An NMR Study of Ionic Motion in Ammonium Ferrocyanide

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A nuclear magnetic resonance study has been made of ionic motion in ammonium ferrocyanide, $(NH_4)_4Fe(CN)_6 \cdot H_2O$. Narrowing of the ^1H steady-state resonance line, corresponding to ionic diffusion, begins near 150°K. Above about 315°K the line is fully narrowed. Analysis of the temperature dependence of the line width gives an Arrhenius activation energy of 19 kJ/mole.

Introduction

Materials showing large values of ionic diffusivity at ambient temperatures are of much interest for potential use in new types of batteries or fuel cells either as the electrolyte or as an electrode component. Because of their high electropositive character and light weight, the alkali metals and hydrogen are the cationic species of greatest promise for use in high energy density systems. Solids of the β-alumina and its magnesia-stabilized modification β″ families are attractive electrolytes for several of the alkali metal ions; however, there is no satisfactory hydrogen ion conducting material known at present which is also an electronic insulator under the requisite thermodynamic conditions.

There have been indications that ammonium compounds might bear investigation in this respect. Herrington and Staveley (*1*) measured the ionic conductivity of ammonium halides and found them to be appreciably higher than that of the related alkali metal compounds and suggested that this might be due to hydrogen ions hopping through the lattice. Fuller and Patten (*2*) confirmed this mechanism, using conductivity measurements on deuterated ammonium chloride. Thus it seems worthwhile to investigate proton transport in ammonium compounds in the search for interesting ionic conductors.

Nuclear magnetic resonance spectroscopy is a particularly powerful method for the study of ionic motion in solids, as it does not require single crystals, and the often difficult electrode problem is not present. Also the hydrogen nucleus

is the most amenable to such a study. In steady-state NMR measurements the proton line width, in ammonium compounds, collapses from values as high as 15–25 G to 1–5 G at the onset of rotation of the ammonium ion upon its crystallographic site. At higher temperatures it is reduced even further, to values less than 0.1 G (the limit imposed by inhomogeneity in the experimental magnetic field), due to motion of the hydrogen species through the lattice, which averages out internal field variations. The temperature dependence of the NMR line width is shown schematically in Fig. 1.

From experimental line width–temperature information, activation energies for both rotational (or oscillatory) and translational motion
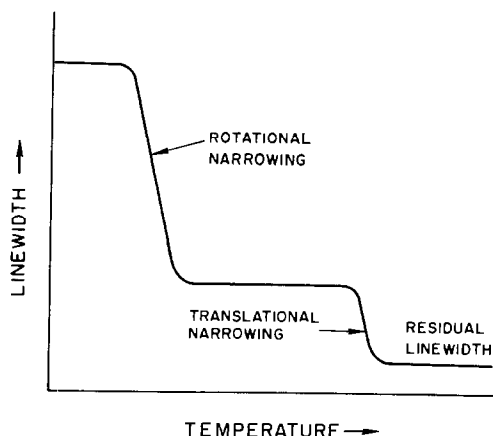

FIG. 1. Schematic representation of the ^1H magnetic resonance line width *vs.* temperature in an ammonium material.

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can be determined, as well as ionic jump frequencies. From knowledge of the crystal structure of the material, the diffusion coefficients can also be calculated. Richards and Schaefer (3) made a survey of the temperature dependence of the line width, between 20 and 295°K, for a large group of ammonium compounds and were able to study the complete rotational narrowing curve in a number of cases; however in several instances the ion was already freely rotating even at 20°K (4, 5). In the simple halides (3, 6–8) the narrowing temperature decreases with increasing size of the anion, as is expected from simple electrostatic considerations. Ammonium fluoroberyllate, NH_4BeF_4, is particularly interesting as the cation is rotating at 20°K and at about 210°K the fluoroberyllate anion begins to rotate (9). Because of the experimental difficulties of working at such low temperatures, rotational motion is more commonly studied using pulsed rather than static NMR techniques. To the authors' knowledge, there is only one case where site-to-site hydrogen transport, i.e., translational narrowing, has been observed by NMR techniques in an ammonium compound; this was in an ammonium tungsten bronze (10, 11), where the ammonium ions reside in channels within the structure (12, 13). This paper discusses steady-state nuclear magnetic resonance experiments on hydrogen transport in ammonium ferrocyanide, $(NH_4)_4$ $Fe(CN)_6 \cdot H_2O$.

Experimental Aspects

The ammonium ferrocyanide used in this work was obtained from Alfa Inorganics as a very fine pale yellow-green powder with the stated formula $(NH_4)_4Fe(CN)_6 \cdot H_2O$. As essentially nothing is known about this material, a full chemical analysis was made of both the initial powder and of single crystals grown from aqueous solutions of the powder. The results in wt% were: powder, 46.0 N, 23.5_5 C, 5.02 H, and 18.6 Fe; single crystal, 46.3_5 N, 23.2 C, 5.67 H, and 18.5 Fe; and calculated for the formula $(NH_4)_4Fe(CN)_6 \cdot H_2O$, 46.36 N, 23.85 C, 6.00 H, and 18.48 Fe. These data clearly show that this is a reasonable formula for this material, and that it cannot, therefore, be isomorphous with the potassium salt, which has three waters of crystallization.

An X-ray analysis was performed on a Picker diffractometer using a solid state detector and $CuK\alpha$ radiation. The only other published X-ray

information on this material is a 1928 powder photograph by Brill and Mark (14), who described it as "aussordentlich linienreich." The values of d, $\sin^2 \theta$, and relative intensity found in this work are given in Table I; and the spectrum is shown

TABLE I

X-RAY POWDER DIFFRACTION DATA
FOR AMMONIUM FERROCYANIDE
$(NH_4)_4Fe(CN)_6 \cdot H_2O$

d	Intensity	$\sin^2 \theta$
6.810	7	0.01281
6.449	100	0.01429[a]
5.324	3	0.02096
4.848	1	0.02529
4.571	18	0.02845[a]
4.212	8	0.03349
4.139	5	0.03470
4.110	2	0.03518
3.715	29	0.04305[a]
3.596	1	0.04596
3.342	15	0.05320
3.235	4	0.05678[a]
3.137	13	0.06038
3.008	6	0.06568
2.964	51	0.06821
2.890	20	0.07115[a]
2.821	3	0.07469
2.698	14	0.08162
2.587	3	0.08878
2.531	3	0.09279
2.487	9	0.09611
2.441	22	0.09974[a]
2.315	1	0.11088
2.280	2	0.11430[a]
2.245	3	0.11793
2.154	7	0.12808[a]
2.119	2	0.13237
2.068	3	0.13894
2.043	7	0.14240[a]
1.971	1	0.15298
1.946	3	0.15690[a]
1.884	1	0.16752
1.864	6	0.17112[a]
1.791	5	0.18534[a]
1.668	6	0.21371[a]
1.614	1	0.22819[a]
1.567	4	0.24188[a]
1.482	5	0.27044[a]
1.445	1	0.28482[a]
1.410	2	0.29879[a]
1.377	1	0.31326[a]
1.347	1	0.32751[a]

[a] The $\sin^2 \theta$ values of these lines are all multiples of 0.01424, and can be fitted to a bcc cell with $a_0 = 9.137$ Å.

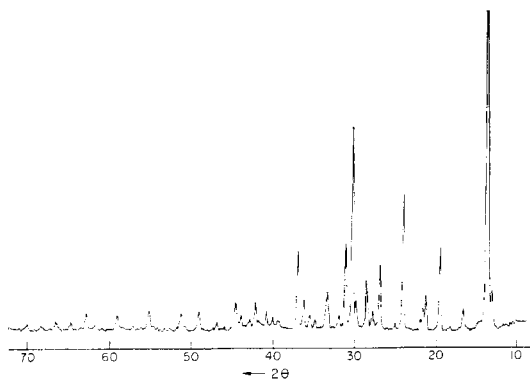FIG. 2. X-Ray diffraction spectrum of ammonium ferrocyanide using Cu$K\alpha$ radiation.

FIG. 3. The temperature dependence of the ^{1}H resonance line for ammonium ferrocyanide.

in Fig. 2. The value 0.01424 is a common factor to almost half the $\sin^2\theta$ values. Despite this, initial attempts to index the pattern have failed and it appears that the crystal symmetry is either monoclinic or triclinic. However, single crystals have now been grown, and further studies are in progress to elucidate the structure.

The NMR spectra were obtained by using a Varian 4200 wide line spectrometer, which employs a crossed-coil probe and phase-sensitive detection, equipped with the Varian variable temperature Dewar. About 2 g of the sample was placed in a sealed quartz tube in direct contact with a copper–constantan thermocouple; the sample was cooled by passing dry nitrogen through a copper coil immersed in liquid nitrogen at various flow rates. During the time it took to record a spectrum, about 10 min, the temperature was constant to within a degree. Radio-frequency field strength, field modulation, and detector time constants were all kept below values producing measurable signal broadening. The cumulative error in line width determination, including measuring and calibration error, was less than 5%. The maximum magnetic field inhomogeneity over the volume of the sample, determined from the spectrum of ^{1}H in H_2O at 300°K, was less than 0.1 G.

NMR Results

The peak-to-peak width of the derivative signal of the ^{1}H resonance line, ΔH, was found to vary with sample temperature as shown in Fig. 3. It is seen that narrowing, typical of motion of the resonant species, occurs between 150 and 315°K. At low temperatures the line width is about 3.5 G, and it becomes half narrowed at
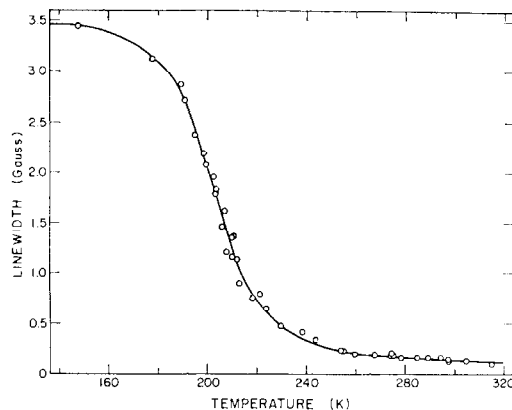
about 200°K. Above 315°K the value of ΔH has reached the limit determined by the magnetic field inhomogeneity. The line shape, as shown in Fig. 4, changes with temperature as well, in accordance with theoretical predictions (15), being Lorentzian when more than half narrowed, and more Gaussian at the lower temperatures.

Data Analysis

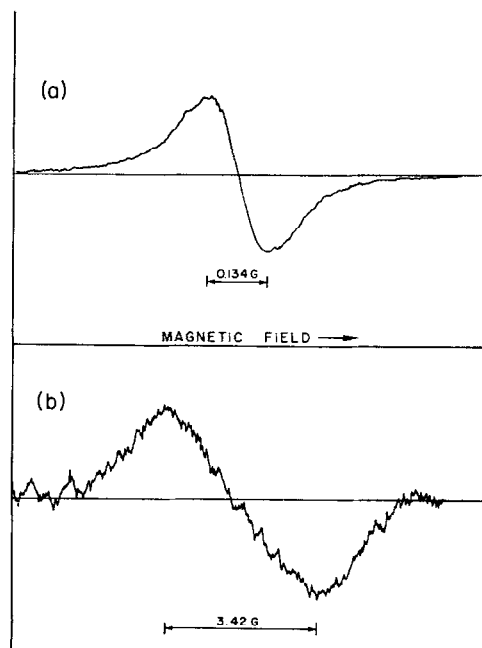In a steady-state experiment of this type, the line width is determined by the value of the

FIG. 4. The ^{1}H derivative spectrum for ammonium ferrocyanide at (a) 296°K and (b) 148°K.

dipolar relaxation time T_2. In the higher temperature portion of the narrowing curve, where the line shape is essentially Lorentzian, indicating the dominance of a single relaxation process, these quantities are related by the expression

$$T_2 = 2/\sqrt{3}\gamma\Delta H_d, \tag{1}$$

where ΔH_d is the dipolar contribution to the width (in gauss) of the line, and γ is the gyromagnetic ratio. The motion of nuclei from site-to-site within the solid, expressed in terms of a jump frequency, ν_j, is directly proportional to the value of T_2, and thus to $(\Delta H_d)^{-1}$. If the temperature dependence of the jump frequency can be represented by

$$\nu_j = \nu_0 \exp(-Q/RT), \tag{2}$$

then

$$\Delta H_d = A \exp(+Q/RT). \tag{3}$$

However, because of the lower limit imposed on the measured line width by inhomogeneity in the magnetic field, a correction must be made to the measured values of ΔH to obtain ΔH_d. In this Lorentzian regime, all contributions to the measured line width are additive, so that

$$\Delta H = \Delta H_d + \Delta H_r, \tag{4}$$

where ΔH_r is the temperature-independent residual line width. The temperature dependence of the line width can thus be expressed in linear form as (16)

$$\ln(\Delta H - \Delta H_r) = \ln(A) + Q/RT. \tag{5}$$

The experimental points were fitted to Eq. (5) by a least-squares regression program. A series of values of ΔH_r were tried in the vicinity of 0.1 G, and the value 0.08 G was found to produce the minimum least-mean-square error, using all but the data at the temperature extremes. The experimental data plotted according to Eq. (5) are shown in Fig. 5. The resulting activation energy Q was 18.9 ± 0.5 kJ/mole, with a pre-exponential factor A of 2.1×10^{-5} G, with a standard error given by $\log(A) = -4.68 \pm 0.12$.

The data can also be analyzed in a different way, using the relation between the jump frequency and experimentally measurable parameters from the "weak collision" theory of Bloembergen, Purcell, and Pound (17), who obtained

$$(\Delta\nu_d)^2 = (\Delta\nu_l)^2 (2/\pi)\tan^{-1}[\alpha(\Delta\nu_d/\nu_j)], \tag{6}$$

where α is a constant, determined by the line shape, whose value falls in the range 1–10 (7),
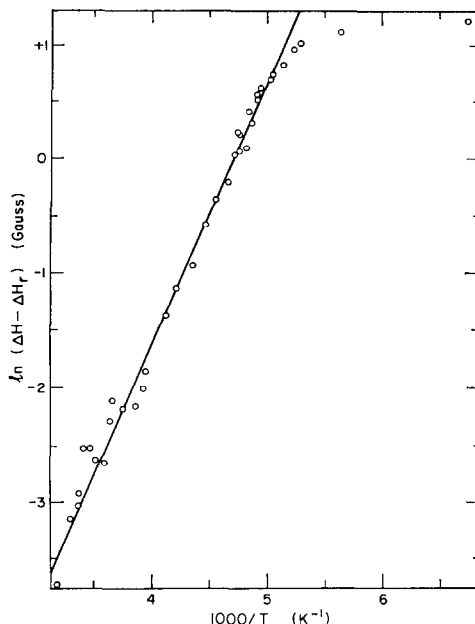

FIG. 5. Arrhenius plot of corrected ^1H line width of ammonium ferrocyanide.

$\Delta\nu_d = \gamma\Delta H_d/2\pi$ is the dipolar line width (in frequency units) at the specified temperature, and $\Delta\nu_l = \gamma\Delta H_l/2\pi$ is the rigid lattice (low temperature) line width.

Rewriting this equation in terms of the experimentally determined line widths, in magnetic field units, correcting for the temperature-independent residual line width in the manner shown above, and rearranging gives (18)

$$\nu_j = \alpha\gamma(\Delta H - \Delta H_r)/(2\pi\tan\{(\pi/2) \times \\ \times [(\Delta H - \Delta H_r)/(\Delta H_l - \Delta H_r)]^2\}). \tag{7}$$

Making the assumption that α is a constant over the entire temperature range, the experimental points were reduced to values of ν_j/α, and fitted to the Arrhenius expression

$$\ln(\nu_j/\alpha) = \ln(\nu_0/\alpha) - Q/RT \tag{8}$$

using a least-squares method for a series of values of ΔH_r about 0.1 G and ΔH_l about 3.5 G. The error was minimized when $\Delta H_r = 0.085$ G and $\Delta H_l = 3.45$ G. The value of activation energy was found to be 19.0 ± 0.3 kJ/mole, and ν_0/α had a value of 1.52×10^9 sec^{-1} with the standard error given by $\log(\nu_0/\alpha) = 9.18 \pm 0.14$. The temperature dependence of the jump frequency, ν_j, obtained from the data in this manner is illustrated in Fig. 6.
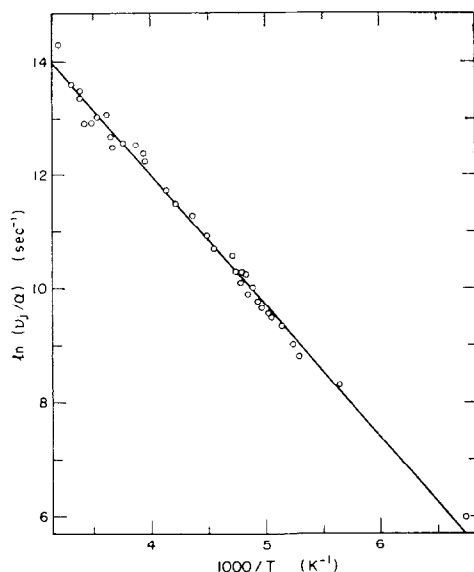
FIG. 6. Arrhenius plot of jump frequency of hydrogen species in ammonium ferrocyanide.

From a random-walk model, the diffusion coefficient, D, is related to the jump frequency, ν_j, the mean jump distance, d, and the number of possible jumps, n_j, by the expression

$$D = d^2 \nu_j / n_j. \qquad (9)$$

For cubic materials n_j is usually 6, but when jumps are constrained to a single direction, it becomes 2. Neglecting the temperature dependence of d, and substituting Eq. (2) into Eq. (9) gives

$$D = D_0 \exp(-Q/RT). \qquad (10)$$

Using the Van Vleck formula (19) for the calculation of the second moment of the resonance line, and the measured rigid lattice line width of 3.45 G, it is clear that the ammonium ions must be closer than 3.5 Å to one another. Taking $n_j = 6$, and assuming for simplicity that α is 1 and d^2 is 10 Å^2, then D_0 has a value of about 3×10^{-7} cm^2/sec, and the diffusion coefficient at 300°K is 1×10^{-10} cm^2/sec.

One major assumption that has been made throughout the above analysis is that the effect of the hydrogens in the water molecule in ammonium ferrocyanide on the line width is negligible. This assumption is probably justified on two grounds. First, there are eight times as many hydrogens in the ammonium groups than in the water. Second, water of hydration is typically held rather rigidly, much more so than the more spherically sym-

metric ammonium ion, so that rotational motion only starts to set in at the temperatures studied here (20–22); thus, Chiba (22) in a study of ammonium oxalate monohydrate found that whereas rotation of the ammonium ions appeared at about 200°K, the water did not start to reorient until 350°K. In potassium ferrocyanide, which contains three waters of hydration, the line width at 300°K, 4–5 G, is indicative of rotational but not translational motion (20–22). It thus seems reasonable to assume that in this case as well, the water is not involved in any translational motion, so that the ^{1}H resonance line for the water should be a few gauss wide; naturally if this water is so rigidly held that it also cannot rotate, then the line width will be much larger. In either instance, such a broad line is expected to cause only a slight drift in the baseline of the much narrower measured ammonium signal.

Discussion

The experiments described here clearly indicate that some sort of motion occurs in ammonium ferrocyanide between 150 and 315°K that involves the hydrogens of the ammonium groups. There are three primary types of motion that can be responsible for narrowing of the ^{1}H NMR signal, rotation of the ammonium ion upon its site, motion of ammonium ions from site to site, or jumping of protons from site to site.

As discussed earlier, rotation of the ammonium ion has been observed in a number of ammonium compounds (3), and this phenomenon typically gives narrowing of NMR signals well below 200°K. In such cases, however, as shown in Fig. 1, the low temperature value below the narrowing is very large, and the signal does not narrow all the way to the instrumental limit. This low temperature line width includes contributions from both intramolecular and intermolecular interactions, and it has been shown (23) that the former contributes about 16 G in the case of a tetrahedral ammonium ion, so that the total line width in this regime must be in excess of 16 G. Thus at the temperatures studied in this experiment the ammonium ion must be freely rotating upon its site, and the narrowing observed here must be due to averaging out of the intermolecular interactions, and related to site-to-site motion of either ammonium ions or protons themselves. On the basis of the information presently available it is not possible to

Compound	Mobile ion	Q (kJ/mole)	$D_{300°K}$ (cm^2/sec)	$\sigma_{300°K}$ (ohm-cm)$^{-1}$	Reference
H_xWO_3	H	5.4	7×10^{-6}	—	(24)
$(NH_4)_xWO_3$	NH_4/H	16.0	—	—	(10, 11)
$NaAl_{11}O_{17}$	Na	15.8	7×10^{-7}	1.4×10^{-2}	(25)
$AgAl_{11}O_{17}$	Ag	16.5	3×10^{-7}	7×10^{-3}	(26)
$KAl_{11}O_{17}$	K	28.4	3×10^{-9}	6.5×10^{-5}	(27)
$RbAg_4I_5$	Ag	7.1	3×10^{-6}	2×10^{-1}	(28)
$(NH_4)_4Fe(CN)_6 \cdot H_2O$	NH_4/H	19.0	1×10^{-10}	1×10^{-5}	This work

differentiate between these two possibilities. Further experiments for this purpose are being undertaken and will be reported at a later date.

If the diffusional process described above is not restricted to local motion within the crystal, such as about a defect, then it will also be responsible for the ionic conductivity, as it is extremely unlikely that any non-hydrogen containing species will contribute to ionic charge transport. Hence the ionic conductivity, σ, of this material at 300°K is 1×10^{-5} (ohm-cm)$^{-1}$, as calculated from the Nernst–Einstein relationship

$$D = \sigma RT/cq^2, \qquad (11)$$

where q is the electronic charge per mole, and c the concentration of ammonium ions per cm^3; the volume of a formula unit of the ferrocyanide was taken as 250 Å^3, which is typical of most hexacyanides.

Most conventional ionic conductors, such as sodium chloride, exhibit at least two conductivity regimes; one, in which the temperature dependence is determined by the enthalpy of motion of the defect, and the other, which occurs at a higher temperature, also includes the enthalpy of formation of the defect. Super ionic conductors on the other hand, have such a high concentration of native "defects" that their numbers are essentially independent of temperature, and their activation energies for conduction, Q, are generally much less than 50 kJ/mole. This is to be compared with about 100 kJ/mole for the intrinsic region of more conventional ionic conductors.

NMR studies of the ammonium halides (3, 6–8) have failed to show any evidence of translational motion of hydrogen species. In agreement with this, Fuller and Patten (2) found an activation energy for conduction of 121 kJ/mole for

ammonium chloride; this dropped to 14 kJ/mole at low temperatures on doping with a divalent cation, but even then the conductivity was less than 10^{-10} (ohm-cm)$^{-1}$ at 350°K. In contrast, it appears that ammonium ferrocyanide has a conductivity more than six orders of magnitude higher, while having a temperature dependence similar to that of the doped chloride. Clearly such a difference in conductivity must be due to differences in crystal structure, the ferrocyanide structure possibly being of a very open nature as found in other superionic conductors such as the β-aluminas and the tungsten bronzes.

The temperature dependence found for the transport process in ammonium ferrocyanide, 19.0 kJ/mole, is in the general range found for ionic motion in several superionic conductors, as indicated in Table II. These data are also consistent with a recent NMR study (10, 11) of ionic motion in an ammonium tungsten bronze, $(NH_4)_xWO_3$, in which evidence was obtained for both rotational movement of the ammonium ion, and ionic translation of the type described here. The half-narrowed temperature and the activation energy for the diffusion process in the bronze were 213°K and 16.0 kJ/mole, compared to 203°K and 19.0 kJ/mole found for ammonium ferrocyanide. Vannice et al. (24), however, found a much lower activation energy, 5.4 kJ/mole, for proton hopping in a hydrogen tungsten bronze, H_xWO_3, also using NMR techniques.

Acknowledgment

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