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Neutron scattering study of the proton dynamics in \( \text{NH}_4^+ \) and \( \text{OH}_3^+ \) \( \beta \) alumina

J. C. Lassègues, M. Fouassier

Laboratoire de Spectroscopie Infrarouge, Associé au CNRS,
Université de Bordeaux I, 351, Cours de la Libération, 33405 Talence Cedex, France

N. Baffier, Ph. Colomban

Laboratoire de Chimie Appliquée de l’Etat Solide, L.A. 302,
E.N.S.C.P., 11, rue Pierre-et-Marie-Curie, 75231 Paris Cedex 05, France

and A. J. Dianoux

Institut Laue-Langevin, 156X, Centre de Tri, 38042 Grenoble Cedex, France

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Résumé. — Des expériences de diffusion quasiélastique des neutrons ont été effectuées à différentes résolutions sur des échantillons en poudre d’alumine \( \beta \) contenant soit des cations \( \text{NH}_4^+ \) soit des cations \( \text{OH}_3^+ \) plus ou moins hydratés.

On confirme l’existence de réorientations des ions \( \text{NH}_4^+ \) avec une vitesse de saut du proton de \( 1.4 \times 10^{12} \text{ s}^{-1} \) à 395 K. On montre en outre que seuls les cations occupant des sites Beevers-Ross (\( \sim 75 \% \)) sont concernés par ce mouvement rapide, en accord avec les prédictions d’études cristallographiques et spectroscopiques antérieures. Aucun mouvement de réorientation n’est détecté dans l’alumine \( \beta \) complètement hydratée. Par contre, un échantillon deshydraté, obtenu par chauffage du précédent au-dessus de 670 K, présente un élargissement quasiélastique qui peut être associé à des rotations par sauts des cations \( \text{OH}_3^+ \) autour de leur axe ternaire. La fréquence de ce mouvement est \( 4.1 \times 10^{11} \text{ s}^{-1} \) à 395 K et \( 4.9 \times 10^{11} \text{ s}^{-1} \) à 485 K. A ces deux températures le pourcentage de cations en rotation (44 \%) reste constant et correspond assez bien à la composition non stoechiométrique attendue : \( 1.33(\text{OH}_3^+)_2\text{O}, 11 \text{Al}_2\text{O}_3 \), pour laquelle un tiers des plans-maille sont occupés par deux cations liés par liaison hydrogène tandis que les deux autres plans sont occupés par un seul cation en interaction faible avec l’environnement.

Le même échantillon se ré-hydrate partiellement à température ambiante ; 24 \% seulement des cations sont en effet impliqués dans un mouvement de réorientation avec une fréquence de \( 2 \times 10^{11} \text{ s}^{-1} \).

Si l’on utilise une résolution de 1 \( \mu \text{eV} \), un autre type d’élargissement semble apparaître dans le cas du dérivé \( \text{NH}_4^+ \). Il pourrait être dû à une diffusion translationnelle par sauts et on peut alors déduire une constante d’auto-diffusion de l’ordre de \( 10^{-8} \text{ cm}^2 \text{ s}^{-1} \). Les mesures de conductivité antérieures rendent ce résultat vraisemblable.

Abstract. — Quasielastic neutron scattering experiments have been performed at different resolutions on powdered samples of \( \beta \) alumina containing either \( \text{NH}_4^+ \) or more or less hydrated \( \text{OH}_3^+ \) cations.

The existence of reorientations with a proton jump rate of \( 1.4 \times 10^{12} \text{ s}^{-1} \) at 395 K is confirmed for the ammonium derivative. Furthermore, it is shown that only the cations occupying Beevers-Ross sites (\( \sim 75 \% \)) are concerned by this fast motion, in agreement with the predictions of previous X-Ray and spectroscopic studies.

No reorientational motion is detected for the fully hydrated \( \beta \) alumina but a dehydrated sample obtained by heating the latter above 670 K presents a quasielastic broadening which can be associated with jump rotations of \( \text{OH}_3^+ \) cations around their threefold axis. The frequency of this motion is \( 4.1 \times 10^{11} \text{ s}^{-1} \) at 395 K and \( 4.9 \times 10^{11} \text{ s}^{-1} \) at 485 K. At these two temperatures the percentage of rotating protons, 44 \%, is constant and corresponds rather well to the expected non stoichiometric composition \( 1.33(\text{OH}_3^+)_2\text{O}, 11 \text{Al}_2\text{O}_3 \) in which one third of the unit cell planes are occupied by two hydrogen bonded cations in middle-oxygen sites, the other two planes being occupied by only one cation relatively free to rotate.

The same sample undergoes a partial rehydration at room temperature. Only 24 \% of the protons are then found to be involved in a reorientational motion with a frequency of \( 2 \times 10^{11} \text{ s}^{-1} \).

With a resolution of the order of 1 \( \mu \text{eV} \), another kind of broadening seems to occur in the case of the ammonium derivative. It could be due to translational jump diffusion characterized by a self-diffusion constant of the order of \( 10^{-8} \text{ cm}^2 \text{ s}^{-1} \). This result is consistent with the conductivity measurements.
1. Introduction. — Superionic conductors have been widely investigated during the last few years owing to their properties of solid electrolytes used in energy storage and conversion systems [1]. β and β" alumina are among the best protonic conductors of large chemical and thermal stability [2-5].

Although these protonic compounds have been studied by a wide range of experimental techniques — optical spectroscopy [6, 7], X-ray diffraction [7, 8], conductivity [4-7], NMR [9] — the mechanism of conduction is not clearly elucidated. Two kinds of explanation have been proposed: in NH₄⁺ and OH₃⁻ β alumina the cation could jump as a whole from site to site whereas in fully hydrated β alumina a proton transfer mechanism is invoked [6, 7].

Quasielastic neutron scattering (QNS) thanks to its ability to investigate dynamical processes both on a time scale of 10⁻⁸ to 10⁻¹³ s and for distances of the order of 0.5 to 10 Å, seems to be one of the best adapted methods of investigation of these mechanisms. Some QNS experiments have already been successfully performed in solid ionic conductor systems such as AgI [10] or La₂O₃ [11].

β alumina compounds containing hydrogenated cations such as NH₄⁺ or OH₃⁻ are in principle rather favourable since these scatterers are highly incoherent. In this case the quasielastic spectral density can be related simply to the self-part of the correlation function of the protons displacement.

The first experiment on NH₄⁺ β alumina with a resolution of 0.06 meV failed to show any quasielastic broadening due to the NH₄⁺ translational process. It was concluded that the self-diffusion coefficient was smaller than 10⁻⁶ cm² s⁻¹ [12]. On the other hand, the NH₄⁺ ions were shown to perform rather fast jumps reorientations (1.0 x 10¹² s⁻¹).

The possibility offered at the Laue-Langevin Institute of performing QNS experiments with resolutions as good as 0.001 meV prompted us to investigate at different temperatures NH₄⁺, OH₃⁻ and H(H₂O)ₙ⁺ β alumina compounds (referred to as βNH₄⁺, βOH₃⁻ and βH(H₂O)ₙ⁺ respectively). The aim of these experiments is to see how the rotational and eventually translational diffusive motions vary according to the nature and stoichiometry of the hydrogenated cations.

2. The structure and conductivity of β alumina. — The structure of β alumina is of hexagonal symmetry (space group P6₃/mmc). The unit cell consists of two spinel-like blocks separated by a mirror plane which contains an oxygen atom and the conducting cation which diffuses easily in the mirror plane. In the non-stoichiometric β alumina, the conducting cations are distributed simultaneously on several allowed crystallographic sites: Beevers-Ross (B-R) site (2d in Wyckoff position), anti Beevers-Ross (aB-R) site (2b position) and middle oxygen (m-O) site (6h position). NH₄⁺ and OH₃⁻ ions occupy mainly Beevers-Ross sites.

The electrical conduction is purely ionic and two-dimensional. Typical values are: 10⁻⁶ Ω⁻¹ cm⁻¹ for βH⁺(H₂O)ₙ⁺, 10⁻⁶ Ω⁻¹ cm⁻¹ for βNH₄⁺ and 10⁻¹¹ Ω⁻¹ cm⁻¹ for βOH₃⁻ at 470 K [6, 7]. These values can be compared with conductivity and self-diffusion measurements reported in figure 1 for other β alumina compounds.

![Fig. 1. — Relationship between conductivities and self-diffusion coefficients for various β alumina compounds. The values are taken from references [1-7] and [19] and are given for a temperature of 500 K. The numbers between parentheses are the activation energies in kcal. mole⁻¹.](image)

3. Sample preparation. — Fully hydrated H⁺(H₂O)ₙ⁺ β alumina was obtained by heating single crystals of non-stoichiometric Na⁺ β alumina of general formula 1.3 Na₂O, 11 Al₂O₃ with concentrated sulphuric acid [6]; the product was washed with boiling water and dried at 320 K. Further heating of the hydrated sample caused a continuous loss of water up to about 700 K where a de-hydrated sample stable up to 1 000 K is obtained. Infrared study shows that the de-hydrated sample contains OH⁻ ions as dominant species while the hydrated ones consist mainly of O₂H⁻ and O₃H⁻ entities.

NH₄⁺ β alumina has been prepared by ionic exchange of Na⁺ β alumina of general formula 1.3 Na₂O, 10.85 Al₂O₃, 0.3 MgO in molten ammonium nitrate at about 470 K. This compound is not hydrated [7]. Our material is completely exchanged, in contrast to Axe's compound of formula (NH₄)₂O₃, 11 Al₂O₃ in which the excess Na⁺ (~ 20 %) was not exchanged [12].

All these materials have been used as powders for the QNS experiments and contained between two circular aluminium plates. A heating wire surrounding...
the aluminium can allowed the samples to be heated up to about 500 K.

4. Experimental conditions for the QNS experiments.
   — The QNS experiments were performed at the Laue-
   Langevin Institute at Grenoble with the multi-chopper
time-of-flight IN5 and back-scattering IN10 spectro-
meters.

   On the latter, a mean resolution of 1 µeV and an
   energy transfer window of ± 12 µeV were used.
   Spectra were taken at seven different scattering angles
   corresponding to elastic momentum transfers \( \hbar |\mathbf{Q}| \)
of 0.130, 0.290, 0.57, 0.924, 1.454, 1.671 and 1.936 Å\(^{-1}\).
   The percentage of transmission of the samples was
   about 87 %.

   On IN5, two different incident wavelengths were
   used : \( \lambda_0 = 9.26 \) and 4.6 Å. They were respectively
   associated with momentum transfer ranges of 0.12
to 1.23 Å\(^{-1}\) and 0.24 to 2.48 Å\(^{-1}\). The mean experi-
mental resolutions were 0.033 meV with \( \lambda_0 = 9.26 \) Å
and 0.275 meV with \( \lambda_0 = 4.6 \) Å. The thickness of the
samples was calculated to give 8 to 10 % of scattering
i.e. to minimize multiple scattering contributions.

   On both spectrometers the scattering angles were
   chosen to avoid the Bragg peaks determined indepen-
dently by a powder diffraction experiment. The
spectra were treated by the standard programs of
correction for detector efficiency, sample container
scattering, absorption and self-shielding. In the case of
\( \beta \text{NH}_4 \), a blank of 1.3 Na\(_2\)O, 11 Al\(_2\)O\(_3\) was subtracted
as both compounds have nearly the same stoicho-
metry and structure whilst Na\(^+\) has a negligible scat-
ering cross-section compared to NH\(_4\)\(^+\). All the spectra
were normalized by comparison to the elastic scattering
from vanadium. Furthermore a careful analysis
of this vanadium elastic peak provides not only the
resolution (F.W.H.M.) but also the analytical curve
which gives the best fit to the experimental vanadium
profile. It is lorentzian in the case of the back-scatter-
ing experiment, very close to a triangle for the time-of-
flight experiment with \( \lambda_0 = 9.26 \) Å and gaussian with
\( \lambda_0 = 4.6 \) Å.

5. Results.
   — 5.1 Time-of-flight experiments with \( \lambda_0 = 4.6 \) Å.
   — Some typical examples of corrected spectra obtained for the
three kinds of \( \beta \) alu-
mina at the same temperature are reported in figure 2.

   The spectrum of \( \beta \text{NH}_4 \) presents very similar
features to those described by Axe \etal. \[12\] : an
elastic peak is superimposed on a broad quasi-
elastic component (Fig. 2a). The quasielastic width
(H.W.H.M. ∼ 1 meV) is independent of the momen-
tum transfer but not the relative fraction of elastic to
quasielastic scattered intensity.

   At the same temperature and angle of scattering, the
\( \beta \text{OH}_3 \) spectrum (Fig. 2b) differs by its less broad
and less intense quasielastic component. Further
experiments performed on \( \beta \text{OH}_3 \) clearly show an
increase of the quasielastic width and intensity at
higher temperature (485 K), and a decrease of these
quantities at lower temperature (291 K).

   Finally, in the case of \( \beta \text{H}_2\text{O} \)\(^+\), no quasielastic
component is detected as shown by a perfect agree-
ment between the experimental points and the gaussian
resolution function (Fig. 2c).

5.2 Time-of-flight experiments with \( \lambda_0 = 9.26 \) Å.
   — As the experimental resolution limits the observa-
tion time, it is important to see whether what we have considered as an elastic peak with a resolution of 0.275 meV remains strictly elastic when the resolution is improved by one order of magnitude. This kind of verification has already been performed by Axe et al. on their βNH₄⁺. So we have concentrated on the other compounds.

Two typical examples of spectra obtained for βOH₃⁻ and βH(H₂O)₆⁺ are presented in figure 3 at the higher scattering angle. Only the energy gain side of the quasielastic part is shown because the energy loss side is rather limited in energy transfer and has poorer statistics. One observes for the βOH₃⁻ spectrum (Fig. 3a) a QNS profile which has roughly the same width as in the previous experiment (Fig. 2b). Obviously the maximum of the elastic peak is now extremely high although its integrated intensity relative to the total scattered intensity is of the same order of magnitude as in the experiment with λ₀ = 4.6 Å.

The spectrum of βH(H₂O)₆⁺ (Fig. 3b) seems also to present a quasielastic component but it is even weaker than for βOH₃⁻. Its integrated intensity is less than 3% of the total scattered intensity. The weakness of this signal makes its origin questionable; it could be due to multiple scattering or simply to the departure from the triangular resolution function.

5.3 BACK-SCATTERING EXPERIMENTS. — A further improvement of the resolution is achieved with the IN10 back-scattering spectrometer. An example of a corrected spectrum is given for βNH₄⁺ in figure 5. The experimental points are compared to the lorentzian resolution profile given by the vanadium. In the present energy transfer range, the broad quasielastic profile observed in figure 2a appears only as a flat background.

When the momentum transfer increases, it seems that the experimental points present a small departure from the vanadium curve. The same kind of situation is found for βH(H₂O)₆⁺, although it is less pronounced. A more quantitative comparison of the vanadium and sample profiles is given in table I in terms of the F.W.H.H. of the best-fitted lorentzians. It is clear that we are just at the limit of detection of a new quasielastic contribution.

6. Discussion. — 6.1 TIME-OF-FLIGHT EXPERIMENTS. — The experiments illustrated in figure 2 can rather easily be interpreted by reference to the numerous examples of QNS studies already performed on disordered phases of ammonium or hydronium salts [13], and especially to the first analysis of βNH₄⁺ by Axe et al. [12]. These authors studied the quasielastic width and intensity in a momentum transfer range extending from 0.3 to 4.2 Å⁻¹ and inferred jump rotations of the NH₄⁺ ions either by 120° about their three-fold axes or by 180° about their two-fold axes. Both models can be written under the general expression:

Table I. — F.W.H.H. (µeV) of the best-fitted Lorentzians through the experimental profiles.

<table>
<thead>
<tr>
<th>Qₑ⁻¹ (Å⁻¹)</th>
<th>Vanadium</th>
<th>βNH₄⁺</th>
<th>βNH₄⁺</th>
<th>βH(H₂O)₆⁺</th>
<th>βH(H₂O)₆⁺</th>
<th>βH₂O⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.130</td>
<td>1.44</td>
<td>1.45</td>
<td></td>
<td>1.47</td>
<td>1.47</td>
<td>1.49</td>
</tr>
<tr>
<td>0.290</td>
<td>1.69</td>
<td>1.75</td>
<td></td>
<td>1.75</td>
<td>1.67</td>
<td>1.73</td>
</tr>
<tr>
<td>0.570</td>
<td>1.01</td>
<td>1.07</td>
<td></td>
<td>1.07</td>
<td>1.07</td>
<td>1.01</td>
</tr>
<tr>
<td>0.925</td>
<td>1.37</td>
<td>1.53</td>
<td></td>
<td>1.49</td>
<td>1.43</td>
<td>1.44</td>
</tr>
<tr>
<td>1.454</td>
<td>0.79</td>
<td>0.94</td>
<td></td>
<td>0.87</td>
<td>0.87</td>
<td>0.74</td>
</tr>
<tr>
<td>1.671</td>
<td>1.02</td>
<td>1.38</td>
<td></td>
<td>1.29</td>
<td>1.24</td>
<td>1.21</td>
</tr>
<tr>
<td>1.936</td>
<td>1.32</td>
<td>1.77</td>
<td></td>
<td>1.63</td>
<td>1.47</td>
<td>1.35</td>
</tr>
</tbody>
</table>
The near-neighbour H-H distance \( a \) is equal to 1.63 Å. 

\( a \) is the H.W.H.H. of the single lorentzian describing the quasielastic profile. It can easily be related to the mean residence time between two reorientations in either model [12].

The intensity of the elastic peak will be governed by the \( Q \) dependent factor \( \frac{1}{4} \left( 1 + \frac{3 \sin Qa}{Qa} \right) \), often referred to as the elastic incoherent structure factor (E.I.S.F.) [14]. This function fits satisfactorily Axe's results (Fig. 2 of Ref. [12]) but figure 4a shows that it is in disagreement with ours : at a momentum transfer \( Q \) of 2.4 Å\(^{-1}\), the experimental value is 0.35 ± 0.03 whereas the theoretical one is 0.13. This difference is well outside the uncertainties that one could arbitrarily associate to the theoretical value by considering slightly different models of reorientation for NH\(_4\)\(^+\).

As already pointed out, the main difference between Axe's experiment and the present one lies in the nature of the \( \beta \)NH\(_4\)\(^+\) compounds. Our compound has been completely exchanged; the dominant species are weakly hydrogen-bonded NH\(_4\)\(^+\) ions in B-R sites, but some other ions occupy either aB-R or m-O sites where they are less free to rotate because of stronger hydrogen bond interactions [7]. As a result, one may only see a fraction \( p \) of the NH\(_4\)\(^+\) ions rotating, the others, \( 1 - p \), appearing to be fixed on the time-scale defined by the experimental resolution [15]. By taking also into account the vibrational contribution to the elastic profile, introducing a Debye-Waller factor, one gets :

\[
S'(Q, \omega) = \exp \left( -\frac{\langle u^2 \rangle}{3} Q^2 \right) \times \\
\times \left[ (1 - p) \delta(\omega) + p S_{\text{ROT}}(Q, \omega) \right] \tag{2}
\]

where \( \langle u^2 \rangle \) is the mean square vibrational amplitude which can be evaluated independently from a plot of the logarithm of the total quasielastic integrated intensity versus \( Q^2 \). We found \( \langle u^2 \rangle = 0.24 \) Å\(^2\) for \( \beta \)NH\(_4\)\(^+\) at 395 K.

To compare the above model with the experimental results, one has then to fold (2) by the resolution function. Furthermore, a scaling factor \( A \) is needed to normalize the calculated intensity to the measured one and a constant base-line \( B \) has to be subtracted to simulate the flat inelastic background in the quasielastic region and eventually a non-negligible multiple scattering contribution.

Finally, for a given scattering angle \( \theta \) the variation of \( Q \) with the energy transfer \( h\omega = E - E_0 \) can be included by the relationship :

\[
Q = \left[ \frac{2m}{\hbar^2} (E_0 + E - 2(E_0 E)^{1/2} \cos \theta) \right]^{1/2} \tag{3}
\]

where \( m \) is the mass of the neutron, leading to the following expression :

\[
S_{\text{EXP}}(Q, \omega) = A \exp \left( -\frac{\langle u^2 \rangle}{3} Q^2 \right) \left\{ (1 - p) + \frac{p}{4} \left( 1 + \frac{3 \sin Qa}{Qa} \right) \right\} \cdot G(\omega) + \\
+ \left[ \frac{3}{4} p \left( 1 - \frac{\sin Qa}{Qa} \frac{1}{\pi \left( \omega^2 + \sigma^2 \right)} \right) \otimes T(\omega) \right\} + B \tag{4}
\]
\(G(\omega)\) is the gaussian elastic resolution function measured for each scattering angle with the vanadium standard. It determines the elastic component profile.

For \(\hbar\omega \neq 0\) the width of the resolution function changes continuously. This variation is known [15] and can be introduced in the folding of the quasi-elastic part. However, to make the calculations easier, the gaussian function can be replaced to a good approximation by a triangular function \(T(\omega)\) of same F.W.H.H. The symbol, \(\mathcal{G}\), in equation (4) stands for the convolution product of the quasielastic part by \(T(\omega)\).

So, all the functions or parameters of (4) are known except \(A\), \(B\), \(p\) and \(\sigma\). In fact \(p\) and \(\sigma\) are the only important quantities which have to be extracted from a fit of (4) to the experimental profiles since \(A\) is just a scaling factor and \(B\) the asymptote to the wings of the quasielastic profile.

The validity of the hypotheses made to interpret the QNS spectra is contained in the constancy of the \(\sigma\), \(p\) and \(A\) values obtained for each individual scattering angle (see also Fig. 4a). One finds

\[
\hbar\sigma = 1.20 \pm 0.15 \text{ meV}, \quad p = 0.75 \pm 0.04
\]

and \(A = \langle A \rangle \pm 5\%\). The \(\hbar\sigma\) value is in good agreement with that of \(1.20 \pm 0.12\) meV given by Axe et al. at 373 K. The corresponding proton jump rate \(\Gamma = 3/4 \sigma\) is \(1.36 \pm 0.14 \times 10^{12} \text{ s}^{-1}\).

On the other hand, the percentage of rotating protons, 75\%, confirms the evaluations made from X-Ray diffraction which gave 72\% of NH\(^+\) in B-R sites against 21\% and 7\% respectively in m-O and aB-R sites [7].

The same kind of analysis can be performed on the \(\beta\text{OH}_3^+\) compound if one assumes that the observed quasielastic profile is due to jump reorientations of the \(\text{OH}_3^+\) cations about their three-fold axis. The starting equation is now:

\[
S^{\text{ROT}}(Q, \omega) = \frac{1}{3} \left[ 1 + 2 \sin \frac{Qa}{Qa} \right] \delta(\omega) + 2 \left( 1 - \frac{\sin \frac{Qa}{Qa}}{\pi \omega^2 + \sigma^2} \right)
\]

where \(a\) is of the order of 1.66 Å [16].

Again one has to take into account the convolution by the experimental resolution, the fraction of rotating protons \(p\) and to introduce the measured value of the Debye-Waller factor \(\langle u^2 \rangle = 0.195\) Å\(^2\). This yields an equation similar to (4) which is fitted to the experimental profiles. One finds at 291 K,

\[
p = 0.26 \pm 0.01 \quad \text{and} \quad \hbar\sigma = 0.22 \pm 0.10 \text{ meV}.
\]

The proton jump rate \(\Gamma = 2/3 \sigma\) is \(2 \pm 1 \times 10^{11} \text{ s}^{-1}\).

When the temperature is increased, the reorientation becomes faster, as expected: \(\hbar\alpha = 0.41\pm 0.10\) meV at 395 K (\(\Gamma = 4 \pm 1 \times 10^{11} \text{ s}^{-1}\)) and 0.48 \pm 0.10 meV at 485 K (\(\Gamma = 4.9 \pm 1.0 \times 10^{11} \text{ s}^{-1}\)). However, at these two temperatures the fraction of rotating protons is found to be similar:

\[
p = 0.44 \pm 0.04.
\]

Figure 4b compares the experimental E.I.S.F. to the theoretical value corresponding to the limiting case where \(p = 1\).

Again these results can be interpreted by reference to the previous spectroscopic and crystallographic studies [6], in terms of more or less hydrogen bonded \(\text{OH}_3^+\) cations interacting either with the surrounding oxygens of \(\beta\) alumina or with near-neighbour water molecules.

It has been shown that \(\beta\text{OH}_3^+\) prepared by heating the fully hydrated \(\beta\text{OH}_3^+\) above 673 K contains \(\text{OH}_3^+\) cations occupying B-R sites as dominant species; m-O sites with single and double occupancy are less populated. Rather strong hydrogen bond interactions occur in the double occupancy case whereas the \(\text{OH}_3^+\) ions are nearly non hydrogen bonded in the B-R and m-O singly occupied sites.

The composition expected for \(\beta\text{OH}_3^+\) corresponds to the non stoichiometric formula \(1.33 (\text{OH}_3^+)\cdot\text{O}, 11 \text{ Al}_2\text{O}_3\) and implies statistically a double occupancy for one third of the unit cell planes. As a result two individual cations would be rather free to rotate whereas two others would form a hydrogen bonded dimer. The percentage of rotating protons found at 291 K (26\%) is much lower than expected (50\%), indicating a partial re-hydration of our powdered sample at room temperature.

However, it seems that by heating above 373 K one nearly reaches the expected composition and no more water is lost between 395 and 485 K. The experiment performed at higher resolution on this compound at 393 K (Fig. 3a) indicates the absence of a slower rotational process. Both, the E.I.S.F. and quasielastic width are of the same order of magnitude as obtained previously. This implies that the cation pairs are rather firmly trapped in the m-O sites.

For \(\beta\text{H}^+(\text{H}_2\text{O})_n\) (Fig. 3b) the reorientational motions, if any, must be slower than \(10^{10} \text{ s}^{-1}\) since a strictly elastic peak is observed with a resolution of 0.033 meV.

6.2 Back-scattering experiments. — The use of an even higher resolution confirms the absence of any significant broadening for \(\beta\text{OH}_3^+\) in the energy transfer window of \(\pm 12\) meV (Table I).

The situation is less clear for the \(\beta\text{NH}_4^+\) and \(\beta\text{H}^+(\text{H}_2\text{O})_n\). As illustrated in figure 5 and in Table I the experimental profiles differ slightly from that of vanadium. If this broadening has a rotational origin, it could concern species until now considered as fixed. In this case the scattering law would take the form of an elastic peak superimposed on a quasielastic profile. On the other hand, if the observed broadening is due to some kind of translational process occurring either
by \( \text{NH}_4^+ \) jump or by a proton transfer mechanism in the case of \( \beta \text{H}^+(\text{H}_2\text{O})_n \), one expects a lorentzian shaped broadening and no elastic component.

Unfortunately, the weakness of the observed effect prevents any reasonable analysis being performed to differentiate between the previous models; the experimental profile can be fitted by one lorentzian as well as by the sum of two lorentzians.

In the optimistic and simplifying assumption of translational diffusion, one can estimate an order of magnitude for the self-diffusion constant \( D_t \) of \( \text{NH}_4^+ \). A plot of \( \Delta E/2 \) versus \( Q^2 \) (Fig. 6) gives a slope of about

\[
9 \pm 3 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}
\]

at 351 K and

\[
7 \pm 3 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}
\]

at 293 K.

Obviously this is only a very rough estimation made on the basis of a \( \Delta E = 2 hQ^2 \) law which is known to hold only for a liquid at low \( Q \) values. To extract the geometrical path of the translational process, it would have been necessary to discuss the \( Q \) dependence of the quasielastic width and intensity in terms of adequate jump models \([17, 18]\). Another limiting case in the framework of these models is that derived in the case of a primitive cubic lattice and for \( Q^2 R^2 < 1 \) where \( R \) is the jump distance \([13]\). One gets

\[
D_t = \frac{R^2}{6 \tau}
\]

where \( \tau \) is the average time between successive jumps. If one considers from table I that the broadening \( \Delta E \) is roughly

\[
0.3 \pm 0.1 \mu\text{eV},
\]

\[
\tau \sim \frac{\hbar}{\Delta E} = 2.2 \pm 0.7 \times 10^{-9} \text{ s}.
\]

The more likely jumps probably occur between B-R/m-O or m-O/aB-R or m-O/m-O sites (\( R = 1.61 \) Å), one obtains respectively \( D_t = 8 \pm 3 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1} \) and

\[
D_t = 2 \pm 1 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}.
\]

All these estimations lead finally to an order of magnitude for \( D_t \) of \( 10^{-8} \text{ cm}^2 \text{ s}^{-1} \), which is reasonable according to the value of the conductivity

\[
(\sim 10^{-5} \Omega^{-1} \text{ cm}^{-1} \text{ at } 351 \text{ K})
\]

and to the relationship between conductivity and self-diffusion coefficient (Fig. 1).

On the other hand, the conductivities of \( \beta \text{OH}_2^+ \) and \( \beta \text{H}^+(\text{H}_2\text{O})_n \) \( 10^{-11} \) and \( 10^{-8} \Omega^{-1} \text{ cm}^{-1} \) at 470 K respectively, would yield \( D_t \) values far too small to give any detectable effect. Such is the case for \( \beta \text{OH}_2^+ \), but a weak broadening is present for \( \beta \text{H}^+(\text{H}_2\text{O})_n \) (Table I). This could be due to a departure from the Nernst-Einstein type of law illustrated on figure 1 or at least to a modification of the parameters entering in this law. Indeed, if the conduction process in \( \beta \text{H}^+(\text{H}_2\text{O})_n \) is associated with a proton transfer mechanism, important quantities such as the density of charge carriers or the proton jump distance are likely to be greatly changed. However, more precise results are needed to draw valuable conclusions on this compound.

7. Conclusion. — The reorientational dynamics of \( \text{NH}_4^+ \) or \( \text{OH}_2^+ \) substituted in \( \beta \) alumina can be rather easily analysed by QNS because these cations, when they are in single occupancy in B-R sites, undergo a rather fast motion whose geometrical pathway is restricted to very few and rather simple possibilities. As a result, interesting complementary information
can be extracted which is the fraction $p$ of rotating protons. This quantity can be usefully compared to the conclusions drawn from X-ray, optical spectroscopy, and NMR on the probability of presence and degree of interaction of the $\text{NH}_4^+$ and $\text{OH}_2^-$ cations in various cristallographic sites [6, 7].

Moreover, the activation energy for the reorientation of the $\text{OH}_2^-$ cations can be extracted from a plot of the logarithm of the quasielastic width versus $1/T$. This yields a value of about 1.3 kcal mole$^{-1}$. Axe et al. found 0.8 kcal mole$^{-1}$ for $\text{NH}_4^+$ [12]. Both values are low and of the same order of magnitude. They contrast with the high value of the conductivity activation energies (11 kcal mole$^{-1}$ for $\beta\text{NH}_4^+$). Also the conductivity of $\beta\text{OH}_2^-$ is smaller than that of $\beta\text{NH}_4^+$ by a factor 10$^3$ whereas the reorientational motions of the $\text{OH}_2^-$ and $\text{NH}_4^+$ ions lie on a similar time scale. One can conclude that the fast reorientational motions found in these compounds has very little influence on the conduction process.

The only indications on this latter process are provided by the high-resolution experiment. An order of magnitude of $10^{-8}$ cm$^2$ s$^{-1}$ is deduced for the self-diffusion coefficient of $\text{NH}_4^+$. As this cation has a similar size to that of $\text{Tl}^+$, one can see from figure 1 that this value is reasonable. As expected, no broadening is detected for $\beta\text{OH}_2^-$ but a small effect is found for $\beta\text{H}^+(\text{H}_2\text{O})_n$ which can just be considered as an encouraging preliminary confirmation for the hypothesis of proton transfer mechanism.

References