



Neutron scattering study of the proton dynamics in NH₄ and OH₃ β alumina

J.C. Lassègues, M. Fouassier, N. Baffier, Ph. Colombar, A.J. Dianoux

► To cite this version:

J.C. Lassègues, M. Fouassier, N. Baffier, Ph. Colombar, A.J. Dianoux. Neutron scattering study of the proton dynamics in NH₄ and OH₃ β alumina. Journal de Physique, 1980, 41 (3), pp.273-280. 10.1051/jphys:01980004103027300 . jpa-00209243

HAL Id: jpa-00209243

<https://hal.science/jpa-00209243>

Submitted on 4 Feb 2008

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Classification
 Physics Abstracts
 66.30H — 35.20Y

Neutron scattering study of the proton dynamics in NH_4^+ and OH_3^+ β 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

(Reçu le 7 août 1979, accepté le 19 novembre 1979)

Résumé. — Des expériences de diffusion quasiélastique des neutrons ont été effectuées à différentes résolutions sur des échantillons en poudre d'alumine β contenant soit des cations NH_4^+ soit des cations OH_3^+ plus ou moins hydratés.

On confirme l'existence de réorientations des ions 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 β 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 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 μeV , un autre type d'élargissement semble apparaître dans le cas du dérivé 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 β alumina containing either NH_4^+ or more or less hydrated 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 β 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 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 μeV , 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 NH_4^+ and OH_3^+ 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 La_2O_3 [11].

β alumina compounds containing hydrogenated cations such as NH_4^+ or OH_3^+ 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 NH_4^+ β alumina with a resolution of 0.06 meV failed to show any quasi-elastic broadening due to the NH_4^+ translational process. It was concluded that the self-diffusion coefficient was smaller than $10^{-6} \text{ cm}^2 \text{ s}^{-1}$ [12]. On the other hand, the NH_4^+ ions were shown to perform rather fast jump reorientations ($1.0 \times 10^{12} \text{ s}^{-1}$).

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 NH_4^+ , OH_3^+ and $\text{H}(\text{H}_2\text{O})_n^+$ β alumina compounds (referred to as βNH_4^+ , βOH_3^+ and $\beta\text{H}(\text{H}_2\text{O})_n^+$ 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 $\text{P6}_3/\text{mmc}$). 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 posi-

tion). NH_4^+ and OH_3^+ ions occupy mainly Beevers-Ross sites.

The electrical conduction is purely ionic and two-dimensional. Typical values are : $10^{-6} \Omega^{-1} \text{ cm}^{-1}$ for $\beta\text{H}^+(\text{H}_2\text{O})_n$, $10^{-4} \Omega^{-1} \text{ cm}^{-1}$ for βNH_4^+ and $10^{-11} \Omega^{-1} \text{ cm}^{-1}$ for βOH_3^+ 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.

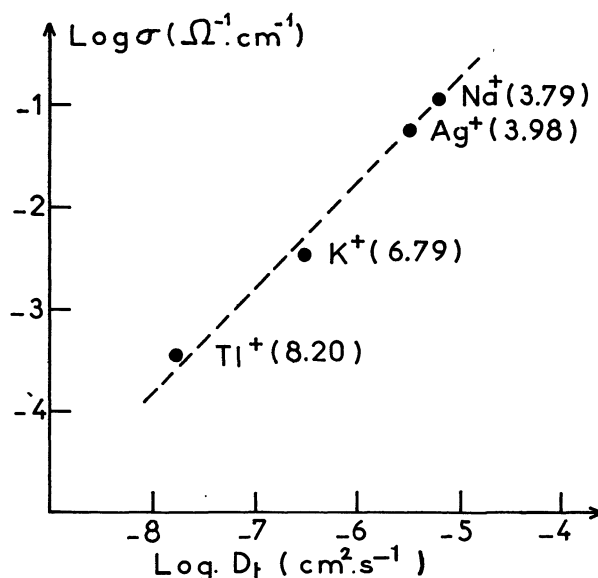


Fig. 1. — Relationship between conductivities and self-diffusion coefficients for various β alumina compounds. The values are taken from references [1-7] and [19] and are given for a temperature of 500 K. The numbers between parentheses are the activation energies in kcal. mole⁻¹.

3. Sample preparation. — Fully hydrated $\text{H}^+(\text{H}_2\text{O})_n$ β alumina was obtained by heating single crystals of non-stoichiometric Na^+ β alumina of general formula $1.3 \text{ Na}_2\text{O}$, $11 \text{ Al}_2\text{O}_3$ 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_3^+ ions as dominant species while the hydrated ones consist mainly of O_2H_5^+ and O_3H_7^+ entities.

NH_4^+ β alumina has been prepared by ionic exchange of Na^+ β alumina of general formula $1.3 \text{ Na}_2\text{O}$, $10.85 \text{ Al}_2\text{O}_3$, 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 $(\text{NH}_4)_2\text{O}$, $11 \text{ Al}_2\text{O}_3$ in which the excess Na^+ ($\sim 20\%$) 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 spectrometers.

On the latter, a mean resolution of 1 μeV and an energy transfer window of $\pm 12 \mu\text{eV}$ were used. Spectra were taken at seven different scattering angles corresponding to elastic momentum transfers $\hbar |\vec{Q}|$ of 0.130, 0.290, 0.57, 0.924, 1.454, 1.671 and 1.936 \AA^{-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 \AA . They were respectively associated with momentum transfer ranges of 0.12 to 1.23 \AA^{-1} and 0.24 to 2.48 \AA^{-1} . The mean experimental resolutions were 0.033 meV with $\lambda_0 = 9.26 \text{\AA}$ and 0.275 meV with $\lambda_0 = 4.6 \text{\AA}$. 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 independently 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 βNH_4^+ , a blank of 1.3 Na_2O , 11 Al_2O_3 was subtracted as both compounds have nearly the same stoichiometry and structure whilst Na^+ has a negligible scattering 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.H.) but also the analytical curve which gives the best fit to the experimental vanadium profile. It is lorentzian in the case of the back-scattering experiment, very close to a triangle for the time-of-flight experiment with $\lambda_0 = 9.26 \text{\AA}$ and gaussian with $\lambda_0 = 4.6 \text{\AA}$.

5. Results. — **5.1 TIME-OF-FLIGHT EXPERIMENTS WITH $\lambda_0 = 4.6 \text{\AA}$.** — Some typical examples of corrected spectra obtained for the three kinds of β alumina at the same temperature are reported in figure 2.

The spectrum of βNH_4^+ presents very similar features to those described by Axe *et al.* [12] : an elastic peak is superimposed on a broad quasi-elastic component (Fig. 2a). The quasielastic width (H.W.H.H. $\sim 1 \text{ meV}$) is independent of the momentum transfer but not the relative fraction of elastic to quasielastic scattered intensity.

At the same temperature and angle of scattering, the βOH_3^+ spectrum (Fig. 2b) differs by its less broad and less intense quasielastic component. Further experiments performed on βOH_3^+ clearly show an increase of the quasielastic width and intensity at

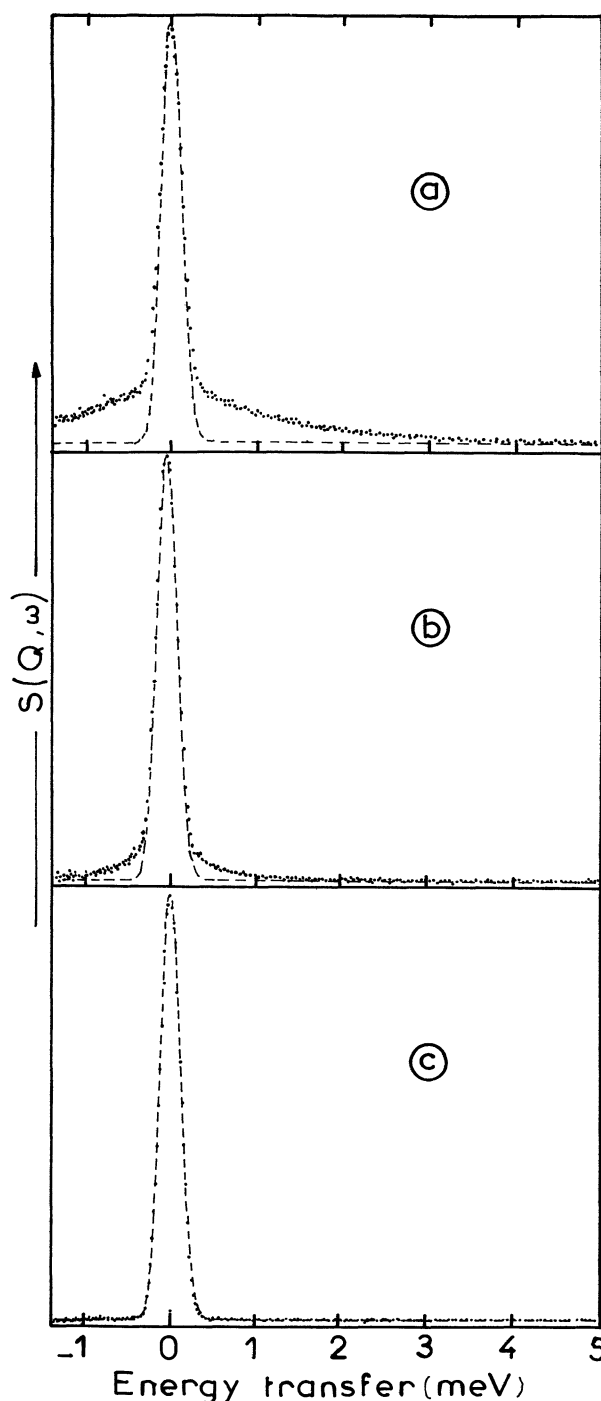


Fig. 2. — Quasielastic neutron scattering spectra taken with $\lambda_0 = 4.6 \text{\AA}$ at a scattering angle of 126° and a temperature of 395 K : a) βNH_4^+ , b) βOH_3^+ , c) $\beta\text{H}(\text{H}_2\text{O})_n^+$. In each case the experimental points are compared with the vanadium elastic peak (dotted line).

higher temperature (485 K), and a decrease of these quantities at lower temperature (291 K).

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

5.2 TIME-OF-FLIGHT EXPERIMENTS WITH $\lambda_0 = 9.26 \text{\AA}$.

— 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 βNH_4^+ . So we have concentrated on the other compounds.

Two typical examples of spectra obtained for βOH_3^+ and $\beta\text{H}(\text{H}_2\text{O})_n^+$ 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 βOH_3^+

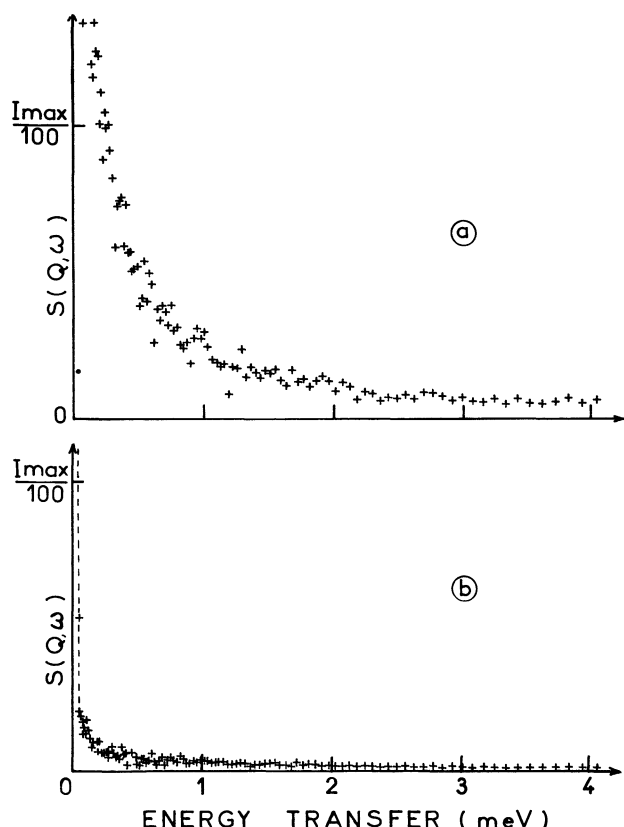


Fig. 3. — Quasielastic neutron scattering spectra taken with $\lambda_0 = 9.26 \text{ \AA}$ at a scattering angle of 130° . a) βOH_3^+ at 339 K, b) $\beta\text{H}^+(\text{H}_2\text{O})_n$ at 293 K. The ordinates are scaled by reference to the maximum of the elastic peak intensity, I_{max} . The resolution is 0.033 meV.

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 $\lambda_0 = 4.6 \text{ \AA}$.

The spectrum of $\beta\text{H}(\text{H}_2\text{O})_n^+$ (Fig. 3b) seems also to present a quasielastic component but it is even weaker than for βOH_3^+ . 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 βNH_4^+ 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 $\beta\text{H}(\text{H}_2\text{O})_n^+$, 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 βNH_4^+ 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 \AA^{-1} and inferred jump rotations of the NH_4^+ 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.

$Q_{\text{el}} (\text{\AA}^{-1})$	Vanadium 293 K	βNH_4^+ 351 K	βNH_4^+ 293 K	$\beta\text{H}(\text{H}_2\text{O})_n^+$ 399 K	$\beta\text{H}_3\text{O}^+$ 293 K
0.130	1.44	1.45	1.47	1.47	1.49
0.290	1.69	1.75	1.75	1.67	1.73
0.570	1.01	1.07	1.07	1.07	1.01
0.925	1.37	1.53	1.49	1.43	1.44
1.454	0.79	0.94	0.87	0.87	0.74
1.671	1.02	1.38	1.29	1.24	1.21
1.936	1.32	1.77	1.63	1.47	1.35

$$S^{\text{ROT}}(Q, \omega) = \frac{1}{4} \left[\left(1 + \frac{3 \sin Qa}{Qa} \right) \delta(\omega) + 3 \left(1 - \frac{\sin Qa}{Qa} \right) \frac{1}{\pi} \frac{\sigma}{\omega^2 + \sigma^2} \right] \quad (1)$$

The near-neighbour H-H distance a is equal to 1.63 Å. σ is the H.W.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 βNH_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 :

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

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 $\langle u^2 \rangle = 0.24 \text{ Å}^2$ for βNH_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

$$S^{\text{EXP}}(Q, \omega) = A \exp \left(- \frac{\langle u^2 \rangle}{3} Q^2 \right) \left\{ \left[(1 - p) + \frac{p}{4} \left(1 + \frac{3 \sin Qa}{Qa} \right) \right] \cdot G(\omega) + \left[\frac{3}{4} p \left(1 - \frac{\sin Qa}{Qa} \right) \frac{1}{\pi} \left(\frac{\sigma}{\omega^2 + \sigma^2} \right) \right] \otimes T(\omega) \right\} + B \quad (4)$$

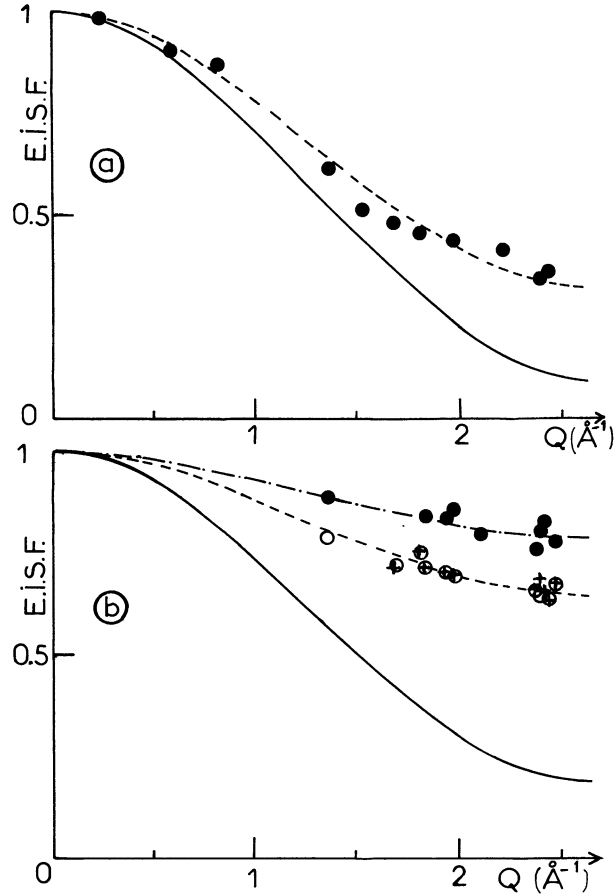


Fig. 4. — Comparison of the theoretical (full and broken lines) and experimental elastic incoherent structure factors (E.I.S.F.) for : a) βNH_4^+ at 395 K, b) βOH_3^+ at 291 K (black circles), 395 K (open circles) and 485 K (crosses). The theoretical full lines correspond to the functions : a) $\frac{1}{4} \left(1 + 3 \frac{\sin Qa}{Qa} \right)$ with $a = 1.63 \text{ Å}$. b) $\frac{1}{3} \left(1 + 2 \frac{\sin Qa}{Qa} \right)$ with $a = 1.66 \text{ Å}$. The theoretical broken lines correspond to the functions : a) $\frac{p}{4} \left(1 + 3 \frac{\sin Qa}{Qa} \right)$ with $p = 0.75$. b) $\frac{p}{3} \left(1 + 2 \frac{\sin Qa}{Qa} \right)$ with $p = 0.26$ which give the best fit to the experimental points.

to simulate the flat inelastic background in the quasi-elastic region and eventually a non-negligible multiple scattering contribution.

Finally, for a given scattering angle θ the variation of Q with the energy transfer $\hbar\omega = E - E_0$ can be included by the relationship :

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

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

$G(\omega)$ 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, \otimes , 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 σ . In fact p and σ 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 σ , 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 $1.20 \pm 0.12 \text{ meV}$ 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_4^+ 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 βOH_3^+ compound if one assumes that the observed quasielastic profile is due to jump reorientations of the OH_3^+ cations about their three-fold axis. The starting equation is now :

$$S^{\text{ROT}}(Q, \omega) = \frac{1}{3} \left[\left(1 + \frac{2 \sin Qa}{Qa} \right) \delta(\omega) + 2 \left(1 - \frac{\sin Qa}{Qa} \right) \frac{1}{\pi} \left(\frac{\sigma}{\omega^2 + \sigma^2} \right) \right] \quad (5)$$

where a is of the order of 1.66 \AA [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 $\langle u^2 \rangle = 0.195 \text{ \AA}^2$. 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 : $\hbar\sigma = 0.41 \pm 0.10 \text{ meV}$ at 395 K ($\Gamma = 4 \pm 1 \times 10^{11} \text{ s}^{-1}$) and $0.48 \pm 0.10 \text{ meV}$

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 cristallographic studies [6], in terms of more or less hydrogen bonded OH_3^+ cations interacting either with the surrounding oxygens of β alumina or with near-neighbour water molecules.

It has been shown that βOH_3^+ prepared by heating the fully hydrated βOH_3^+ above 673 K contains 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 OH_3^+ ions are nearly non hydrogen bonded in the B-R and m-O singly occupied sites.

The composition expected for βOH_3^+ corresponds to the non stoichiometric formula $1.33 (\text{OH}_3^+)_2\text{O}$, $11 \text{ Al}_2\text{O}_3$ 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} 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 βOH_3^+ in the energy transfer window of $\pm 12 \text{ \mu eV}$ (Table I).

The situation is less clear for the βNH_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

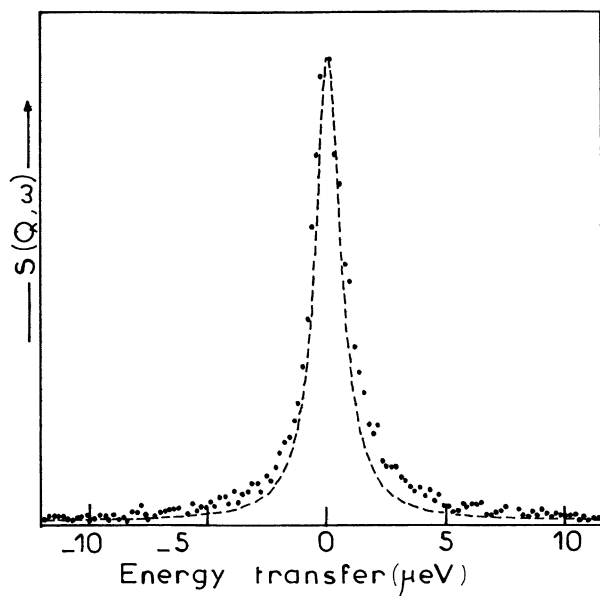


Fig. 5. — Comparison of the vanadium (dotted line) and βNH_4^+ spectra taken at room temperature and 351 K, respectively, at a scattering angle of 150° ($Q = 1.936 \text{ \AA}^{-1}$). The two peaks have been normalized to the same maximum intensity.

by 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 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

$$7 \pm 3 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1} \text{ at } 293 \text{ K}.$$

Obviously this is only a very rough estimation made on the basis of a $\Delta E = 2 \hbar D Q^2$ 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 $Q^2 R^2 \ll 1$ where R is the jump distance [13]. One gets $D_t = \frac{R^2}{6\tau}$ where τ is the average time between successive jumps. If one considers from table I that the broadening ΔE is roughly $0.3 \pm 0.1 \text{ \mu eV}$,

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

The more likely jumps probably occur between B-R/aB-R or m-O/m-O sites ($R = 3.2 \text{ \AA}$), or between

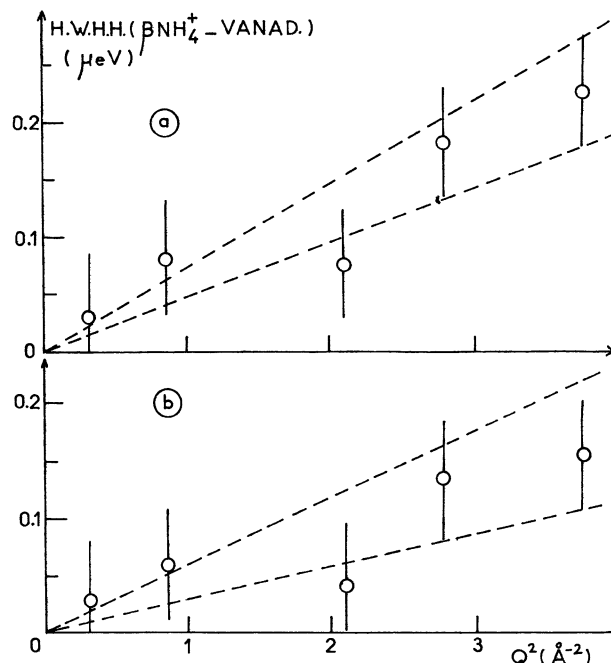


Fig. 6. — Comparison of the best-fitted Lorentzian profiles to the vanadium and βNH_4^+ peaks in terms of width difference versus Q^2 at 351 K (a) and 293 K (b).

B-R/m-O or m-O/aB-R sites ($R = 1.61 \text{ \AA}$). 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 βOH_3^+ and $\beta\text{H}^+(\text{H}_2\text{O})_n$, 10^{-11} and $10^{-6} \Omega^{-1} \text{ cm}^{-1}$ at 470 K respectively, would yield D_t values far too small to give any detectable effect. Such is the case for βOH_3^+ , 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 NH_4^+ or OH_3^+ substituted in β 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 NH_4^+ and OH_3^+ cations in various cristallographic sites [6, 7].

Moreover, the activation energy for the reorientation of the OH_3^+ cations can be extracted from a plot of the logarithm of the quasielastic width versus $1/T$. This yields a value of about $1.3 \text{ kcal mole}^{-1}$. Axe *et al.* found $0.8 \text{ kcal mole}^{-1}$ for 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 ($11 \text{ kcal mole}^{-1}$ for βNH_4^+). Also the conductivity of βOH_3^+ is smaller than that of

βNH_4^+ by a factor 10^7 whereas the reorientational motions of the OH_3^+ and 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 $10^{-8} \text{ cm}^2 \text{ s}^{-1}$ is deduced for the self-diffusion coefficient of NH_4^+ . As this cation has a similar size to that of Ti^+ , one can see from figure 1 that this value is reasonable. As expected, no broadening is detected for βOH_3^+ 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

- [1] HAGENMULLER, P. and VAN GOOL, W., *Solid Electrolytes* (Academic Press, New York) 1978.
- [2] COLOMBAN, P., KAHN, A., BOILOT, J. P. and LUCAZEAU, G., *Second International Meeting on Solid Electrolytes*, St. Andrews, Scotland 1978.
- [3] COLOMBAN, P., BOILOT, J. P., CHAGNON, P., GUILLOTEAU, G., *Bull. Soc. Fr. Ceram.* (1978) 119.
- [4] FARRINGTON, G. C., BRIANT, J. L. and STORY, H. S., *Second International Meeting on Solid Electrolytes*, St. Andrews, Scotland 1978.
- [5] FARRINGTON, G. C., BRIANT, J. L., BREITER, M. W. and ROTH, W. L., *J. Sol. State Chem.* **24** (1978) 311.
- [6] COLOMBAN, P., LUCAZEAU, G., MERCIER, R. and NOVAK, A., *J. Chem. Phys.* **67** (1977) 5244.
- [7] COLOMBAN, P., BOILOT, J. P., KAHN, A. and LUCAZEAU, G., *Nouv. J. Chim.* **2** (1978) 21.
- [8] ENGLAND, W. A., JACOBSON, A. J. and TOFIELD, B. C., *J. Chem. Soc. (Chem.-Comm.)* (1976) 895.
- [9] GOURIER, D. and SAPOVAL, B., *J. Phys. C* **12** (1979) 3587.
- [10] ECKOLD, G., FUNKE, K. and LECHNER, R. E., *J. Phys. Chem. Sol.* **37** (1976) 1097.
- [11] ALDEBERT, P., DIANOUX, A. J. and TRAVERSE, J. P., *J. Physique* **40** (1979) 1005.
- [12] AXE, J. D., CORLISS, L. M., HASTINGS, J. M., ROTH, W. L. and MULLER, O., *J. Phys. Chem. Sol.* **39** (1978) 155.
- [13] SPRINGER, T., *Dynamics of Solids and Liquids by neutron scattering* Eds. Lovesey, S. W. and Springer, T. (Springer-Verlag, Berlin, New York) 1977, p. 225.
- [14] VOLINO, F. and DIANOUX, A. J., *Organic liquids* Eds. Buckingham, A. D., Lippert, E. and Bratos, S. (John Wiley and Sons, New York) 1978, p. 17.
- [15] VOLINO, F., DIANOUX, A. J., LECHNER, R. E. and HERVET, H., *J. Physique Colloq.* **36** (1975) C1-84.
- [16] LUNDGREN, J. D. and WILLIAMS, J. M., *J. Chem. Phys.* **58** (1973) 788.
- [17] CHUDLEY, C. T. and ELIOTT, R. J., *Proc. Phys. Soc.* **77** (1961) 353.
- [18] GISSLER, W. and STUMP, N., *Physica* **65** (1973) 109.
- [19] KUMMER, J. T., *Prog. Solid State Chem.* **7** (1972) 141.