

## Ammonium-ion reorientations in $(\text{NH}_4)_2\text{SbF}_5$

R. Mukhopadhyay and P. S. Goyal

*Solid State Physics Division, Bhabha Atomic Research Centre, Trombay, Bombay 400 085, India*

C. J. Carlile

*ISIS Pulsed Neutron Facility, Rutherford Appleton Laboratory, Didcot, Chilton, OXON, OX11 0QX, United Kingdom*

(Received 9 November 1992)

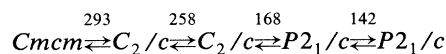
The reorientation of ammonium ions in ammonium pentafluoro antimonate,  $(\text{NH}_4)_2\text{SbF}_5$ , is studied with quasielastic neutron scattering in the temperature range from 40 to 300 K.  $(\text{NH}_4)_2\text{SbF}_5$  has two crystallographically inequivalent  $\text{NH}_4^+$  ions in the unit cell, the hydrogen-bonded (type-I) and the non-hydrogen-bonded (type-II) ions. Usually it is difficult to obtain reorientation times associated with the two reorienting units in a quasielastic-scattering experiment. Two different energy resolutions and the variation of the ratio of elastic to quasielastic intensities with wave-vector transfer have been exploited to obtain the reorientation times  $\tau^{\text{I}}$  and  $\tau^{\text{II}}$  for the two ions in the above salt at different temperatures. It is seen that the hydrogen-bonded  $\text{NH}_4^+$  ion rotates more slowly than the non-hydrogen-bonded ion. Information about the geometry of reorientation of the  $\text{NH}_4^+$  ions has also been extracted. In particular, it has been shown that there is a change in geometry of reorientation of  $\text{NH}_4^+$  (II) when the compound undergoes a phase transition at 168 K. The activation energies have been obtained from the observed variations of  $\tau^{\text{I}}$  and  $\tau^{\text{II}}$  with temperature.

### I. INTRODUCTION

The study of reorientational motion of molecules and molecular groups in solids is a subject of immense interest both theoretically and experimentally.<sup>1,2</sup> Several experimental techniques such as NMR,<sup>3</sup> Raman scattering,<sup>4</sup> and neutron scattering<sup>5</sup> have been used for these studies. The reorientations in the case of hydrogenous molecules or molecular groups are quite fast because of the low moment of inertia of these molecules and can thereby be studied using a quasielastic-neutron-scattering (QENS) technique. This technique has been extensively used for studying reorientational motions of  $\text{CH}_4$ ,  $\text{CH}_3$ , and  $\text{NH}_4^+$  in solids.<sup>6</sup> In most of the systems studied so far, there is only one type of molecular group that undergoes reorientations. The data analysis procedures for such situations are simple and are now well established.<sup>6</sup> In the case of solids where there are two different types of molecular groups [as is the case of  $(\text{NH}_4)_2\text{SbF}_5$ , where the unit cell contains two crystallographically inequivalent  $\text{NH}_4^+$  ions], it is, however, not straightforward to separate out the contribution from the two reorienting units to the quasielastic scattering. In an earlier work on  $(\text{NH}_4)_2\text{SO}_4$ , Goyal and Dasannacharya<sup>7</sup> have shown that in suitable cases it is possible to obtain the relative values of the different reorientation times  $\tau^{\text{I}}$  and  $\tau^{\text{II}}$  for the two  $\text{NH}_4^+$  ions by examining the ratio of elastic to quasielastic intensities as a function of wave-vector transfer,  $Q$ . The present paper deals with study of  $\tau^{\text{I}}$  and  $\tau^{\text{II}}$  for the  $\text{NH}_4^+$  ions in  $(\text{NH}_4)_2\text{SbF}_5$ . In order to separate out the contribution from two  $\text{NH}_4^+$  ions in quasielastic-scattering experiments, we not only exploit the ratio of elastic to quasielastic intensities but also use two different energy resolutions for the experiments.

Ammonium pentafluoro antimonate,  $(\text{NH}_4)_2\text{SbF}_5$ , belongs to a family of  $M_2\text{SbF}_5$ - ( $M = \text{Na}, \text{K}, \text{NH}_4, \text{Rb}, \text{Cs}$ ) type compounds. It shows phase transformations at 292, 257, 168, and 142 K as observed by heat-capacity measurements and many other techniques.<sup>8,9</sup> The transitions are believed to be connected with the motions of the  $\text{NH}_4^+$  and  $\text{SbF}_5^-$  groups. The transition at 168 K, in particular, is believed to be connected with the reorientational motion of one type of ammonium group.<sup>8</sup> The other important transition is the one at 257 K where it undergoes a transition to a two-dimensional superionic conductor which is related to the dynamics of the  $\text{SbF}_5$  group.

At room temperature,  $(\text{NH}_4)_2\text{SbF}_5$  has orthorhombic structure (space group  $Cmcm$ ,  $Z=4$ ) with four formula units per cell. The x-ray studies<sup>10,11</sup> suggest that there exist two inequivalent ammonium ions (types I and II) in the unit cell. The first crystallographic type  $\text{NH}_4^+$  (I) positioned at the relatively short distance of 2.75 Å from the fluorine atom involving the hydrogen bond and the other type  $\text{NH}_4^+$  (II) is located at more than 3 Å. A single-crystal x-ray-diffraction study at low temperatures<sup>12</sup> gives



as the probable transition scheme. All the transitions are of the second kind. It also showed that there exist two inequivalent ammonium ions in the unit cell down to 123 K. It is of interest to know whether the reorientational dynamics of the two  $\text{NH}_4^+$  ions are similar. In particular, one would like to know the changes in dynamics of  $\text{NH}_4^+$  ions as the system goes through the phase transition at 168 K. The NMR and NQR (Refs. 8 and 13) studies suggested that  $\text{NH}_4^+$  ions experience a low rotational barrier

and are quite free to rotate. The  $^1\text{H}$  spin-lattice relaxation study<sup>14,15</sup> showed a nonexponential recovery of magnetization above 200 K suggesting crossrelaxation between  $^1\text{H}$  and  $^{19}\text{F}$ . Further, Kobayashi *et al.*<sup>15</sup> found the minimum value (4.7 msec) of  $T_1$  to be twice as long as that ( $\approx 2$  msec) obtained from simple Bloembergen-Percell-Pound (BPP) theory. From this, they concluded that the two  $\text{NH}_4^+$  ions rotate at different rates. One type of  $\text{NH}_4^+$  ion shows minima in  $T_1$  at 120 K and the other below 80 K.

In an earlier work, we reported the results of QENS measurements at room temperature.<sup>16</sup> The resolution ( $\Delta E \approx 200 \mu\text{eV}$ ) used in that experiment was not very good. This paper reports a detailed neutron-quasielastic-scattering study of the reorientational motions of  $\text{NH}_4^+$  ions in  $(\text{NH}_4)_2\text{SbF}_5$  at several temperatures in the temperature range 40–300 K. Measurements have been made using two different resolutions ( $\Delta E = 15$  and  $50 \mu\text{eV}$ ). The details of these experiments are given in Sec. II. Theoretical aspects are given in Sec. III. The analysis of the data is given in Sec. IV and the results and discussion are in Sec. V. Section VI gives the summary. A preliminary version of the work has been reported earlier.<sup>17</sup>

## II. EXPERIMENTAL DETAILS

Ammonium pentafluoro antimonate was prepared and characterized using the procedure as described in the earlier paper.<sup>16</sup> The powder samples were packed in a standard flat aluminum sample holder and placed in a variable temperature helium cryostat. The thickness of the sample used was 1 mm (transmission  $\approx 77\%$ ). The neutron incoherent quasielastic-scattering experiments were carried out using the high-resolution spectrometer IRIS at the ISIS pulsed neutron facility at Rutherford Appleton Laboratory, England.<sup>18</sup> IRIS is a time-of-flight backscattering spectrometer with an array of pyrolytic graphite and mica analyzers. The different reflections ( $hkl$ ) of the analyzers offer different instrumental resolution. In the present experiment, (002) and (004) reflections of the graphite analyzer were used. The (002) reflection provides an energy resolution  $\Delta E$  of  $15 \mu\text{eV}$  at a fixed final energy of 1.82 meV with a  $Q$  range  $0.3$ – $1.85 \text{ \AA}^{-1}$  and the (004) reflection provides  $\Delta E$  of  $50 \mu\text{eV}$  at a fixed final energy of 7.3 meV with a  $Q$  range  $0.6$ – $3.7 \text{ \AA}^{-1}$ . The availability of two different resolutions in the same instrument proved to be very useful in unraveling details of the  $\text{NH}_4^+$  ion reorientations as described in later sections. The quasielastic spectra were measured at 40, 100, 160, 200, 260, and 300 K using both (002) and (004) reflections of the graphite analyzer in the  $Q$  ranges  $0.89$ – $1.83$  and  $1.75$ – $3.66 \text{ \AA}^{-1}$ , respectively. Typical spectra obtained from the two different settings are shown in Figs. 1–3. The raw data in time of flight are normalized with respect to monitor counts and converted to  $S(Q, \epsilon)$  using standard programs. Multiple-scattering corrections have not been carried out. Figure 1 shows the spectra obtained at 100 and 160 K with the PG(002) analyzer at  $Q = 1.42 \text{ \AA}^{-1}$ . A broad quasielastic com-

ponent below the elastic peak is clearly seen. The measurement with the PG(004) analyzer did not show any broadening at these temperatures. The spectra at 200 and 260 K are shown in Fig. 2. Data with PG(002) at  $Q = 1.42 \text{ \AA}^{-1}$  are shown in Fig. 2(a) and that with PG(004) at  $Q = 3.13 \text{ \AA}^{-1}$  are shown in Fig. 2(b). At these temperatures, quasielastic broadening is seen both with the PG(002) and PG(004) analyzers. At 300 K, data with PG(002) did not show any quasielastic broadening [Fig. 3(a)]. As we see later, it has perhaps merged in the background. However, a well-defined quasielastic component below the elastic line is seen with PG(004) data as shown in Fig. 3(b) at  $Q = 3.13 \text{ \AA}^{-1}$ . The widths of the quasielastic component seen in the PG(004) data [Figs. 2(b) and 3(b)] are considerably more than those seen with PG(002) data [Figs. 1 and 2(a)]: It should be noted that different  $x$ -axis scales have been used in the two cases.

## III. THEORETICAL ASPECTS

The neutron-scattering signal from  $(\text{NH}_4)_2\text{SbF}_5$  originates mainly from the hydrogens of the  $\text{NH}_4^+$  ions and is incoherent. That is, the shape of the measured spectra is

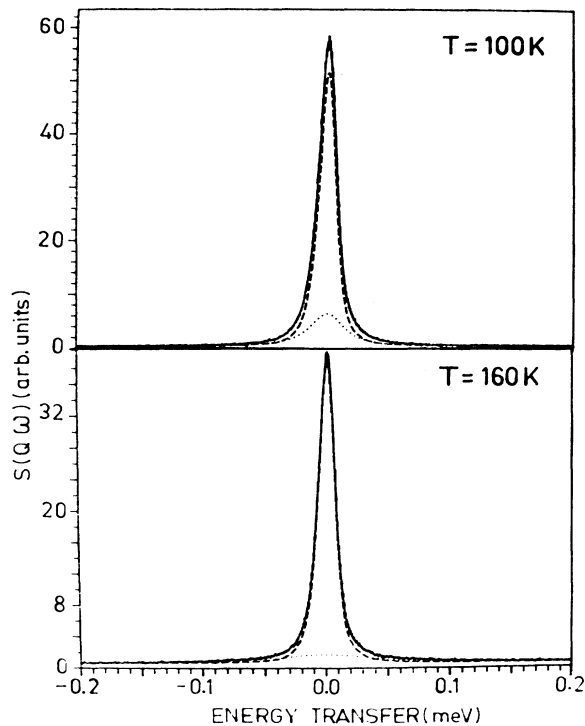


FIG. 1. Fitted spectra from  $(\text{NH}_4)_2\text{SbF}_5$  at 100 and 160 K obtained with the PG(002) analyzer at a  $Q$  of  $1.42 \text{ \AA}^{-1}$ . Experimental points are shown by vertical bars (signifying errors at each point), but being very small it has almost coincided with the fitted curve shown by the solid line. The quasielastic components are shown by dotted lines and the elastic components by dashed lines.

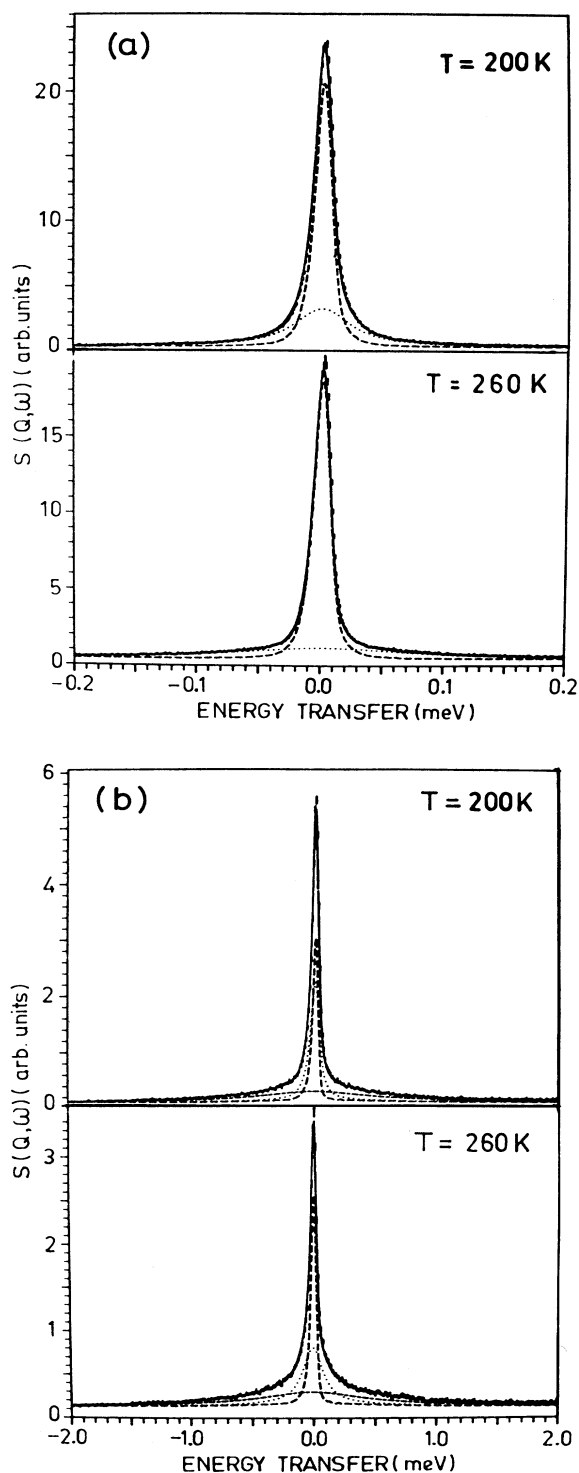


FIG. 2. Fitted spectra from  $(\text{NH}_4)\text{SbF}_5$  at 200 and 260 K. (a) Obtained with the PG(002) analyzer at a  $Q$  of  $1.42 \text{ \AA}^{-1}$  and (b) obtained with the PG(004) analyzer at a  $Q$  of  $3.13 \text{ \AA}^{-1}$ . Experimental points are shown by vertical bars (signifying errors at each point), but being small it has almost coincided with the fitted curve shown by the solid line. Quasielastic components are shown by dotted lines and elastic components by dashed lines.

decided by the dynamics of the  $\text{NH}_4^+$  ions. Because large energies are associated with the lattice modes of the crystal (translational or librational) and the internal vibrations of the ions, these inelastic excitations do not contribute to the intensity of neutron scattering in the energy region under discussion. The broadening of the elastic peak, seen in the present measurements, is connected only with the reorientational motion of  $\text{NH}_4^+$  ions. Analysis of the data is carried out on the basis of a jump diffusion model<sup>1,5-7</sup> to describe the reorientations of the  $\text{NH}_4^+$  ions. In this model one assumes that an  $\text{NH}_4^+$  ion oscillates about an equilibrium orientation for an average time  $\tau$  and then instantaneously reorients to a new equilibrium orientation. The average value of the residence time  $\tau$  is referred to as the reorientational relaxation time. The reorientation geometry of the ammonium ion in a crystal is generally described in terms of jumps between equilibrium orientations. The tetrahedral  $\text{NH}_4^+$  ions can reorient in many ways without violating the crystal symmetry. There are three possible ways an ion can reorient to an indistinguishable configuration: model A,  $120^\circ$  rotation about only one of the N—H bonds; mod-

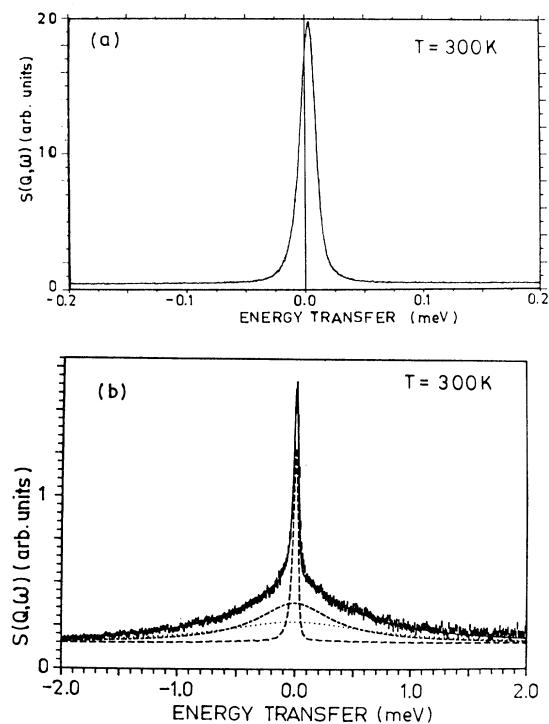


FIG. 3. Fitted spectra at 300 K. (a) Obtained with the PG(002) analyzer, where only an elastic line was able to be fitted. Experimental points are shown by vertical bars (signifying errors at each point), but being small it has almost coincided with the fitted curve shown by the solid line. (b) Obtained with the PG(004) analyzer; experimental points are shown by vertical bars (signifying errors at each point), and the fitted curve is shown by the solid line. Two different quasielastic components associated with the two  $\text{NH}_4$  ions are shown by the dotted line and short-dashed line. The elastic component is shown by the dashed line.

el  $B$ ,  $120^\circ$  rotation about any of the four N—H bonds; model  $C$ ,  $180^\circ$  rotation about an axis bisecting any of the four  $\angle \text{H—N—H}$  angles. As already mentioned, there are two crystallographically distinct types of ammonium ions  $[\text{NH}_4^+(\text{I})$  and  $\text{NH}_4^+(\text{II})]$  in  $(\text{NH}_4)_2\text{SbF}_5$ . In general, they could have different reorientation rates and possibly also different geometries of reorientation. Let  $\tau^{\text{I}}$  and  $\tau^{\text{II}}$  be the reorientational relaxation times for  $\text{NH}_4^+(\text{I})$  and  $\text{NH}_4^+(\text{II})$ , respectively. We assume that both of the  $\text{NH}_4^+$  ions reorient to indistinguishable configurations of the type discussed above. In the following, we give expressions for the relevant scattering laws  $S(Q, \epsilon)$ . First we give  $S(Q, \epsilon)$  for a system which contains only one type of  $\text{NH}_4^+$  ions. The expressions are then generalized in Sec. III B to apply to a system like  $(\text{NH}_4)_2\text{SbF}_5$ , where there are two types of  $\text{NH}_4^+$  ions.

#### A. Systems containing one type of $\text{NH}_4^+$ ion

We assume that  $S(Q, \epsilon)$  in the quasielastic region is decided only by the reorientational motion of the  $\text{NH}_4^+$  ions. Let  $\tau$  be the reorientation time for the  $\text{NH}_4^+$  ion. For the reorientational models under discussion, it can be shown that  $S(Q, \epsilon)$  for a polycrystalline sample is given by<sup>6</sup>

$$S(Q, \epsilon) = C \{ A_{\text{el}}(Q) \delta(\epsilon) + A_{\text{qel}}(Q) L(\Gamma, \epsilon) \}, \quad (1)$$

where  $C$  is a constant that depends on sample volume, scattering cross section, etc. We note that  $S(Q, \epsilon)$  consists of two parts. The first term is the contribution from the elastic scattering and the second is from the quasielastic scattering. The quasielastic part is Lorentzian in shape and is given by

$$L(\Gamma, \epsilon) = \frac{\Gamma}{\Gamma^2 + \epsilon^2}. \quad (2)$$

Here  $Q$  and  $\epsilon$  denote the wave vector and the energy transferred by the neutrons to the sample and  $\Gamma$  is the FWHM of the Lorentzian. The reorientation time  $\tau$  is related to the inverse of  $\Gamma$ . It can be shown that  $\Gamma = 3h/2\tau$  for model  $A$  and  $\Gamma = h/\tau$  for models  $B$  and  $C$ .<sup>6</sup> The elastic incoherent structure factor (EISF),  $F$ , giving the geometry of reorientation of the ion is defined as<sup>6</sup>

$$F(Q) = \frac{A_{\text{el}}(Q)}{A_{\text{el}}(Q) + A_{\text{qel}}(Q)}, \quad (3)$$

where  $A_{\text{el}}$  and  $A_{\text{qel}}(Q)$  are the *total* integrated intensities corresponding to the elastic and quasielastic parts, respectively. It may be noted that for the model under discussion it can be shown that

$$A_{\text{el}}(Q) = e^{-Q^2 \langle u^2 \rangle} F(Q)$$

and

$$A_{\text{qel}}(Q) = e^{-Q^2 \langle u^2 \rangle} \{ 1 - F(Q) \}, \quad (4)$$

where  $\langle u^2 \rangle$  is the mean-square amplitude of vibration of the hydrogen atom in the  $\text{NH}_4^+$  ion. It is, however, easier to calculate the EISF using Eq. (3) since, in that case, a knowledge of the Debye-Waller factor is not required.

EISF should be different for different geometries of reorientation. It can be shown<sup>1,6,7</sup> that, for model  $A$ ,

$$F(Q) = \frac{1}{2} \left[ 1 + \frac{\sin(QR)}{QR} \right], \quad (5)$$

and that, for models  $B$  and  $C$ ,

$$F(Q) = \frac{1}{4} \left[ 1 + 3 \frac{\sin(QR)}{QR} \right]. \quad (6)$$

Here  $R$  is the proton-proton distance in the  $\text{NH}_4^+$  ion. Thus, usually one expects that in the measured spectrum the elastic component would be riding on top of a broader quasielastic component. This will, of course, depend on the instrumental resolution. In many cases, one observes a broad continuous distribution and the elastic and quasielastic components are separated only by least-squares fitting. In any case, it is clear that to see the quasielastic component or to study the reorientational motion, the instrumental resolution ( $\text{FWHM} = \Delta E$ ) should be comparable to the width ( $\Gamma$ ) of the quasielastic line. That is, the time window of the spectrometer  $\tau_R (h/\Delta E)$  should, in general, be comparable to the reorientation time  $\tau$ . If  $\tau$  and  $\tau_R$  are not comparable, one might not see the quasielastic component.<sup>19,20</sup> For example, if the  $\text{NH}_4^+$  ions are reorienting very slowly ( $\tau \gg \tau_R$ ), the quasielastic part will be very narrow and would merge in the elastic component. On the other hand, if  $\text{NH}_4^+$  ions are undergoing fast reorientation ( $\tau \ll \tau_R$ ), the quasielastic component will be very broad and will merge in the background. That is, both for  $\tau \gg \tau_R$  and  $\tau \ll \tau_R$ , the measured spectra would show only elastic scattering; though the variation of the elastic intensity with  $Q$  would be different in the two cases. The intensity of the elastic peak will be given by  $e^{-2w}$  for  $\tau \gg \tau_R$  and by  $F e^{-2w}$  for  $\tau \ll \tau_R$ , where  $w = Q^2 \langle u^2 \rangle$ ,  $\langle u^2 \rangle$  being the mean-square amplitude of vibration. This suggests one should not attempt to obtain the EISF from the  $Q$  variation of the elastic intensity. In view of the above, and in view of the Debye-Waller factor corrections [Eq. (4)] it is common practice to extract the EISF using Eq. (3). This would be a reasonable method of extracting the EISF even if the quasielastic component consists of more than one Lorentzian function provided that the elastic and quasielastic components are well separated. In particular, we note that if there is a quasielastic broadening observed from a system where there is only one type of  $\text{NH}_4^+$  ion, then the ratio of elastic to quasielastic components gives the EISF for  $\text{NH}_4^+$  ion; this will not always be the case if there are two  $\text{NH}_4^+$  ions as discussed below.

#### B. Scattering law for systems consisting of two types of $\text{NH}_4^+$ ions

As was the case in Sec. III A, here we also assume that quasielastic scattering is determined by the reorientational motion of the  $\text{NH}_4^+$  ions; the lattice vibrations contribute through the Debye-Waller factor  $e^{-2w}$ . Let  $\tau^{\text{I}}$  and  $\tau^{\text{II}}$  be the reorientation times for the two  $\text{NH}_4^+$  ions and  $F_1$  and  $F_2$  the EISF's for them. It is reasonable to assume

that the Debye-Waller factor  $e^{-2w}$  is the same for the two  $\text{NH}_4^+$  ions because x-ray structure analysis at room temperature<sup>11</sup> showed that the values of  $\langle u^2 \rangle^{\text{I}}$  and  $\langle u^2 \rangle^{\text{II}}$  for the hydrogen nuclei in the two ammonium ions are 0.31 and 0.29  $\text{\AA}^2$ , respectively, and are not very different. The scattering law can then be written as

$$S(Q, \epsilon) = \frac{1}{2} C e^{-2w} [F_1(Q) \delta(\epsilon) + \{1 - F_1(Q)\} L(\Gamma^{\text{I}}, \epsilon)] \\ + \frac{1}{2} C e^{-2w} [F_2(Q) \delta(\epsilon) \\ + \{1 - F_2(Q)\} L(\Gamma^{\text{II}}, \epsilon)] . \quad (7)$$

In a fitting process it is not possible to obtain  $F_1$  and  $F_2$  separately. The elastic scattering will be the composition of the two contributions. Therefore, in essence, the scattering law consists of a  $\delta$  function and two Lorentzians and is given by

$$S(Q, \epsilon) = A_1(Q) \delta(\epsilon) + A_2 L(\Gamma^{\text{I}}, \epsilon) + A_3 L(\Gamma^{\text{II}}, \epsilon) , \quad (8)$$

where

$$A_1(Q) = \frac{1}{2} \{F_1(Q) + F_2(Q)\} e^{-2w} , \quad (9)$$

$$A_2(Q) = \frac{1}{2} \{1 - F_1(Q)\} e^{-2w} , \quad (10)$$

$$A_3(Q) = \frac{1}{2} \{1 - F_2(Q)\} e^{-2w} . \quad (11)$$

Then the ratio of the elastic to quasielastic intensity is defined as

$$R(Q) = \frac{A_1(Q)}{A_2(Q) + A_3(Q)} . \quad (12)$$

In particular we note that if the two  $\text{NH}_4^+$  ions have similar reorientation geometries (i.e.,  $F_1 = F_2 = F$ ), the elastic intensities from the two  $\text{NH}_4^+$  ions would be identical and we will have  $A_1 = F e^{-2w}$ . In general,  $A_1$  is decided by the effective structure factor  $F_{\text{eff}} = (F_1 + F_2)/2$ . Even though the two inequivalent ions can have different geometries of reorientation, we make the simplifying assumption that  $F_1 = F_2 = F$ . This also implies that  $A_2 = A_3$ . The justification for this assumption is given in Sec. V.

It may be pointed out that, while one has to use an  $S(Q, \epsilon)$  consisting of two Lorentzians for obtaining  $\tau^{\text{I}}$  and  $\tau^{\text{II}}$ , it is possible to get the relative intensities  $I_{\text{el}}$  and  $I_{\text{qel}}$  of the elastic and the quasielastic parts even for the present case assuming  $S(Q, \epsilon)$  is of the type

$$S(Q, \epsilon) = I_{\text{el}}(Q) \delta(\epsilon) + I_{\text{qel}} L(\Gamma_{\text{eff}}, \epsilon) , \quad (13)$$

where the quasielastic part has been represented by a single Lorentzian function having a width  $\tau_{\text{eff}}$ . The relative intensities of the elastic and the quasielastic components will depend very much on the instrumental resolution. For example, if  $\Delta E \simeq \Gamma^{\text{I}} \simeq \Gamma^{\text{II}}$ , both  $\text{NH}_4^+$  ions contribute to the quasielastic scattering. However, only one type of  $\text{NH}_4^+$  ion (say type I) will contribute to quasielastic scattering if  $\Delta E \ll \Gamma^{\text{II}}$  or  $\Delta E \gg \Gamma^{\text{II}}$  (see discussion in Sec. III A). Thus, if a broadening is seen in a spectrum, one can only say that at least one type of  $\text{NH}_4^+$  ion has a reorientation time comparable to  $\tau_R$ . Let us assume that  $\tau^{\text{I}} \simeq \tau_R$ , in which case we will obtain experimentally the

following three situations.

Case 1.  $\tau^{\text{I}} \simeq \tau_R$ ,  $\tau^{\text{II}} \simeq \tau_r$ :

$$R(Q) = \frac{F(Q)}{1 - F(Q)} . \quad (14)$$

Case 2.  $\tau^{\text{I}} \simeq \tau_R$ ,  $\tau^{\text{II}} \ll \tau_R$ :

$$R(Q) = \frac{2F(Q)}{1 - F(Q)} . \quad (15)$$

Case 3.  $\tau^{\text{I}} \simeq \tau_R$ ,  $\tau^{\text{II}} \gg \tau_R$ :

$$R(Q) = \frac{1 + F(Q)}{1 - F(Q)} . \quad (16)$$

Thus, a comparison of the *experimental*  $R(Q)$  with Eqs. (14)–(16) will provide an estimate for the relative values of  $\tau^{\text{I}}$  and  $\tau^{\text{II}}$ . This will also reveal if the observed quasielastic scattering arises from one or two  $\text{NH}_4^+$  ions.

#### IV. DATA ANALYSIS

The analysis of the data involved convoluting the appropriate scattering law  $S(Q, \epsilon)$  with the instrumental resolution function and then obtaining the parameters by least-squares fitting of the calculated spectra to the measured one. The instrumental resolution is generally obtained by measuring the spectra from a standard vanadium sample. In this experiment, it is found that data from  $(\text{NH}_4)_2\text{SbF}_5$  at 40 K with both PG(002) and PG(004) do not show any broadening over the instrumental resolution indicating that  $\text{NH}_4^+$  reorientations are frozen at this temperature. These data have been used as the resolution for the higher-temperature data which thus minimizes other systematic effects such as those arising from sample geometry, Bragg scattering from the sample holder, etc.

The present measurements show that quasielastic broadening is seen at all temperatures between 100 and 300 K. At some temperatures it is seen in the PG(002) data, at some in the PG(004) data, and at some in both. Broadly the data can be divided into three temperature regions.

(a)  $100 < T(\text{K}) < 160$ . Quasielastic broadening is seen only in the good resolution [PG(002) analyzer] data (Fig. 1).

(b)  $200 < T(\text{K}) < 260$ . Quasielastic broadening is seen both in the good and the poor resolution [PG(002) and (004) analyzers] data (Fig. 2).

(c)  $T = 300$  K. Quasielastic broadening is seen only in the poor resolution [PG(004) analyzer] data (Fig. 3).

The data have been analyzed using the following procedure. First they have been analyzed using Eq. (13) with  $I_{\text{el}}$ ,  $I_{\text{qel}}$ ,  $\Gamma_{\text{eff}}$ , as parameters. The background is taken to be a straight line having a constant value  $a$  at zero energy transfer with slope  $b$ .  $a$  and  $b$  are also parameters in the fit. Knowing the value of  $I_{\text{el}}$  and  $I_{\text{qel}}$ , the experimental  $R(Q)$  is computed. This is compared with those obtained from Eqs. (14)–(16). In this way, we are able to decide whether the quasielastic component contains one or two Lorentzians. Data are then analyzed in terms of Eq. (8). If the measured distribution has contributions from one  $\text{NH}_4^+$  ion only,  $A_3$  becomes identically zero and the data then are analyzed using Eq. (8) with  $A_1$ ,  $A_2$ ,  $\Gamma^{\text{I}}$ ,

and the background are parameters. This was the case at 100 and 160 K in the PG(002) data. When the quasielastic component is seen to have contributions from both the  $\text{NH}_4^+$  ions, the data have again been analyzed using Eq. (8) with  $A_1$ ,  $A_2$ ,  $A_3$ ,  $\Gamma^I$ ,  $\Gamma^{II}$ , and the background as parameters. This was the case at 300 K with the PG(004) data. Sometimes at a given temperature ( $T=200$  and 260 K) data from the PG(002) analyzer have contributions from one  $\text{NH}_4^+$  ion and the PG(004) data have contributions from both  $\text{NH}_4^+$  ions. In that case,  $\Gamma^I$  is first obtained from the PG(002) data and then kept as a fixed parameter for the analysis of the PG(004) data in order to obtain the other parameters.

## V. RESULTS AND DISCUSSIONS

For the sake of clarity in presentation, first results at intermediate temperature (region *b*) then at higher temperature (region *c*) and lastly at low temperature (region *a*) are presented.

### A. Region (*b*): Intermediate temperatures

In this temperature region, measurements have been carried out at 200 and 260 K. As already mentioned, data with both good and poor resolutions show broadening at these temperatures. This indicates that at least one type of  $\text{NH}_4^+$  ion is contributing to the quasielastic scattering in both of these data sets. To examine whether only one or both of the  $\text{NH}_4^+$  ions contribute to the quasielastic scattering,  $R(Q)$  is studied. The ratio  $R(Q)$ , of the elastic to quasielastic intensity has been obtained using Eq. (12). Results are shown in Fig. 4 at a sample temperature of 200 K. The solid circles (●) and crosses (×) in Fig. 4 correspond to good and poor resolution data, respectively. The solid lines are the calculated curves [Eqs.

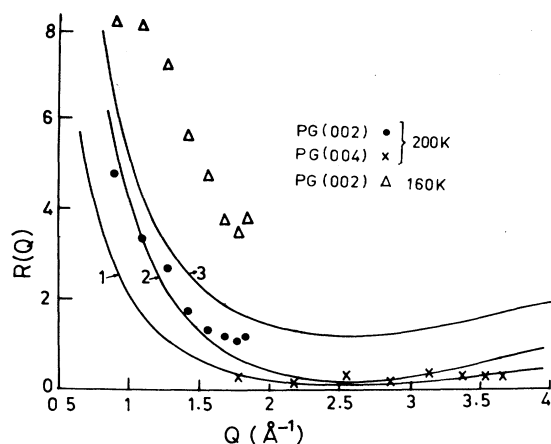


FIG. 4. The ratio  $R(Q)$  of elastic to quasielastic intensities as a function of  $Q$ . Calculated  $R(Q)$ 's corresponding to the three cases described in the text using model  $B/C$  are shown by solid lines. Experimental points at 200 K are shown by solid circles (●) and by crosses (×) for the PG(002) and PG(004) data, respectively. At 160 K the data are shown by triangles (Δ) as obtained with the PG(002) analyzer.

(14)–(16)] for the three cases mentioned in Sec. III B. In these calculations model  $B/C$  has been assumed, and it is shown later that this assumption is not unreasonable. It is seen that good resolution data agree with curve 2 (i.e.,  $\tau^I \simeq \tau_R$  and  $\tau^{II} \ll \tau_R$ ) and the poor resolution data agree either with curve 1 (i.e.,  $\tau^I \simeq \tau_R$  and  $\tau^{II} \simeq \tau_R$ ) or with curve 2, but not curve 3. Thus, we can conclude that the hydrogen-bonded  $\text{NH}_4^+$ (I) alone contributes to the quasielastic scattering in the PG(002) experiments and possibly both hydrogen-bonded  $\text{NH}_4^+$ (I) and the nonhydrogen-bonded  $\text{NH}_4^+$ (II) contribute to the quasielastic scattering in the PG(004) experiments. Therefore,  $A_3$  takes a zero value while fitting Eq. (8) to the PG(002) data. The resultant reorientational relaxation time of  $\tau^I = 188$  psec is obtained for  $\text{NH}_4^+$ (I) from the analysis of the PG(002) data. Having obtained this value of  $\tau^I$  (or  $\Gamma^I$ ), the PG(004) data were then analyzed, again in terms of Eq. (8) with  $A_1$ ,  $A_2$ ,  $A_3$ , and  $\Gamma^{II}$  as parameters, the value of  $\Gamma^I$  being kept fixed at the value obtained from the PG(002) data. The reorientational relaxation time is obtained to be 8.5 psec and it should correspond to  $\tau^{II}$  of the  $\text{NH}_4^+$ (II) ion. It may be mentioned that the least-squares fit shows that  $A_2 = A_3$  (within 5%) suggesting that the two  $\text{NH}_4^+$  ions have similar reorientation geometries. The assumption made in Sec. III B and used to separate the elastic and quasielastic components is now justified. Knowing the values of  $A_1$ ,  $A_2$  (and  $A_3$ ), the EISF for either of the two  $\text{NH}_4^+$  ions has been obtained using  $F = A_1 / (A_1 + 2A_2)$ . The comparison of the experimental and the calculated EISF is shown in Fig. 5. The solid circles (●) and crosses (×) in this figure correspond to good and poor resolution data at 200 K. The solid and dashed lines are the calculated EISF's for models  $A$  and  $B/C$ , respectively. The experimental data clearly favor model  $B/C$ . This is the

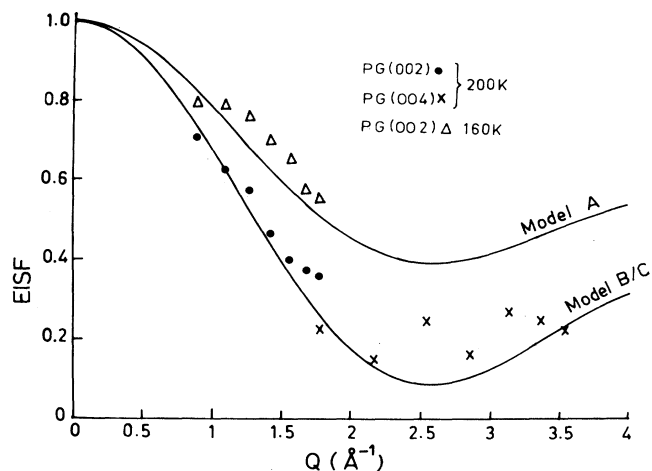


FIG. 5. The measured structure factor associated with the elastic part (EISF),  $F(Q)$ , is shown as a function of  $Q$ . The calculated  $F(Q)$  for model  $A$  and for models  $B/C$  are shown by solid lines. Experimental points are shown by solid circles (●) and by crosses (×) at 200 K for the PG(002) and PG(004) analyzers, respectively, and by triangles at 160 K for the PG(002) analyzer.

model which has been used to calculate the theoretical curves for  $R(Q)$  (Fig. 4). Thus, the above analysis show that the two  $\text{NH}_4^+$  ions have similar reorientation geometries and that they are either reorienting by  $120^\circ$  rotation about any of the three-fold axes or by  $180^\circ$  rotation about any of the two-fold axes.

The data at 260 K have also been analyzed in a similar fashion. The EISF at this temperature is very similar to that at 200 K. The reorientation times obtained are  $\tau^I=51.7$  psec and  $\tau^{II}=9$  psec. We note that there is therefore no major change in pattern of  $\text{NH}_4^+$ -ion reorientations at phase transition of 257 K. The change in value of  $\tau^I$  and  $\tau^{II}$  in going from 200 to 260 K may be purely a temperature effect. That is, the reorientations of the  $\text{NH}_4^+$  ions do not seem to play any significant role in the transition from normal to superionic conductor at 257 K. This is in agreement with earlier studies which suggested that this transition is connected with dynamics of  $\text{SbF}_5$  groups.<sup>8</sup>

### B. Region (c)

The data at 300 K with PG(002) do not show any broadening indicating that the reorientation times of both  $\text{NH}_4^+$  ions are too small to be seen in this time window of the spectrometer [Fig. 3(a)]. The spectra from PG(004), however, show a well-defined quasielastic component [Fig. 3(b)]. In principle, this could be either from one or both of the  $\text{NH}_4^+$  ions. A study of the ratio of the elastic to quasielastic intensities  $R(Q)$  revealed that both of the  $\text{NH}_4^+$  ions are contributing to the quasielastic scattering. The data were thus analyzed using Eq. (8) with  $A_1$ ,  $A_2$ ,  $A_3$ ,  $\Gamma^I$ , and  $\Gamma^{II}$  as parameters. The EISF is again found to follow model  $B/C$ . The value of the reorientation times obtained are  $\tau^I=12$  psec and  $\tau^{II}=6$  psec. The  $\tau$ 's obtained at 300 K are in very good agreement with the earlier data<sup>16</sup> at room temperature, where an effective reorientation time of 10 psec for the two  $\text{NH}_4^+$  ions was obtained. The reorientational geometry obtained from the present data is also in agreement with the earlier reported<sup>16</sup> results.

### C. Region (a)

At 160 K, the results are significantly different from those of regions  $b$  and  $c$ . The  $R(Q)$ , obtained from the PG(002) data at 160 K are shown in Fig. 4 by triangles ( $\Delta$ ). The experimental  $R(Q)$  do not agree with any of the calculated curves. This suggests that the model  $B/C$  may not be the right one to describe the  $\text{NH}_4^+$  reorientations at 160 K. In view of this,  $R(Q)$  were calculated for all three cases discussed in Sec. III B, using model  $A$  and compared with the experimental  $R(Q)$ . Results are shown in Fig. 6. It is seen that experimental  $R(Q)$  follows curve 3. That is, one of the reorientation times has become so large that it has merged into the elastic line. We assign the value 138 psec of the reorientation time obtained from the above data to  $\tau^{II}$ . This value cannot be associated with the hydrogen-bonded  $\text{NH}_4^+$ (I) as it had a value of 188 psec at 200 K and it is highly unlikely that it has reduced to 138 psec at 160 K. The EISF

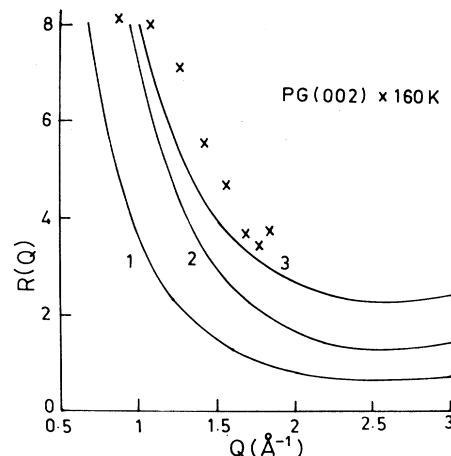


FIG. 6. The ratio  $R(Q)$  of elastic to quasielastic intensities as a function of  $Q$ . Calculated  $R(Q)$ 's corresponding to the three cases described in the text using model  $A$  are shown by the solid lines. Experimental points at 160 K are shown by crosses ( $\times$ ) as obtained with the PG(002) analyzer.

[ $F=(A_1 - A_2)/(A_1 + A_2)$ ] obtained at 160 K shown in Fig. 5 (by triangles) indicates that it now favors model  $A$ , i.e., the reorientation geometry has really changed in passing into the crystalline phase below 168 K. The  $\text{NH}_4^+$  ion has a higher probability of rotating by  $120^\circ$  about only one of the four N—H bonds. Our results suggest that  $\text{NH}_4^+$ (II) is hydrogen bonded below 168 K so that only uniaxial rotation is possible. To confirm this a detailed neutron structure analysis is planned.

It may be recalled that earlier NMR experiments<sup>8</sup> had suggested that the transition at 168 K is related to the reorientational motion of one type of  $\text{NH}_4^+$  ion. The present results not only confirm that but also provide much more detailed information. While at 200 K, the nonhydrogen-bonded  $\text{NH}_4^+$ (II) ions could reorient about any N—H bond, they can only reorient about a fixed N—H bond at 160 K. The hydrogen-bonded  $\text{NH}_4^+$ (I) also reorients about any N—H bond at 200 K; however, it is frozen at 160 K on our time scale and is not seen in this experiment.

The data at 100 K gave results which are very similar to those at 160 K. The EISF does not change in going from 160 to 100 K. The reorientation time  $\tau^{II}$  obtained at 100 K is 622 psec.

Table I gives the values of the reorientation times ( $\tau^I$

TABLE I. Reorientation times ( $\tau^I$  and  $\tau^{II}$ ) at different temperatures.

Temperature (K)	$\tau^I$ (psec)	$\tau^{II}$ (psec)
100		622
160		138
200	188	8.5
260	52	9
300	12	6

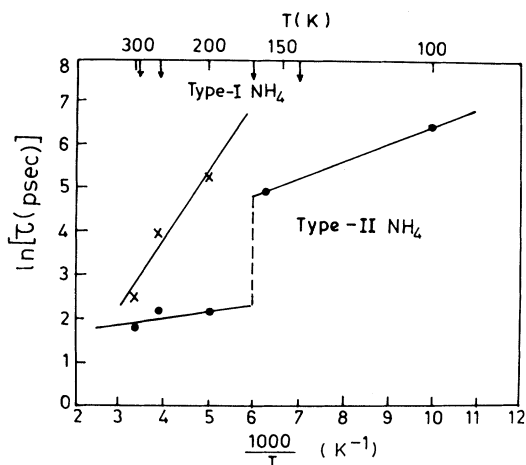


FIG. 7. The Arrhenius plots of  $\ln(\tau)$  vs inverse temperature. The solid lines are obtained by least-squares fitting. The arrows indicate the transition temperatures.  $\tau^{\text{II}}$  changes discontinuously at the phase transition temperature of 168 K where  $\text{NH}_4^+(\text{II})$  changes its geometry of reorientation.

and  $\tau^{\text{II}}$ ) associated with  $\text{NH}_4^+(\text{I})$  and  $\text{NH}_4^+(\text{II})$  ions at different temperatures. Figure 7 shows the variation of the reorientation time with inverse temperature. Assuming an Arrhenius relationship

$$\tau = \tau_0 e^{E_a/KT}, \quad (17)$$

the activation energy  $E_a$  and the prefactor  $\tau_0$  have been obtained from Fig. 7 by least-squares fitting. In the temperature range 200–300 K,  $E_a = 3.09$  Kcal/mol and  $\tau_0 = 0.09$  psec for type-I  $\text{NH}_4^+$  ions and  $E_a = 0.32$  Kcal/mol and  $\tau_0 = 3.93$  psec for type-II  $\text{NH}_4^+$  ions have been obtained. In the temperature range 100–160 K only one type of ion is reorienting within the time frame of the instrument and it is type-II; the reorientation time of type I becomes very large and gives no contribution to the quasielastic part.  $E_a = 0.79$  Kcal/mol and  $\tau_0 = 11.02$  psec have been obtained for type-II  $\text{NH}_4^+$  ions in this temperature range. It may be noted that the barrier for rotation is an order of magnitude larger in the case of the hydrogen-bonded  $\text{NH}_4^+$  as compared to that for the nonhydrogen-bonded  $\text{NH}_4^+$  and there is a factor of 2 change in the barrier in going through the transition at 168 K for  $\text{NH}_4^+(\text{II})$ . The phase transitions at 142, 257, and 292 K do not affect the quasielastic scattering in any perceptible way.

## VI. SUMMARY

The reorientational motion of ammonium ions in  $(\text{NH}_4)_2\text{SbF}_5$  has been investigated by quasielastic neutron scattering in the temperature range 40–300 K.  $(\text{NH}_4)_2\text{SbF}_5$  has two crystallographically inequivalent  $\text{NH}_4^+$  ions in the unit cell. Two different energy resolutions and the variation of the ratio of elastic to quasielastic intensities with wave-vector transfer have been exploited to obtain the reorientational relaxation times  $\tau^{\text{I}}$  and  $\tau^{\text{II}}$  for the two ions in the above salt at different temperatures. The hydrogen-bonded  $\text{NH}_4^+$  ion (type I) rotates slower than the nonhydrogen-bonded ion (type II). The information about geometry of reorientation of the  $\text{NH}_4^+$  ions has also been obtained. Both  $\text{NH}_4^+$  ions reorient by  $120^\circ$  rotations about any of the N—H bonds or by  $180^\circ$  rotations about any of the bisector of  $\angle \text{H—N—H}$  at temperatures above 168 K. It has been found that there is a change in geometry of reorientation of the  $\text{NH}_4^+(\text{II})$  ion when the compound undergoes a phase transition at 168 K. At temperatures below 168 K, the  $\text{NH}_4^+(\text{II})$  ion reorients about a fixed N—H bond instead of any of the N—H bonds as is the case in higher temperature. This suggests that one of the hydrogens of  $\text{NH}_4^+(\text{II})$  becomes hydrogen bonded below 168 K. The variation of  $\tau^{\text{I}}$  and  $\tau^{\text{II}}$  with temperature shows that  $\tau^{\text{II}}$  changes discontinuously at the phase transition temperature of 168 K. The activation energies have been obtained using the Arrhenius law. The activation energy of reorientation for  $\text{NH}_4^+(\text{I})$  (hydrogen bonded) has been found to be 3.09 Kcal/mol. Whereas  $\text{NH}_4^+(\text{II})$  (nonhydrogen bonded) has an activation energy of 0.32 Kcal/mol above 168 K and 0.79 Kcal/mol below 168 K. That is, the rotational barrier does change but not dramatically on going through the transition for  $\text{NH}_4^+(\text{II})$ . The barrier of rotation for hydrogen-bonded  $\text{NH}_4^+$  ion is an order of magnitude higher than that for a nonhydrogen-bonded  $\text{NH}_4^+$  ion.

## ACKNOWLEDGMENTS

Encouragement and support from Dr. B. A. Dasannacharya and Dr. K. R. Rao are greatly acknowledged. We thank Dr. R. M. Kadam of Radio Chemistry Division of BARC for preparing the sample and Dr. W. S. Howells is thanked for his help with the data analysis program. We also acknowledge SERC for access to the pulsed neutron source, ISIS, at UK.

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