55	0.22
3	0.27	0.83	0.53	0.30

these values being satisfactory. Then, each of the three models is chemically acceptable.

One must mention that the OH and H_2O relative number resulting from NMR models 1 and 3 are in good agreement with the results of the mass spectrometry analysis of the deuterated phase II with the previously proposed assumption that the mass value 18 in Table I represents only OD species (see Introduction).

Discussion

Our purpose is to discuss the compatibility of ND with NMR results considering successively the location of H_2O and OH groups. This leads us to retain only the NMR model 1. Then, some of the intergroup H–H distances resulting from the proposed location have to be compared with those of the NMR model. Finally, we discuss the limits of the NMR model.

NMR models 1, 2, and 3 allow us to find n-H_2O, the r values of which lie between 1.65 and 1.58 Å (Table VI). We will show that these values are consistent with ND results: 1.65 Å corresponds to H_2O molecules, the O atom of which is located in 32(e) sites as explained in the ND section. Water molecules with $r = 1.58$ Å would result, for example, from contraction of the OH distances from 0.98 to 0.95 Å at constant HOH angle value. The corresponding actual H position would then be less than 0.07 Å apart from the 96(g) site.

Considering the total number of n-H_2O found by NMR model 1 (0.50 per formula unit, Table VII) one sees that this number is in good agreement with the number of D_2O located in 32(e) sites by ND (0.48); it is nearly equal to its maximum value (0.49, 0.50), which is itself equal to the number of vacancies due to the impossibility of location of two O atoms in 32(e) sites each on one side of the vacancy (see Neutron Diffraction Study).

Such an agreement does not occur by comparison of NMR model 2 or 3 with ND results. For this reason, we shall no longer take these NMR models into account.

Although no D atoms have been located in the vicinity of the O 8(b) by ND, we assume that these O atoms belong to water molecules. Then, they would be some of the s-H_2O identified by NMR. The H atoms may be opposite to the cations, near the O 8(b)–O 48(f) directions, although the shortest distance 3.30 Å between these atoms precludes any hydrogen bond between them. However, if these water H atoms were exactly along the 8(b)–48(f) directions, they would be also in 48(f) sites and the H–O 8(b)–H angle would be 90°, which is unacceptable from the works of Ferraris *et al.* (*10, 11*). From these authors, the smallest possible HOH angle and OH distances are 101° and 0.89 Å, respectively. The shortest r value, 1.40 Å, found by NMR (model 1, Table VI) is compatible with an HOH angle of 101° for OH equal to 0.91 Å. Then each H atom would be 0.09 Å apart from a 48(f) site. Ferraris *et al.* (*10, 11*) mention that such water molecules with small HOH angle and short OH distances are coordinated to two monovalent ions (class 2A). In the present work the considered water molecules are coordinated to three cations (K or Bi). So it seems reasonable that they are s-H_2O.

OD group deuterium atoms do not appear in ND patterns, but, as said above, the NMR results give their number.

Recent ND and NMR studies of $HTaWO_6$ and $H_2Ta_2O_6$ pyrochlores (*29–31*) led to the OH group protons localization in 48(f) sites, these protons being bound in statistical distribution to some of the O 48(f) atoms of the BO_6 array. The same repartition appears reasonable in (K, Bi^{III}, Bi^{V}) pyrochlores, too.

Such a statistical repartition would set OH groups not far from H_2O 32(e) as well as from H_2O 8(b) molecules. Then, we have to calculate the expected value for the shortest distance between an OH proton and a H_2O one to compare with NMR results. Assuming for simplicity H atoms of H_2O 32(e) in 96(g) sites, this distance is 2.51 Å to compare with the r' value of the T configuration of model 1 (Table VI): 2.29 Å, which is about 0.2 Å too small. We discuss this result later. Similarly, the shortest distance between a H atom of an OH group and another of a H_2O 8(b) molecule assumed in a 48(f) site is 2.50 Å. Within model 1, which does not account directly for such a situation, this value is in good agreement with the X value of the D_1 configuration (2.55 Å).

A better simulation would be expected if H atoms of OH groups were associated in isosceles triangular magnetic configuration both with n-H_2O 32(e) and with s-H_2O proportionally to the number of water molecules of each type. But increasing the number of used configurations to simulate the experimental spectrum would become unrealistic. Moreover, one of the results of this study is that all the positions of s-H_2O have not been defined by ND; so several triangular configurations of spins would be necessary only for s-H_2O and the associated OH.

We must then mention that the NMR model 1 which gives the best results is the one which associates protons of OH group to the water molecule of the more numerous type n-H_2O.

The r' and X values for the T configuration are about the same (Table VI, model 1) because of the imposed requirement $r' < X$ (see Method under Proton Magnetic Resonance Study). Indeed the simulation of the experimental spectrum looks improved when the r' value becomes larger than the X value, all other parameters being constant. So the main reason for the smallness of r' is this restriction on the value of X, which is probably due to an enlargement of the T configuration spectrum to compensate some defects of the whole calculated spectrum.

Then, to sum up, each of the three NMR models lead to an acceptable chemical composition, but the above results show that the NMR model 1 is in better agreement with ND structure results than models 2 and 3; it gives:

- the actual number of OH and H_2O groups so that all the X_6-type sites of the theoretical $A_2B_2X_6X'$ formulation are occupied by O atoms or OH groups;
- the correct number of n-H_2O molecules (one per 16(d) vacancy);
- a s-H_2O molecules number compatible with the 8(b) localization of some of their O atoms.

Conclusion

The existence of large intramolecular H–H distance water molecule located by ND at 5 and 290 K has been quantitatively confirmed by 4 K rigid lattice proton NMR technique in (K, Bi^{III}, Bi^{V}) pyrochlores. Their O atoms are located in 32(e) sites and the H atoms near 96(g) positions. The protons of other water molecules, the O atom of which are in 8(b) and in other unknown higher multiplicity positions, have not been located by ND. The interpretation of the NMR spectrum indicates that these water molecules have short intramolecular HH distance. The NMR experiments give the actual formulation of the compound, including OH groups. However, by simulation of the NMR spectrum requiring addition of the contributions of three different magnetic configurations (using 8 to 9 independent parameters), three acceptable simulated spectra were obtained and the choice of the best solution necessitates using the diffraction results. The final formulation and the localization of the atoms of the compound used for the NMR study are proposed as

$$\underset{16(d)}{(\mathrm{K}_{1.14}\mathrm{Bi}^{\mathrm{III}}_{0.37}\square_{0.49})}\underset{16(c)}{(\mathrm{Bi}^{\mathrm{III}}_{0.27}\mathrm{Bi}^{\mathrm{V}}_{1.73})}\underset{48(f)}{\mathrm{O}_{5.70}(\mathrm{OH})_{0.30}}\;\underset{8(b)\;+\;.\;.32(e)}{(\mathrm{H_2O})_{0.32}(\mathrm{H_2O})_{0.50}}.$$

It should be mentioned that in a previous study of thermal decomposition of these phases (*32*), it was noticed that oxygen evolution occurred in two steps, the first one being associated with water emission. It was suggested that this step was an oxidation of OH groups by Bi(V) ions. About 7% of the total oxygen was then evolved. This is in fair agreement with the proposed formula since 8.5% of the total oxygen emission would result from the oxidation of OH groups.

Acknowledgment

We gratefully acknowledge Dr. Jean Pannetier (Institut Laue–Langevin, Grenoble) for the neutron diffraction experiments and for many helpful discussions.

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