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^{1}H NMR observation of the critical slowing down in ammonium chloride

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We have studied the λ transition in ammonium chloride (NH_4Cl) by means of ^{1}H NMR. In previous reports, the ^{1}H NMR spin-lattice relaxation time (T_1) did not show the critical slowing down, whereas the Cl^{35} NMR spin-lattice relaxation time revealed a sharp λ transition at the critical temperature. Our measurements of the ^{1}H solid echo decay constant (T_{2E}) and the second moment near the critical temperature manifest the critical slowing down, and the temperature dependence of the T_{2E} is well explained by the dynamic Ising model.

I. INTRODUCTION

Recently there has been considerable interest in the order-disorder phase transitions, e.g., in the ferroelectric phase transition.[1] Ammonium halides are the typical materials which show the order-disorder phase transitions and have been widely investigated.[2–5]

Since the early days of NMR, a variety of NMR studies of the phase transition in ammoniun halides have been reported.[6–12] The ammonium ions in the CsCl structure are oriented in the unit cell so that the hydrogen atoms point toward four of the eight chlorine atoms at the corner of the cube. This gives two possible orientations for the ammonium ions. In the disordered phase the ammonium ions are randomly distributed in the two orientations, while they are in only one orientation in the completely ordered phase.[2–12]

The proton spin-lattice relaxation in ammonium chlorides arises from three types of the reorientations of an ammonium ion;[7–12] a 120°-flip motion about the threefold axes, and 180° and 90° flips about the twofold axes. The 120°- and 180°-flip motions are possible in the ordered phase. However, the 90°-flip motion is not possible in the completely ordered phase, since it represents the motion of the order variable.

The degree of order in ammonium chloride is closely related to the 90°-flip motion of the ammonium ions, and the ^{35}Cl NMR spin-lattice relaxation time manifests the critical slowing down as it is determined solely by that motion.[9,13,14] On the other hand, the proton spin-lattice relaxation time shows only a slight anomaly at the λ point.[11,12,14,15] The critical slowing down due to the collective motion of the order variable seems to be obscured in the proton spin-lattice relaxation time measurement because it is determined by the combined motion of the three types of the reorientation including the flip-flops of the order parameter variable. Some authors successfully explained the spin-lattice relaxation times of both ^{1}H and ^{35}Cl NMR with the reorientation of the NH_4^+ ions only,[13] while others could explain only that of ^{35}Cl NMR with the critical dynamics.[14] Thus it has been controversial whether the critical dynamics or the molecular motions are dominant near the critical temperature. It is the purpose of this paper to test if the proton spin-spin relaxation shows the critical slowing down in ammonium chloride, which was not observed in the proton spin-lattice relaxation, by measuring the solid echo decay constant near the critical temperature T_c.

II. THEORY

The solid echo decay rate arises from two different origins in ammonium choride. One is the 180°- and the 120°-flip motions which are dominant away from T_c and the other is the 90°-flip motion, which has to do with the collective order-disorder dynamics near T_c. Then it is assumed that the solid echo decay rate T_{2E}^{-1} can be written as

$$T_{2E}^{-1}=T_{2N}^{-1}+T_{2C}^{-1}\,, \tag{1}$$

where T_{2N}^{-1} is the contribution from the intramolecular dipole-dipole interaction which is modulated by the thermally activated molecular motion, and T_{2C}^{-1} is the contribution from the collective critical dynamics.

For the intramolecular dipole-dipole interaction, the spin-spin relaxation rate T_{2N}^{-1} is expressed as[17–19]

$$T_{2N}^{-1}=\frac{1}{3}\gamma^2\langle\delta H^2\rangle\left[3\tau_C+\frac{5\tau_C}{1+(\omega\tau_C)^2}+\frac{2\tau_C}{1+(2\omega\tau_C)^2}\right], \tag{2}$$

$$\tau_c=\tau_0 e^{E/RT}, \tag{3}$$

where E is the activation energy. In the limit $\omega\tau_c \ll 1$, the spin-spin relaxation rate is proportional to the correlation time and is expressed as

$$T_{2N}^{-1}\propto e^{E/RT}. \tag{4}$$

According to previous reports the fast motion limit condition is fulfilled in ammonium chloride in our temperature range and the activation energies are 6.9 kcal/ mole in the ordered phase, and 4.7 kcal/ mole in the disordered phase.[15]

The dynamical susceptibility in the dynamic Ising model can be written in the form

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$$X(\vec{q},\omega)=\frac{X(\vec{q},0)}{1+i\omega\tau(\vec{q})}, \tag{5}$$

and the imaginary part of the dynamical susceptibility becomes, in the limit $\omega\tau(\vec{q})\ll 1$,

$$\mathrm{Im}[X(\vec{q},\omega)]=-\omega\tau(\vec{q})X(\vec{q},0). \tag{6}$$

According to the fluctuation-dissipation theorem, the imaginary part of the dynamical susceptibility is related to the spectral density. Then the spin-spin relaxation rate T_{2C}^{-1} becomes[14]

$$T_{2C}^{-1}\propto\sum_{\vec{q}}\frac{kT}{N^2}\tau(\vec{q})X(\vec{q},0). \tag{7}$$

In order to perform the summation in Eq. (7), we will apply the static and dynamical scaling hypotheses,[20] which allow us to write

$$X(\vec{q},0)=\chi_0 t^{-\gamma}f(q/\chi), \tag{8}$$

$$\tau(\vec{q})^{-1}=\tau_0^{-1}t^{\Delta}g(q/\chi), \tag{9}$$

where τ_0 is the correlation time of the Ising variable, t is given by

$$t=\left|\frac{T-T_c}{T_c}\right|, \tag{10}$$

and the inverse correlation length χ is given by

$$\chi=\chi_0 t^{\nu}. \tag{11}$$

$\tau(\vec{q})^{-1}$ diverges approaching T_c, which is the origin of the critical slowing down.

In the disordered phase and in the limit $\omega\tau(\vec{q})\ll 1$, from Eqs. (7)–(11), we have, as derived by Michel,[14]

$$T_{2C}^{-1}\propto t^{\nu d-\Delta-\gamma},\quad T>T_c, \tag{12}$$

where we have used

$$\int fg^{-1}d\vec{q}\propto\chi^d. \tag{13}$$

In the ordered phase and in the limit $\omega\tau(\vec{q})\ll 1$, it can be assumed that[21]

$$X(\vec{q},0)\tau(\vec{q})=\chi_0\tau_0 fg^{-1}t^{-\Delta-\gamma}(1-\langle s\rangle^2), \tag{14}$$

where $\langle s\rangle$ is the order parameter. Then we have

$$T_{2C}^{-1}\propto t^{\nu d-\Delta-\gamma}(1-t^{2\beta}),\quad T<T_c, \tag{15}$$

where β is a critical exponent of the order parameter.

III. EXPERIMENT

A powder sample of ammonium chloride was commercially available and was carefully sealed in dry argon atmosphere for NMR measurements. A home-built NMR spectrometer was employed for the measurements at the Larmor frequency of 45 MHz in the temperature range 220–270 K. The conventional solid echo pulse sequence $90°\text{-}\tau\text{-}90°_{(90)}$ was used for the solid echo decay constant and the second moment.

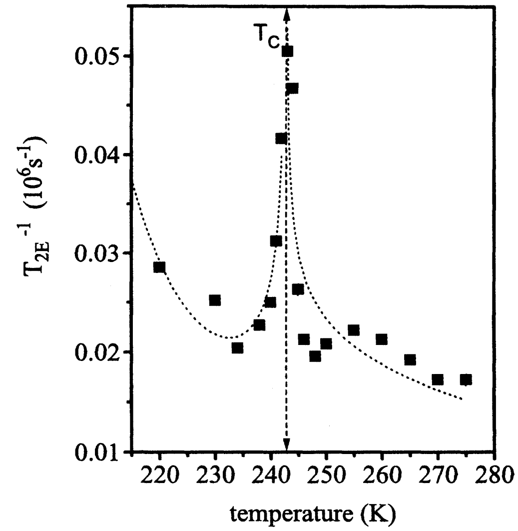

FIG. 1. The solid echo decay rate ($1/T_{2E}$) as a function of temperature. The dotted line is fitted with Eqs. (16) and (17).

IV. RESULTS AND DISCUSSION

The proton spin-spin relaxation rate ($1/T_{2E}$) is shown in Fig. 1 as a function of temperature around the phase transition temperature. It shows a sharp increase approaching the critical temperature. Away from the transition, it increases with decreasing temperature. In contrast to the spin-lattce relaxation, it sharply shows the critical slowing down near T_c. In previous reports, the proton spin-lattice relaxation time measurement showed that on decreasing temperature the correlation time of the proton motion increased discontinuously across T_c.[15] In the fast motion limit, as was dis-

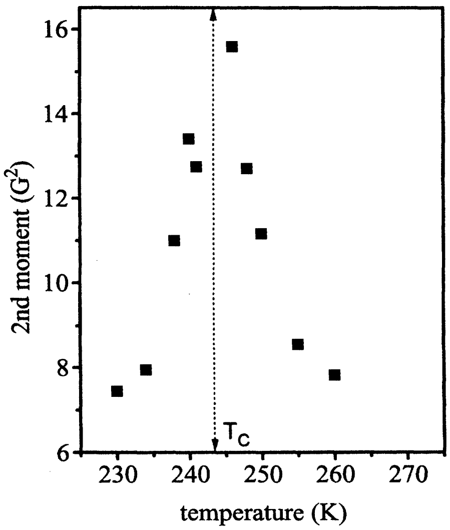

FIG. 2. The second moment as a function of temperature.

cussed, the spin-spin relaxation rate due to the molecular motions is proportional to the correlation time, and should behave in the same manner as the correlation time. However, the solid echo decay rate in our study cannot be described correspondingly. It can then be concluded that the solid echo decay time is dominated not by the thermal motion of the NH_4^+ ion, but by the critical dynamics.

The second moment measurement is shown in Fig. 2. The second moment also increases sharply approaching the critical temperature from either direction. We can see that the second moment of ^1H NMR lineshape also reflects the 90° flip motion of the NH_4^+ ions, which is related to the order-disorder critical dynamics. Then we can analyze the sharp increase of the solid echo decay rate in the light of the dynamic Ising model.

Considering the cubic structure of ammonium chloride, the three-dimensional Ising model is appropriate for our analysis. While the three-dimensional dynamic Ising model has not been exactly solved,[21] the critical exponents have been numerically calculated; $\nu=0.63$, $d=3$, $\gamma=1.25$, and $\beta=0.33$. Using the mean field approximated value $\Delta=1$ because no Δ value is available in the three-dimensional dynamic Ising model, we have $\nu d-\Delta-\gamma = -0.36$. Then we can obtain the best fit with the combination of the three-dimensional Ising model and the molecular motions, combining Eqs. (4), (12), and (15);

$$T_{2E}^{-1}=ae^{E/RT}+bt^{\nu d-\Delta-\gamma},\quad T>T_C, \tag{16}$$

$$T_{2E}^{-1}=a'e^{E/RT}+b't^{\nu d-\Delta-\gamma}(1-t^{2\beta}),\quad T<T_C, \tag{17}$$

where a, b, a', and b' are the appropriate coefficients. The dotted line in Fig. 1 shows the result of the fitting according to Eqs. (16) and (17).

It is worth considering what makes the solid echo decay rate reflect the critical slowing down, which is not reflected in the ^1H spin-lattice relaxation time; while the higher order correlations may smear the critical slowing down in the spin-lattice relaxation time, it may be reflected in the spin-spin relaxation time T_{2E}, since the solid echo refocusses only the two-spin correlations.[16-19]

In summary, we have observed the critical slowing down in the measurements of the ^1H NMR solid echo decay rate and the second moment in ammonium chloride, and explained the temperature dependence of the solid echo decay rate with the three-dimensional Ising model near T_c, and with the molecular motions away from it.

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