

## Pulsed NMR Study of $\text{NH}_4^+$ $\beta$ -Alumina

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Proton NMR relaxation times  $T_2$ ,  $T_1$ , and  $T_{1\rho}$  are reported for  $\text{NH}_4^+$   $\beta$ -alumina powder in the temperature range  $77 \text{ K} < T < 500 \text{ K}$  at 16 MHz. The measurements show that the  $\text{NH}_4^+$  ions both reorient and translate. The translational process can be characterized by the parameters  $E = 20 \text{ kJ mole}^{-1}$  and  $\tau_d^0 = 3 \times 10^{-11} \text{ sec}$ . Relaxation at high temperatures is dominated by dipolar coupling to paramagnetic impurities. Reasons for the different activation energies measured using NMR and other techniques for  $\beta$ -alumina compounds are discussed.

### Introduction

The name  $\beta$ -alumina is applied to a group of nonstoichiometric layered materials, the parent compound being  $\text{Na}^+$   $\beta$ -alumina. Isomorphs in which  $\text{Na}^+$  is replaced by other univalent cations (e.g.,  $\text{Li}^+$ ,  $\text{K}^+$ ,  $\text{Ag}^+$ ,  $\text{NH}_4^+$ ) are formed by ion exchange (1). Interest in these compounds is great because  $\text{Na}^+$   $\beta$ -alumina is used as the solid electrolyte in the sodium-sulfur battery.

The principal features of the structure of  $\beta$ -alumina are well known (2) and, for the  $\beta$  form, are illustrated in Fig. 1. The mobile alkali metal ions occupy several sites in the interlayer region, which is the conduction plane. Stoichiometric  $\beta$ -alumina may be formulated as  $\text{M}_2\text{O} \cdot 11\text{Al}_2\text{O}_3$ , but samples

are usually nonstoichiometric and this arises from extra  $\text{M}^+$  and  $\text{O}^{2-}$  within the conduction plane (see, e.g. (3)).

Studies of  $\text{NH}_4^+$   $\beta$ -alumina by electron and X-ray diffraction, and IR and Raman spectroscopy, have been reported by Colomban *et al.* (4). The cation distribution in  $\text{NH}_4^+$   $\beta$ -alumina is similar to that in  $\text{Ti}^+$   $\beta$ -alumina (4, 5), reflecting the similarity of the ionic radii ( $\text{Ti}^+ = 1.50 \text{ \AA}$ ,  $\text{NH}_4^+$  is effectively  $1.48 \text{ \AA}$ ). Hydrogen atoms were not located by X-ray diffraction, but IR vibrational bands characteristic of  $\text{NH}_4^+$  ion were seen.

Studies of ionic motion in  $\beta$ -alumina have mostly been concerned with  $\text{Na}^+$   $\beta$ -alumina, information having come from electrical, tracer diffusion, and NMR measurements.  $\text{NH}_4^+$   $\beta$ -alumina is particularly suitable for study by NMR because the large number of hydrogen atoms per carrier cation increases the sensitivity of the technique. In this work,

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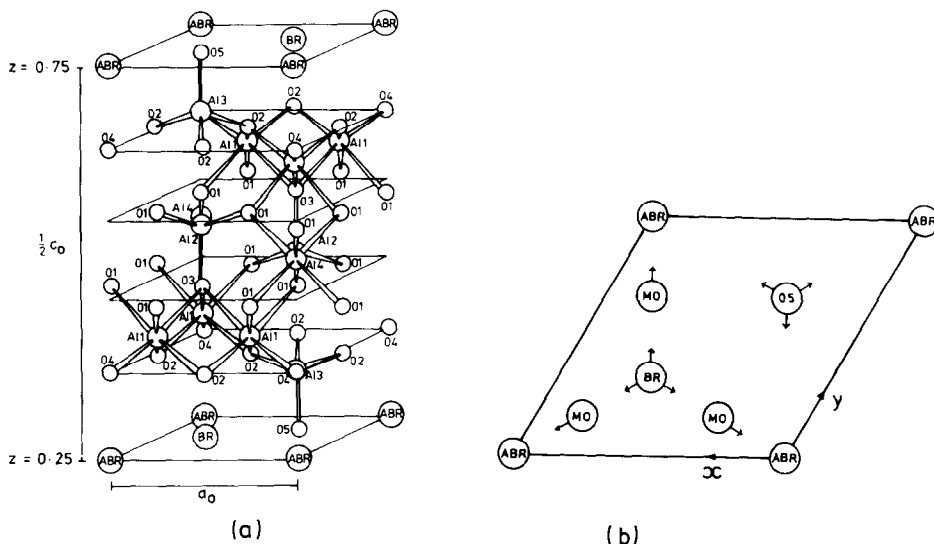


FIG. 1. A schematic diagram of the  $\beta$ -alumina structure. (a) One-half of a unit cell is shown. Four close-packed layers of oxygen atoms lie between mirror planes at  $z = 0.25$  and  $z = 0.75$ . The interior aluminum atoms, Al(4) and Al(2), have, respectively, octahedral and tetrahedral coordination. Octahedral Al(1) and tetrahedral Al(3) are coordinated to oxygen atoms which border the mirror plane, and the latter also to O(5) within the mirror plane. The Beevers-Ross (BR) and anti-Beevers-Ross (ABR) positions in the mirror plane are shown. (b) The conducting plane with mid-oxygen (MO) positions also shown. Small displacements from the ideal positions which are generally found are indicated. All metal ion sites are to a greater or lesser extent occupied in the various  $\beta$ -aluminas.

measurements of  $^1\text{H}$  relaxation times are used to study motions of  $\text{NH}_4^+$  ion in  $\beta$ -alumina.

Some information about ion transport in  $\text{NH}_4^+$   $\beta$ -alumina has come from electrical measurements. Radzilowski *et al.* (6) deduced an activation energy of  $46 \text{ kJ mole}^{-1}$  from dielectric loss measurements. Colomban *et al.* (4) give brief details of conductivity measurements which apparently give a similar activation energy, but their graphs appear somewhat idealized. The conductivity at 400 K appears to be about  $5 \times 10^{-5} \text{ ohm}^{-1} \text{ cm}^{-1}$ , and therefore  $\text{NH}_4^+$   $\beta$ -alumina is a poorer ionic conductor than  $\text{Na}^+$   $\beta$ -alumina (2).  $\text{NH}_4^+$  ion is believed to be the conducting species and it is difficult to envisage an alternative long-range charge transfer process.

Axe *et al.* (7) have studied apparently stoichiometric  $\text{NH}_4^+$   $\beta$ -alumina using

inelastic neutron scattering. They deduced that the correlation time for translational jumps in  $\text{NH}_4^+$   $\beta$ -alumina must be  $> 6 \times 10^{-11} \text{ sec}$  at temperatures  $< 473 \text{ K}$  and interpreted their results in terms of a rapid jump reorientation of  $\text{NH}_4^+$  ions with correlation time  $\tau_r \sim 10^{-11} \text{ sec}$  at room temperature. The results given suggest that  $E_r = 3.5 \pm 0.5 \text{ kJ mole}^{-1}$  and  $\tau_r^0 \approx 2 \times 10^{-13} \text{ sec}$  for the reorientation process.

### Material

$\text{NH}_4^+$   $\beta$ -alumina was prepared from commercial  $\text{Na}^+$   $\beta$ -alumina by ion exchange using a large excess ( $\sim 10^3$  times) of  $\text{NH}_4\text{NO}_3$  melt at  $190^\circ\text{C}$  for 24 hr, followed by decantation and washing with water.

The X-ray powder pattern (recorded using a Stoe Guinier camera,  $\text{CuK}\alpha$  radiation, and KCl as internal standard) for  $\text{NH}_4^+$   $\beta$ -alu-

mina corresponded to a pure, well-crystallized  $\beta$  phase uncontaminated with  $\beta''$  phase. The refined hexagonal lattice parameters were  $a = 5.613 \pm 0.001 \text{ \AA}$  and  $c = 22.845 \pm 0.004 \text{ \AA}$ . These values are, respectively, 0.02 and 0.04  $\text{\AA}$  larger than the lattice parameters given by Colomban *et al.* (4). The discrepancy may be due to lithia and magnesia additions in the starting material.

Thermal decomposition of two samples of  $\text{NH}_4^+$   $\beta$ -alumina (by heating to 1000°C on a vacuum microbalance) gave weight losses of 6.01 and 6.28%, corresponding to  $(\text{NH}_4)_2\text{O} \cdot x\text{Al}_2\text{O}_3$  with  $x = 7.79 \pm 0.18$ . The X-ray powder pattern of the product was that of  $\alpha$ -alumina. The absence of lines attributable to  $\text{Na}^+$   $\beta$ -alumina, which is stable at the decomposition temperature, indicates that complete exchange had been achieved in preparation.

Samples of  $\text{NH}_4^+$   $\beta$ -alumina were sealed under vacuum in glass ampoules (about  $1 \text{ cm}^3$  in volume).

### NMR Methods

The proton relaxation times  $T_2$ ,  $T_1$ , and  $T_{1\rho}$  were measured in the temperature range  $77 \text{ K} < T < 500 \text{ K}$  using a modified Polaron spin-echo spectrometer (operating at  $\omega_0/2\pi = 16 \text{ MHz}$ ) and a Varian Associates Fieldial magnet. The spectrometer is described in detail elsewhere (8). The signal-to-noise ratio was improved by routine use of a Datalab DL905 transient recorder interfaced with a Datalab DL102 averager. The spin-lattice relaxation time,  $T_1$ , was measured using a  $90^\circ - \tau - 90^\circ$  pulse sequence.  $T_{1\rho}$ , the spin-lattice relaxation time in the rotating frame, was measured using the method of Hartmann and Hahn (9). The  $B_1$  field strength, determined from the length of a  $90^\circ$  pulse, was 8 G. In the motionally narrowed region ( $T > 250 \text{ K}$ ),  $T_2$ , the spin-spin relaxation time, was measured from free-induction-decay (FID) measurements (if  $T_2 < 200 \text{ \mu sec}$ ) or by the Carr-Purcell-Mei-

boom-Gill (CPMG) pulse sequence (10). At lower temperatures (in the rigid lattice region),  $T_2$  was measured using the zero-time-resolution (ZTR) method (11),  $T_2$  being taken as the time for the solid echo to decay to  $1/e$  of its maximum height, as is done conventionally. The second moment,  $M_2$ , was determined using the ZTR technique from the curvature of the solid echo at its maximum (12).

### Results

Figure 2 shows the temperature dependence of the relaxation times  $T_2$ ,  $T_1$ , and  $T_{1\rho}$  for  $\text{NH}_4^+$   $\beta$ -alumina. Spin-spin relaxation in the line narrowing region ( $T > 250 \text{ K}$ ) was exponential. At temperatures above 250 K spin-lattice relaxation was also exponential, in both the laboratory and rotating frames, whereas at lower temperatures the relaxation was nonexponential. Data were analyzed using least-squares fitting procedures. In cases of nonexponential spin-lattice relaxation,  $T_1$  and  $T_{1\rho}$  were defined, respectively, as the times for  $(M(\infty) - M(\tau))$  and the initial magnetization after the spin-locking pulse to decrease to  $1/e$  of their initial values.

The low-temperature observed second moment,  $M_2$ , was  $1.2 \pm 0.1 \text{ G}^2$ .

### Discussion

The relaxation behavior of  $\text{NH}_4^+$   $\beta$ -alumina can be accounted for with two mechanisms: reorientation of the  $\text{NH}_4^+$  ion and translational diffusion of the  $\text{NH}_4^+$  ion. Reorientation modulates the (intra)molecular dipolar coupling within each  $\text{NH}_4^+$  ion. The second moment,  $M_2^{\text{molec}}$ , associated with the molecular coupling is about  $50 \text{ G}^2$  (13). Translation modulates the intermolecular dipolar coupling between  $^1\text{H}$  nuclei on different  $\text{NH}_4^+$  ions and also the paramagnetic dipolar coupling between  $^1\text{H}$  nuclei and paramagnetic (impurity) centers. The

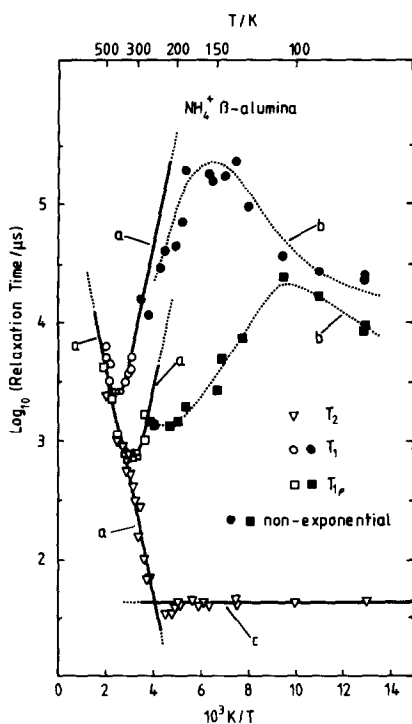


FIG. 2. Temperature dependence of relaxation times for  $\text{NH}_4^+$   $\beta$ -alumina. (a)  $T_1$ ,  $T_2$ ,  $T_{1\rho}$  are determined by hydrogen-paramagnetic dipolar coupling ( $C = 71 \text{ G}^2$ ) modulated by translation of  $\text{NH}_4^+$ . The solid curves are calculated using Eqs. (1) and (2) with  $\tau_d^0 = 2.8 \times 10^{-11} \text{ sec}$  and  $E_d = 19.6 \text{ kJ mole}^{-1}$ . (b) Relaxation is nonexponential, for both  $T_1$  and  $T_{1\rho}$ , and determined by modulation of the molecular hydrogen-hydrogen coupling ( $M_2^{\text{molec}} \approx 50 \text{ G}^2$ ) by reorientation of  $\text{NH}_4^+$ . (c)  $T_2$  is determined by "rigid" intermolecular dipolar interactions ( $M_2^{\text{inter}} = 1.2 \text{ G}^2$ ). The molecular dipolar interaction is wiped out by reorientation of  $\text{NH}_4^+$ . The solid line was calculated using the formula  $T_2 = (2\gamma^2 M_2^{\text{inter}} / \pi)^{-1/2}$  (i.e., assuming a Gaussian lineshape).

paramagnetic centers originate in the  $\alpha$ -alumina used to prepare  $\text{Na}^+$   $\beta$ -alumina, which commonly contains iron and other transition metals as impurities.  $M_2^{\text{inter}}$ , the intermolecular second moment, was calculated using van Vleck's formula to be  $1.06 \text{ G}^2$  and comprises a homonuclear part of  $0.29 \text{ G}^2$  and a heteronuclear part of  $0.76 \text{ G}^2$ . The calculation was done, using the atom coordinates of Colombari *et al.* (4), for

a stoichiometric  $\text{NH}_4^+$   $\beta$ -alumina with the  $\text{NH}_4^+$  ions in *BR* sites and the  $^1\text{H}$  nuclei in their average positions over random reorientations (i.e., at the centers of the ions).

### Reorientation

At low temperatures reorientation of  $\text{NH}_4^+$  ion about random axes is fast enough to wipe out the molecular coupling so that the temperature-independent  $T_2$  is determined by intermolecular coupling. The discrepancy between the measured second moment ( $1.2 \text{ G}^2$ ) in this region and the calculated  $M_2^{\text{inter}} = 1.06 \text{ G}^2$  may be explained by the excess of  $\text{NH}_4^+$  ions in the conduction plane over the ideal stoichiometry and could also be due to the assumption of random reorientation.

The reorientational parameters deduced from the work of Axe *et al.* (7) suggest that minima in  $T_1$  and  $T_{1\rho}$  would be observed at temperatures lower than those in this work and the low-temperature trends in  $T_1$  and  $T_{1\rho}$  are consistent with this. Relaxation can be nonexponential if a significant fraction of the relaxation arises from reorientation. We have considered a number of possible explanations for this behavior (see e.g., (14)):

- If correlated motion of more than two nuclei in the reorienting group ( $\text{NH}_4^+$ ) is important, the relaxation is the sum of a number of exponentials, none of which dominates the others (15).
- If quantum mechanical tunneling is important, nonexponential relaxation may occur (16, 17). The barrier to  $\text{NH}_4^+$  reorientation in  $\text{NH}_4^+$   $\beta$ -alumina is apparently low (7) and hence tunneling splittings of hindered rotational levels may be large. The temperatures in this work are, however, higher than those where tunneling is generally important.
- If ions reorient on different sites, their reorientation rates will differ and, if

they relax independently of each other, nonexponential relaxation will be observed.

The occupation of several sites and the presence of charge defects in  $\text{NH}_4^+$   $\beta$ -alumina imply a distribution in attempt frequencies and activation energies and explanation (c) is preferred.

### Translation

The relaxation behavior at temperatures above 450 K ( $T_1 \approx T_2 = T_{1\rho}$ ) clearly shows the effects of strong motional narrowing by translational diffusion. The  $T_1$  minimum at 2.6 msec is, however, too low to arise from the modulation of the intermolecular interaction. For  $M_2^{\text{inter}} = 1.2 \text{ G}^2$  one would expect, using Torrey's formulas, a  $T_1$  minimum at about 130 msec. The required strong interaction could be provided by paramagnetic impurities. We have used the model used by Resing and Thompson in their study of  $\text{SF}_6$  adsorbed on Faujasite (18) to analyze our data.

The model assumes a uniform paramagnetic jelly which fills all space beyond a certain distance of closest approach, approximated by  $p\lambda$ , from the center of the rapidly reorienting  $\text{NH}_4^+$  ions, which undergo jumps of length  $\lambda$  in random directions. The relaxation times for a nuclear spin  $I$  coupled to an electronic spin  $S$  are given by Eqs. (1) and (2) of Ref. (18) (with  $\omega_I \ll \omega_e$ )

$$1/T_1 = 0.75\gamma_I^2 C [J(\omega_I)], \quad (1)$$

$$1/T_2 = 0.125\gamma_I^2 C [3J(\omega_I) + 4J(0)], \quad (2)$$

where

$$J(\omega) = 2\tau_d / (1 + \omega^2\tau_d^2)$$

and

$$C = \frac{4}{15}\gamma_e^2 \hbar^2 S(S+1) [4\pi N / 3(p\lambda)^3], \quad (3)$$

where  $\tau_d$  is the time between jumps,  $p$  is crystal structure dependent, and  $N$  is the number of paramagnetic centers per unit volume. For measurements at 16 MHz the

model predicts a  $T_1$  minimum at

$$(T_1)_{\text{min}} = 186/C \text{ msec G}^2.$$

Using the data of Fig. 2 we deduce  $C = 71 \text{ G}^2$ , which on substitution into Eq. (3) gives

$$S(S+1)N/(p\lambda)^3 = 1.84 \times 10^{41} \text{ cm}^{-6}, \quad (4)$$

the sum of the contributions of all the paramagnetic centers present. Iron is the predominant paramagnetic impurity in the material used in this work. According to Akridge *et al.* (19), it occupies only the tetrahedral sites in  $\beta$ -alumina and, when prepared in an oxidizing atmosphere,  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  are present in roughly equal proportions. They further suggest that  $\text{Fe}^{2+}$  is most likely to be present only on the Al(2) site (5.7 Å from the ions in the mirror plane, see Fig. 1), while  $\text{Fe}^{3+}$  can be present on either Al(2) or Al(3) (3.6 Å from mobile ion sites).

We have assumed that the iron impurities are distributed as described in the previous paragraph and also that:

- (1)  $S(\text{Fe}^{2+}) = 1$  (its usual spin state in oxide crystal fields (20));
- (2)  $S(\text{Fe}^{3+}) = \frac{5}{2}$ ;
- (3)  $\text{Fe}^{3+}$  is equally distributed between Al(2) and Al(3) (the calculation is much more sensitive to the distance between nuclear and paramagnetic spins than to the number of the latter present).

A simple calculation assuming iron to be the only paramagnetic impurity present gave  $N(\text{Fe}) \sim 3 \times 10^{18} \text{ cm}^{-3}$ , where  $N(\text{Fe})$  is the total number of iron atoms per unit volume. This would correspond to 0.008% by weight of iron, which is in fact low for commercial-grade alumina. However, bearing in mind the limitations of the model, notably that

- (a) the "uniform paramagnetic jelly" is in fact two infinite hemispheres separated at the important region near the nuclear spins by an interlayer region containing no paramagnetic species, and

(b) the ions are not free to jump in any direction but rather in just three directions in the mirror plane, we regard the result as strong evidence for paramagnetic impurities determining the position of the  $T_1$  minimum.

The presence of paramagnetic impurities in  $\text{NH}_4^+$   $\beta$ -alumina was confirmed by recording ESR spectra. No signal could be seen at room temperature, but at 140 K a weak signal was observed which had features in common with the spectra obtained by Barklie and O'Donnell (21) for  $\text{Mn}^{2+}$  in  $\text{Na}^+$   $\beta$ -alumina.

The trace amount of iron present can dominate the relaxation only when the  $\text{NH}_4^+$  ions are diffusing fast enough to come close to an iron atom many times in a relaxation time. At low temperatures, as pointed out by Resing (22), diffusion is so slow that most  $\text{NH}_4^+$  ions are not able to couple with a paramagnetic center but reach a common nuclear spin temperature by intermolecular dipolar coupling, as we have previously assumed.

The time,  $\tau_d$ , between translational jumps in  $\text{NH}_4^+$   $\beta$ -alumina was evaluated over a range of temperature from  $T_2$  data in the line narrowing region and from  $T_1$  around the minimum using Eqs. (1) and (2). Figure 3 shows that the temperature dependence of  $\tau_d$  has an Arrhenius form with  $E_d = 19.6 \pm 0.8 \text{ kJ mole}^{-1}$  and  $\tau_d^0 = (2.8 \pm 0.2) \times 10^{-11} \text{ sec}$ .

### $T_{1\rho}$ Behavior

Below about 100 K reorientation is the dominant mechanism and  $T_{1\rho}$  decreases toward a probable low-temperature minimum. The contribution to relaxation from reorientation is found to be nonexponential.

Above about 100 K, modulation of the intermolecular coupling by translational diffusion becomes the dominant relaxation mechanism. Jones's treatment (23) of  $T_{1\rho}$  has been generalized in terms of Torrey's random walk diffusion theory (24, 25).

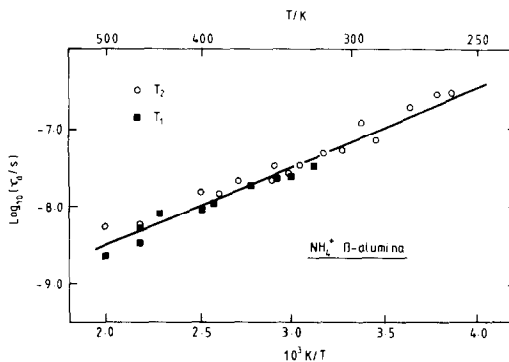


FIG. 3. Temperature dependence of translational jump correlation time for  $\text{NH}_4^+$   $\beta$ -alumina.  $\tau_d$  values are calculated using, in the line narrowing region ( $T > 250 \text{ K}$ ), Eqs. (1) and (2), which apply to relaxation brought about by translational modulation of the dipolar interaction between  $^1\text{H}$  nuclei and paramagnetic (impurity) centers. The temperature dependence has an Arrhenius form, the least-squares line shown giving  $E_d = 19.6 \pm 0.8 \text{ kJ mole}^{-1}$  and  $\tau_d^0 = (2.8 \pm 0.3) \times 10^{-11} \text{ sec}$ .

Assuming  $M_2^{\text{inter}} = 1.2 \text{ G}^2$  and with  $B_1 = 8 \text{ G}$ , a  $T_{1\rho}$  minimum of 1.1 msec at 198 K ( $10^3 \text{ K}/T = 5.06$ ) is predicted, which coincides with the position of the shoulder in the  $T_{1\rho}$  curve. Torrey's theory is valid in the weak collision limit, i.e.,  $B_L' \ll B_1$  where  $B_L'$  is the local intermolecular dipolar field in the rotating frame and is given by  $B_L' = (\frac{1}{3}M_2^{\text{inter}})^{1/2}$ . In this case,  $B_L' = 0.6 \text{ G}$  and therefore Torrey's formula is valid.

At temperatures above the shoulder,  $T_{1\rho}$  is dominated by modulation of the paramagnetic coupling by translational diffusion. The paramagnetic centers are fixed and the correlation time for the paramagnetic interaction is therefore twice that for the intermolecular interaction and consequently the minimum in  $T_{1\rho}$  due to paramagnetic coupling is shifted to a higher temperature. We have estimated the local paramagnetic field by assuming that  $B_L^{\text{para}} = (\frac{1}{3}C)^{1/2} = 4.9 \text{ G}$ . This shows that weak collision theories are invalid in this case and, as far as we are aware, no other satisfactory theory is available.

No further analysis of the data was attempted because of the nonexponentiality of some of the relaxation.

### Diffusion in $\text{NH}_4^+$ $\beta$ -Alumina

$\tau_d^0$  for translational jumps in  $\text{NH}_4^+$   $\beta$ -alumina is of the same order of magnitude as that measured by NMR for  $\text{Na}^+$  ion translation in  $\text{Na}^+$   $\beta$ -alumina (26, 27), which is evidence that a similar process occurs in both compounds. The diffusion mechanism involves jumps between *BR* and *ABR* sites via intervening *MO* sites (jump distance 1.61 Å). Assuming a random walk model, the two-dimensional self-diffusion coefficient,  $D$ , is related to  $\tau_d$  by

$$D = \lambda^2 / 4\tau_d,$$

where  $\lambda$  is the jump distance. Using the values of  $\tau_d^0$  and  $E_d$  found in this work,  $D$  at 400 K is  $6.5 \times 10^{-9} \text{ cm}^2 \text{ sec}^{-1}$ .  $D$  is related to the ionic conductivity,  $\sigma$ , by the Nernst-Einstein relationship

$$\sigma/D = Ne^2 / (kTH_R),$$

where  $N$  is the number of charge carriers per unit volume,  $e$  is the charge on a proton,  $k$  is the Boltzmann constant, and  $H_R$  is the Haven ratio for the process. Yao and Kummer (1) found  $H_R \approx \frac{1}{3}$  for  $\text{Na}^+$   $\beta$ -alumina and, assuming this to be true for  $\text{NH}_4^+$   $\beta$ -alumina also, the ionic conductivity at 400 K is estimated to be  $4 \times 10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}$ . This value can, in principle, be compared with the values determined by Colomban *et al.* (4) for their nonstoichiometric material. However, the data in Figs. 10 and 11 of their paper are not consistent, giving  $\sigma(400 \text{ K}) \approx 10^{-3}$  and  $5 \times 10^{-5} \text{ ohm}^{-1} \text{ cm}^{-1}$ , respectively. The value calculated here is within that range. The value of  $\tau_d$  at 473 K in  $\text{NH}_4^+$   $\beta$ -alumina is here calculated to be  $4 \times 10^{-9} \text{ sec}$ , which is consistent with the conclusion of Axe *et al.* (7) that  $\tau_d > 6 \times 10^{-11} \text{ sec}$  at temperatures

less than 473 K, albeit for apparently different (stoichiometric) material.

The activation energy for diffusion found in this work is  $20 \text{ kJ mole}^{-1}$ , which is lower than that measured by dielectric loss ( $46 \text{ kJ mole}^{-1}$ , Ref. (6)). The agreement between  $E_d$  for diffusion and dielectric loss was found also to be poor for  $\text{K}^+$  and  $\text{Rb}^+$   $\beta$ -alumina (6), but a satisfactory explanation was not found. Some NMR studies of  $\text{Na}^+$   $\beta$ -alumina (27–30) have suggested an  $E_d$  for  $\text{Na}^+$  translation of  $10 \text{ kJ mole}^{-1}$ , whereas tracer diffusion studies give  $E_d = 16 \text{ kJ mole}^{-1}$  (2). In this work three possible causes of the discrepancy must be considered:

- (1) dielectric loss and NMR are measuring different motions;
- (2) the materials are different;
- (3) there is a wide distribution of correlation times.

Explanation (1) is regarded as unlikely, but (2) and (3) are worthy of further consideration.

The polycrystalline material used in this work contained phase-stabilizing dopants and had the formula  $1.4(\text{NH}_4)_2\text{O} \cdot 11\text{Al}_2\text{O}_3$ , approximately the same composition as the starting sodium material. However, the polycrystalline material prepared by Axe *et al.* (7), of the same initial composition as here, was apparently stoichiometric in  $\text{NH}_4^+$  content after exchange, i.e., had the formula  $(\text{NH}_4)_2\text{O} \cdot 11\text{Al}_2\text{O}_3$ . Colomban *et al.* (4) prepared from single crystals of initial formula  $1.3\text{Na}_2\text{O} \cdot 11\text{Al}_2\text{O}_3$  an  $\text{NH}_4^+$  compound of the same stoichiometry. Radzilowski *et al.* (6) used Monofrax crystals and the same exchange procedure as all subsequent workers and it is presumed that the exchanged material had the same stoichiometry as the starting material. It is not clear why some materials exchange with a retention of (non)stoichiometry while others exchange to the stoichiometric composition. That this is indeed possible, however, is demonstrated by Colomban

*et al.* (4), who, by various heat treatments, appear to produce both stoichiometric and nonstoichiometric  $\text{NH}_4^+$  doped compounds with various activation energies and conductivities: their initially exchanged material has an activation energy close to that reported here according to their Fig. 11 (about  $22 \text{ kJ mole}^{-1}$ ), but not according to Fig. 12 (about  $32 \text{ kJ mole}^{-1}$ ). As one would intuitively expect, and as has been shown for  $\text{Na}^+$   $\beta$ -alumina (31), stoichiometric material appears to have a lower preexponential factor and higher activation energy than the nonstoichiometric compound. Clearly the apparent confusion illustrated above in both material and data can only be resolved by further definitive material characterization and measurement.

The occupation of several sites and the presence of charge defects in  $\beta$ -aluminas imply a distribution of jump frequencies ( $1/\tau_d$ ) and activation barrier heights, and experimental evidence for this distribution has come from NMR (25, 26) and conductivity dispersion (32) measurements. In materials where such a distribution occurs, simple theories of the type used in this work have generally been found unable to correlate satisfactorily activation energies from NMR and dielectric measurements (33). Walstedt *et al.* (26) interpreted  $T_1$  data for various  $\text{Na}^+$   $\beta$ -aluminas in terms of distributions in barrier heights. They also point out that as temperature is lowered an increasing number of mobile ions become virtually immobilized by high energy barriers and consequently a distribution of  $T_1$  values (rather than an average) occurs leading to nonexponential relaxation, which cannot be simply interpreted. The nonexponential relaxation in this work can therefore be attributed to both reorientation and to partial freezing out of translational motions. In this work there is insufficient exponential spin-lattice relaxation data to carry this analysis further.

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