

Computer Simulation of the Order-Disorder Transition in Ammonium Chloride

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The phase transition at $T_c = 243$ K in ammonium chloride is well established to be of the order-disorder type. The ammonium chloride has a CsCl-type cubic structure with hydrogen atoms pointing toward four of the eight chloride ions at the corners of the unit cell. This means that there are two possible orientations of ammonium tetrahedron; a and b . In the ordered phase below the T_c temperature all ammonium ions have the same, let it be a , orientation. Above the T_c temperature ions are randomly distributed among the two possible orientations a and b . An attempt was made to correlate such structural transition with the second moment of the proton NMR absorption line. This approach was chosen because the second moment is the parameter of the NMR line for which the exact theoretical formula exist, and which is mainly a function of the structure and the reorientational state of the studied material. It was found that the NMR second moments calculated for the described above model of the structural transition properly reflect the changes of the experimental NMR second moments measured at temperatures below and above this transition.

Key words: NMR, Ammonium chloride, Phase transition, Simulation.

1. Introduction

Ammonium compounds have been a subject of extensive studies by different experimental techniques [1], with NMR methods being one of the most proliferated. Researcher's interest in the ammonium ion is due to its unique properties in a wide temperature range, from liquid helium to room temperature. Ammonium chloride is one of the simplest compounds in this family and one of the most extensively studied by a wide range of experimental and theoretical methods. It is probably the most often studied ammonium compound if one considers ^1H and ^2H NMR techniques. The interest of NMR researcher's in NH_4Cl does not decrease with time, and papers on the subject have been published since 1954 [2–6]. One of the main points of interest is the lambda-type transition at 243 K discovered in NH_4Cl in 1992 [7]. It is now well established that this transition is of the order-disorder type [8].

We have made a successful attempt to correlate this structural transition with the second moment of the proton NMR absorption line. This approach was chosen because the second moment is the parameter of the NMR line for which the exact theoretical formula exists [9], and it is mainly a function of the structure

and the reorientational state of the studied material. By reorientational state we understand the frequency and geometry of the reorientation as well as the model of motion involved. For the model of motion we chose instantaneous jumps between allowed positions of atoms with correlation frequency $\nu_c = 1/(2\pi\tau_c)$ where the correlation time τ_c is the average time spent in the equilibrium (allowed) position.

2. Order-Disorder Transition in NH_4Cl

X-ray studies have shown [10] that on both sides of the transition temperature $T_c = 243$ K the ammonium chloride has the CsCl-type cubic structure. The ammonium ions in this cubic structure are oriented in such a way that hydrogen atoms point toward four of the eight chloride ions at the corners of the unit cell. This leads to two possible orientations of the ammonium tetrahedron; we call them a and b . If we look down the z axis, the orientation b can be obtained from a by rotating the ammonium ion by 90° around this axis.

In the ordered phase below the temperature T_c all ammonium ions have the same orientation, let it be a . All proton-proton vectors in every plane perpendicular to the z -axis are parallel. Vectors from the nearest neighboring (along the z -axis) planes are of

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course perpendicular to themselves. Above the temperature T_c ions are randomly distributed among the two possible orientations a and b . This gives a structure with the consecutive proton-proton vectors in each plane mentioned above being perpendicular to each other. The transition from the ordered to the disordered state is interpreted as the onset of ammonium ion rotation about the three fourfold axes C_4 , with the potential curve for this rotation having two sets of wells with different depth. The C_4 rotation changes the degree of order in the lattice as defined by the number of ions in the allowed (a or b) positions.

From early NMR studies [2, 3] it is known that on both sides of the transition temperature T_c ammonium ions undergo hindered rotation around C_3 axes of symmetry. This rotation has a correlation frequency ν_c of the order of 10^9 s^{-1} , and from the ^1H NMR point of view it is high enough for this geometry of motion, to result in the maximum averaging of dipol-dipol interaction. It is important to notice that C_3 -rotation does not affect, contrary to the C_4 rotation, the degree of order in the lattice as it does not change the position of ammonium ion from a to b or vice versa.

This model of structure and reorientation can easily be simulated on the computer, and Van Vleck's second moment can be calculated for the ordered and disordered phase. On the other hand, the experimental values of the ^1H NMR second moments in single crystal samples of NH_4Cl differ for ordered and disordered phases [3, 4], giving the possibility of confirming or rejecting the models of structure and order-disorder transition assumed for second moment calculation.

3. Second Moment Calculation

Van Vleck's formula for the second moment was originally derived for rigid structures [9]. In the NMR context rigid structure means that any reorientation occurring in the sample must have a frequency much lower than the absorption line-width in frequency unit. The formula for the second moment of the NMR absorption spectrum arising from single crystal of the ammonium chloride (rigid structure), when only hydrogen and nitrogen atoms are taken into account, can be written as

$$M_2^{\text{rig}} = N_{\text{HI}}^{-1} C_{\text{HH}} \sum_{i=1}^{N_{\text{HI}}} \sum_{j=1}^{N_{\text{HT}}} B_{ij}^2 + N_{\text{HI}}^{-1} C_{\text{HN}} \sum_{i=1}^{N_{\text{HI}}} \sum_{k=1}^{N_{\text{NT}}} B_{ik}^2, \quad (1)$$

where N_{HI} is the number of protons in a single ion, N_{HT} the total number of protons considered in the calculation and N_{NT} the total number of nitrogen considered in the calculation.

The index i describes protons from the single ion for which the second moment is calculated, j describes all protons (including those denoted by the index i) taken into account in the calculation, and k describes all nitrogen atoms considered in the calculation. This definition of the indexes means that the value calculated from formula (1) is the second moment of one ammonium ion, arbitrarily chosen from the block of unit cells taken for calculation. At the same time it is a second moment for the macroscopic single crystal sample of ammonium chloride. The last statement is true if we take for the calculation a reasonably large block of unit cells and choose our single ion (with proton indexes i) to be in the center of this block.

The meaning of the other symbols in (1) are as follows:

$$C_{\text{HH}} = \frac{3}{4} \gamma_{\text{H}}^2 \hbar^2 I(I+1), \quad (1a)$$

$$C_{\text{HN}} = \frac{1}{3} \gamma_{\text{N}}^2 \hbar^2 S(S+1), \quad (1b)$$

$$B_{i\alpha} = \frac{3 \cos^2 \Theta_{i\alpha} - 1}{r_{i\alpha}^3}, \quad (1c)$$

with γ_{H} and γ_{N} being the magnetogyric ratio of the hydrogen and nitrogen nucleus, respectively. $I = 1/2$ denotes the proton spin and $S = 1$ the spin of ^{14}N , as only this isotope of nitrogen is included in the calculation. $\Theta_{i\alpha}$ are the angles between the nucleus-nucleus vector and the direction of the external magnetic field H_0 , $r_{i\alpha}$ are the nucleus-nucleus distances. The index α should be replaced by j for protons or k for nitrogens.

To calculate the second moments for ammonium chloride with NH_4^+ ions reorienting one must replace the B_{ij} and B_{ik} terms in (1) with their values averaged by reorientation – $\langle B_{ij} \rangle_{\text{rot}}$ and $\langle B_{ik} \rangle_{\text{rot}}$ [11–13]. These averaged values can be calculated from the expression

$$\langle B_{i\alpha} \rangle_{\text{rot}} = N_{\text{p}}^{-1} \sum_{m=1}^{N_{\text{p}}} \frac{3 \cos^2 \Theta_{izm}^{-1}}{r_{izm}^3}, \quad (2)$$

where N_{p} is the number of positions taken by atoms in the course of reorientation, which averages the $B_{i\alpha}$ term. The index m denotes successive positions taken in the course of reorientation, and index α has the same meaning as before (j for protons, k for nitrogens).

The angles Θ and the distances r are defined as in (1). For practical application of (2) it is very convenient to express these values as a functions of Cartesian coordinates (x, y, z) , and this can symbolically be written as

$$\Theta_{iam} = f_{\Theta}(x_{iam}, y_{iam}, z_{iam}), \quad (2a)$$

$$r_{iam} = f_r(x_{iam}, y_{iam}, z_{iam}). \quad (2b)$$

The functions f_{Θ} and f_r are simple relations from analytical geometry.

The only difficulty connected with the evaluation of $\langle B_{iam} \rangle_{\text{rot}}$ from (2) is the necessity of knowing the x_m, y_m, z_m coordinates for all atoms considered in the calculation at each position m taken in the course of reorientation. In case of ammonium ion reorientation, due to the high symmetry of all possible atom positions, this is a trivial task. If we construct a cube with protons of the ammonium ion at four of its corners, than any type of the allowed reorientation, described in Part 2 can be realized by proper permutation of the protons between the eight corners of this cube. The analogous procedure of "rotating" the benzene molecules is detailedly described in [14].

There is one question to be answered. How to simulate reorientation with a frequency much higher than the NMR line-width for the rigid structure? The answer can be found through the following reasoning. The FID signal from the sample with transverse relaxation time T_2 lasts for the order of T_2 before it falls below noise level of the apparatus. Therefore the total time of recording the NMR signal can be assumed to be of the order of T_2 . If during that time all molecules (ions or atoms) do not change their position, the spectrum resulting from the experiment (after performing Fourier transform of the FID) will be the "rigid structure" spectrum. If, however, during the recording of the FID signal molecules will perform a number of reorientational jumps, the shape of the FID, and consequently the frequency spectrum will be affected by these jumps. Therefore the frequency of jumps required to influence the line shape and width can be "translated" into the number of positions N_p taken for averaging of the terms B defined by (2).

For practical reasons, the calculation of the second moment is often divided into two parts: calculation of the intra- and intermolecular (or intra- and interionic) contributions. We also followed this scheme, which required the summations in (1) over i, j , and k to be split into two parts. This procedure was introduced at the stage of writing the computer program and can be

considered as a simple technical detail of the calculation, not needed to be described here.

For the ammonium ion the number of positions required for averaging is as small as $N_p = 3$ if one is interested in intraionic contributions, but must be a few hundred to give the maximum possible averaging of the interionic contribution. As we want to calculate the total (intra- plus interionic) second moment to be compared with the experimental values, we have to choose N_p large enough to get maximum averaging of the final M_2 .

It is worth reminding that for each geometry of motion there is a maximum averaging obtainable at a certain frequency of reorientation, and further increasing this frequency (number of positions N_p in calculation) does not have any other effect except increasing the CPU time required for performing the calculation.

To make the simulation of the reorientation as close to reality as possible, the frequency of reorientation, and following from it the number of positions N_p , were calculated on the basis of an Arrhenius relation, assuming values of activation energy E_a and preexponential factor ν_0 close to the values given in [15]. This was done to follow in the calculation the real situation in which the frequencies of C_3 and C_2 reorientations increase continuously with temperature, while above the temperature T_c the C_4 type of rotation is released. The number of positions N_p as a function of temperature was calculated from the equation

$$N_p = T_{2\text{exp}}^{\text{rig}} \nu_c \cong (\gamma_H \sqrt{M_{2\text{exp}}^{\text{rig}}})^{-1} \nu_0 \exp(-E_a/RT), \quad (3)$$

where $\text{exp } r$ denotes experimental values, rig stands for rigid structure and ν_c is the correlation frequency of reorientation. Other symbols used in this equation have already been explained in the text.

It is necessary to point out that (3) is not used for any type of fitting procedure, aimed at evaluating the activation energy E_a or correlation frequency ν_c . It is only a tool to relate the calculated second moment to the temperature. In the vicinity of the transition temperature $T_c = 243$ K, the second moment is already averaged to the lowest possible value and does not change with temperature, which is the case in the experiment as well as in our calculation.

With $M_{2\text{exp}}^{\text{rig}} = 40 \times 10^{-8} T^2$, $E_a = 13$ kJ/mol, and $\nu_0 = 1.0 \times 10^{11} \text{ s}^{-1}$ the N_p value changes from about 1000 at 200 K to about 8000 at 250 K. The $N_p = 1000$ gives nearly maximum possible averaging of the second moment. An increase of N_p to 8000 diminished the calculated value of M_2 by less than 0.5%.

4. Numerical Calculation

The calculation of the second moment was performed for a block of 1331 ($11 \times 11 \times 11$) unit cells, assuming the N–H distance to be 0.103 nm and the lattice constant $a = 0.387$ nm. On both sides of the transition temperature the rotation of ammonium ions about four C_3 axes and three C_2 axes was simulated. The number of positions N_p calculated from (3) at 243 K was about 5000. The second moment was evaluated for the magnetic field H_0 parallel to the c -axis of the unit cell of the ammonium chloride crystal.

The order-disorder transition was simulated through rearranging the ammonium ions in such a way that some of them, taken randomly, were rotated by 90° around the C_2 symmetry axis. The disorder parameter η was introduced, and it was defined as the percentage of ammonium ions which rotate by 90° around the C_2 axis at the order-disorder transition. Therefore the complete ordered state has $\eta = 0$, and the “ideal” disordered state has $\eta = 0.5$. The calculated second moment was compared with experimental values taken from [3]. A reasonably good agreement between the experimental and calculated values was achieved for the ordering parameter being in the range

$0.3 \leq \eta \leq 0.35$. Figure 1 presents results of the calculation together with experimental values of the second moment.

5. Conclusions

The procedure for confirming the structure and dynamics of solids on the basis of the second moment calculations seems to be very promising. With the computational power of modern computers the evaluation of the second moment, which takes into account a few thousand atoms and allows different types of reorientation to be introduced, is now feasible and can be exploited for many types of materials, including biomolecules. It must be pointed out that Van Vleck's formula for the second moment is correct on the basis of quantum mechanical calculations.

If one is able to perform a calculation based on this formula, up to the nuclei-nuclei distances of the order of 5.0 nm, then the error due to truncating the summation before the number of nuclei reaches infinity is less than 0.1%. With the typical experimental error in second moment measurements of the order of 5%, the calculations can be considered as more than satisfactory.

The numerical calculations described in this paper give nearly exact values for the total (intra- and inter-ionic) second moment. This is a very important remark, as most of the calculations presented before give only the intraionic (or intramolecular) part of the second moment in the case of reorientation of the atoms. On the other hand, the measured values of the second moment are, of course, the total values arising from intra- and intermolecular interactions, and for quantitative analysis must be compared with the total values calculated from Van Vleck's formula.

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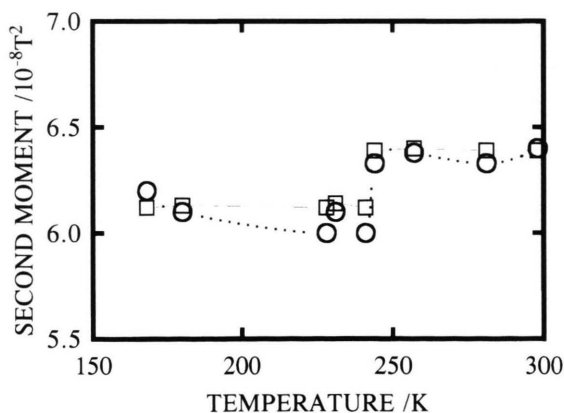


Fig. 1. Proton NMR second moment versus temperature for ammonium chloride in the vicinity of the order-disorder transition for the H_0 direction along the unit cell axis. Circles: experimental values from [3], squares: values calculated as described in the text with $\eta = 0.32$. The dotted and continuous lines are added to guide the eye.

- [1] D. Smith, Chem. Rev. **94**, 1567 (1994).
- [2] H. S. Gutowsky, G. E. Pake, and R. Bersohn, J. Chem. Phys. **22**, 643 (1954).
- [3] R. Bersohn and H. S. Gutowsky, J. Chem. Phys. **22**, 651 (1954).
- [4] J. Itoh, R. Kusaka, and Y. Saito, J. Phys. Soc. Japan **17**, 463 (1962).
- [5] T. Kodoma, J. Magn. Reson. **7**, 137 (1972).
- [6] F. I. Bashirov, J. Magn. Reson. **A 122**, 1 (1996).
- [7] F. Simon, Ann. Physik **68**, 4 (1922).
- [8] H. A. Levy and S. W. Peterson, Phys. Rev. **86**, 766 (1952).
- [9] J. H. Van Vleck, Phys. Rev. **74**, 1168 (1948).
- [10] R. W. G. Wyckoff, Crystal Structures, Vol. I, Table III, Interscience Publishers, Inc., New York 1951.
- [11] A. Abragam, The Principles of Nuclear Magnetism, University Press, Oxford 1961.
- [12] E. R. Andrew, J. Magn. Res. **9**, 108 (1973).
- [13] A. Watton, E. C. Reynhardt, and H. E. Petch, J. Chem. Phys. **65**, 4370 (1976).
- [14] R. Goc, Z. Naturforsch. **52a**, 477 (1997).
- [15] D. E. Woessner and B. S. Snowden, Jr., J. Phys. Chem. **71**, 952 (1967).