Rotating Frame Nuclear Magnetic Relaxation in TlH_2AsO_4

Cheol Eui Lee,* C. H. Lee, and J. H. Kim
Department of Physics, Korea University, Seoul 136-701, Korea

K.-S. Lee
Department of Physics, Inje University, Kimhae 621-749, Korea

(Received 13 June 1995)

We have studied phase transitions in TlH_2AsO_4 using 200 MHz ^1H pulsed NMR. The rotating frame spin-lattice relaxation data fitted the stretched-exponential type, $M(t) = M_0 \exp[-(t/T_{1\rho})^{1-n}]$, below the ferroelastic phase transition temperature, and double-exponential type above that temperature. The exponent n behaved as an order parameter.

PACS numbers: 64.70.Kb, 76.60.–k, 77.80.–e

Thallium dihydrogen arsenate (TlH_2AsO_4, abbreviated as TDA hereafter) is closely related to the KH_2PO_4- (KDP-) type crystals. The KDP-type crystals are the typical hydrogen-bonded materials undergoing structural phase transitions accompanied by ferroelectricity or antiferroelectricity [1]. In these crystals, it is known that protons in double well potentials on the hydrogen bonds undergo a phase transition accompanied by displacements in the heavy atom (K,P,O) structure. One outstanding phenomenon is the proton-deuteron "isotope effect" that raises the transition temperature by about 100 K and decreases the pressure dependence of this transition temperature.

TDA and its isomorph TDP (TlH_2PO_4) undergo two major phase transitions [2–9]. The room temperature phase (phase II) is known to be paraelectric and ferroelastic, while the low temperature phase (phase III) is believed to be antiferroelectric. The antiferroelectric phase transition in TDA is comparable to the antiferroelectric phase transition in ammonium dihydrogen arsenate and to the ferroelectric phase transition in potassium dihydrogen arsenate [6].

The high temperature phase (phase I) is known to be paraelectric and paraelastic. TDA has a monoclinic crystal structure in phases II and III, and an orthorhombic structure in phase I [2–4,9,10]. The II–III phase transition is associated with a doubling of the primitive cell along the *a* and the *b* axis. The II–III phase transition occurs at 251 K (T_c) and is known to be of weak first order, while the I–II phase transition occurs at 391 K (T_c') and is known to be of second order [3,7].

TDP has three different crystallographic hydrogen bonds as determined by neutron diffraction [10]. The two shorter bonds are centrosymmetric and form zigzag chains along the *c* axis. Protons of these bonds are at special positions at a center of inversion and undergo an order-disorder phase transition through the transition temperature T_c [11]. The longest bond is asymmetric along the *b* axis and the protons are at a general position and are ordered both above and below T_c. The very short hydrogen bond lengths and the very heavy mass of Tl^+ ions are peculiar to the TDA and TDP. These features do play an important role in the phase transitions of the TDA.

Protons play a main role in the physical properties and the phase transition mechanism in the KDP-type hydrogen-bonded ferroelectrics in any model, and nuclear magnetic resonance (NMR) and nuclear quadrupole resonance (NQR) studies are essential in probing the proton motions [1]. Few NMR reports on the TDA are found [9], while NMR experiments for KDP have been a subject of much interest [12–15]. Some experiments seem to indicate that selective sites undergo the order-disorder transition in phases II and III [9–17].

Prior to the present work, 45 MHz laboratory frame spin-lattice relaxation measurements were made on TDA and TDP in an effort to understand the proton dynamics, in which no peculiarities attributable to the phase transitions or the proton motions were found. If the proton dynamics does play an important role, this could mean that the protons have quite different correlation times than can be probed in the rf range. Indeed, if the proton motions have much longer correlation times, they would be detected at much lower frequencies, only accessible by the rotating frame experiments.

Thus in the present work we have investigated the rotating frame spin-lattice relaxation in the phases I, II, and III of the TDA in order to probe the ultralow frequency components of the spectral density of the proton motions. From these experimental results, the microscopic proton environments and local dynamics are discussed in the view of successive ordering through the phase transitions.

A polycrystalline sample of TDA was made and investigated in this work using a 200 MHz ^1H pulsed NMR spectrometer. The $T_{1\rho}$ data were obtained by applying a 90° pulse, immediately followed by a long spin-locking pulse, phase shifted by 90° with respect to the 90° pulse. The 90° pulse width used for the $T_{1\rho}$ was 4.7 μs, which gives the frequency of the rotating frame $\omega_1/2\pi = 53.2$ kHz. The $T_{1\rho}$ data were obtained by varying the length of the spin-locking pulse.

0031-9007/95/75(18)/3309(3)$06.00

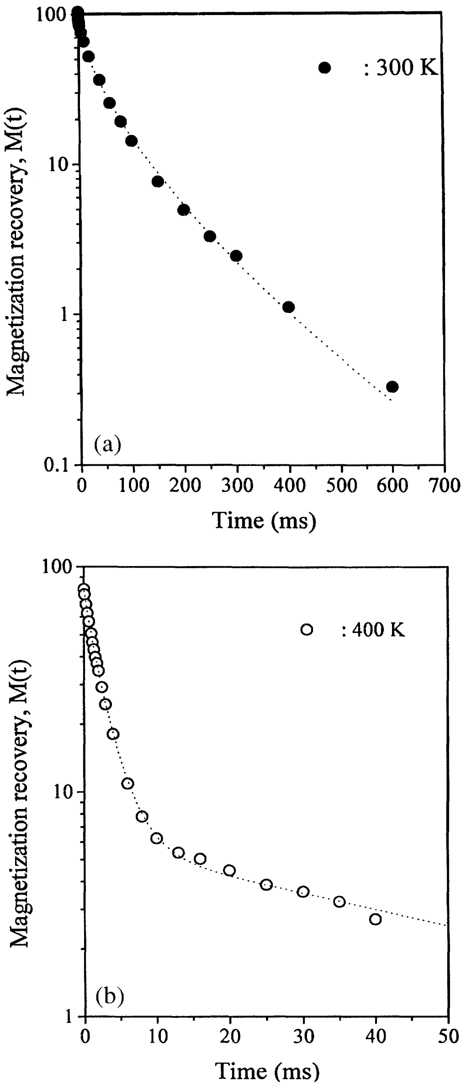

FIG. 1. Rotating frame spin-lattice relaxation of TDA at (a) room temperature and (b) 400 K.

The rotating frame relaxation data obviously deviated from the simple single-exponential form. In phases II and III below T_c', the stretched-exponential type, $M(t) = M_0 \exp[-(t/T_{1\rho})^{1-n}]$, had to be adopted to fit the relaxation data. This is characteristic of a random distribution of the correlation time τ_c for the proton motions. The values of $T_{1\rho}$ and n were obtained by computer fitting. The room temperature relaxation is shown in Fig. 1(a). In phase I above T_c', however, they were well fitted into a double-exponential form, as shown in Fig. 1(b), giving two time constants $T_{1\rho}^{(1)}$ and $T_{1\rho}^{(2)}$. The temperature dependences of $T_{1\rho}$ and n are shown in Figs. 2 and 3, respectively. It is shown that T_1 and n both reflect the critical phenomena around the T_c'.

Recently, the stretched-exponential-type relaxation was found in the glassy systems, notably in the ferroelectric-antiferroelectric mixed crystal $Rb_{1-x}(NH_4)_xH_2AsO_4$, so-called the proton pseudo-spin-glass [18]. Sobol *et al.* attributed the nonexponentiality in that system to a distribution of the microscopic correlation time. The nonexponentiality in our TDA system may be understood in conjunction with the ferroelasticity in phases II and III. The distribution of the spontaneous strain in the ferroelastic microdomains will result in a distribution of the proton double wells each with a characteristic correlation time for the proton motions. The exponent n can reflect the degree of randomness of the proton double well potential, and thus can represent the order in the system.

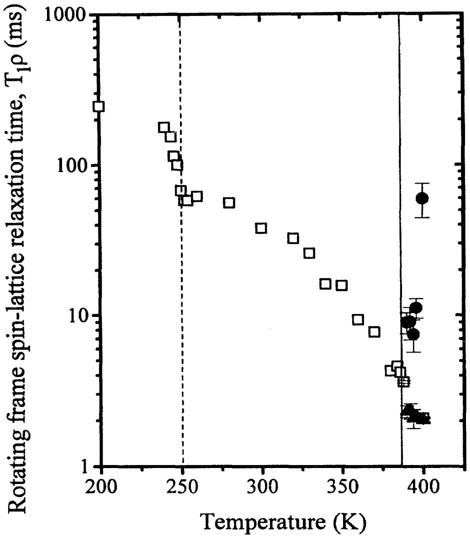

FIG. 2. Temperature dependence of the rotating frame spin-lattice relaxation times.

A random distribution of the proton correlation time as suggested by the stretched-exponential type of relaxation in the TDA, and the observation that the relaxation appears

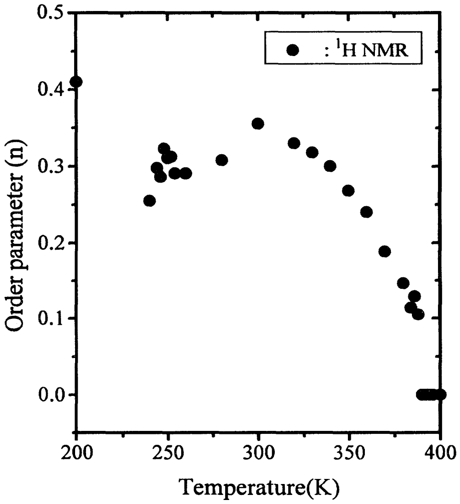

FIG. 3. Temperature dependence of the exponent n.

to be governed by the proton motions associated with the correlation times, apparently supports the dynamic order-disorder model as suggested by related works [8,11].

According to the order-disorder model suggested by the NQR measurements of ^{75}As in TDA [8] and ^{17}O NQR in TDP [11], the O—H · · O hydrogen bonds are "disordered" with symmetric equilibrium sites in the high temperature phases, and in the lower temperature phases some of them become "ordered" or "frozen" in the time scale probed by the NQR. The ordered state corresponds to the asymmetric proton potential wells where the occupation probabilities are not the same between the two sites. The occupation probabilities for the two inequivalent equilibrium proton sites can be written as $(1 + S)/2$ and $(1 - S)/2$, where S can be taken as an order parameter [8]. A small value of S means that the two asymmetric hydrogen bonds are only slightly asymmetric.

Between room temperature and $T_c^{\prime}$ the exponent n in our work showed a temperature dependence of $(T_c^{\prime} - T)^{0.5\pm0.1}$ in comparison to that of $(T_c^{\prime} - T)^{0.55}$ observed by Seliger *et al.* for the order parameter S in the ^{75}As NQR work mentioned above [7]. This similar temperature dependence of n to that of the order parameters S, together with the above observation that it represents the order of the proton double well potential distribution, indicates that the exponent n can be taken as an order parameter.

While the dynamic order-disorder mechanism was supported by experimental observations in TDP [11], another "static" model, in which the high temperature transition is associated with displacements of hydrogens from the central position in the O—H · · O hydrogen bonds, was not completely ruled out by ^{75}As NQR frequency data in TDA although they were well explained by the order-disorder model [8]. However, our rotating frame ^{1}H NMR data, which directly probe the proton motions, warrant exclusion of static types of models, since an excellent fit by a single stretched-exponential function of the proton spin-lattice relaxation of all temperatures below $T_c^{\prime}$ can only be explained by the "dynamic" order-disorder model, which is compatible with our data as well as with previous works. The cross relaxation with ^{75}As, which occurs well outside the range of our NMR frequencies, would not be able to explain our data [8,9].

The double-exponential type of spin-lattice relaxation above $T_c^{\prime}$ may be indicative of the existence of two distinct types of ferroelastic domain structure reported in TDA and TDP single crystals [3,16]. According to previous observations, only one type of the domain structures undergoes the ferroelastic-paraelastic phase transition at T_c, and the other ferroelastic domain structure is retained above $T_c^{\prime}$. Indeed, in Fig. 2 one of the relaxation times above $T_c^{\prime}$ is in continuation with that below $T_c^{\prime}$, whereas the other shows a discontinuous transition. They can be attributed to the ferroelastic and paraelastic domain structures above $T_c^{\prime}$, respectively.

In summary, we have studied the rotating frame spin-lattice relaxation in a polycrystalline sample of $\mathrm{TlH_2AsO_4}$ using 200 MHz ^{1}H pulsed NMR. It was described by a stretched-exponential form in the ferroelastic phase $T_c^{\prime}$ and by a double-exponential form in the paraelastic phase above $T_c^{\prime}$. The exponent n was taken as an order parameter for the order-disorder proton motions. Anomalies in T_1 and n could also be observed around the phase transition temperatures, and our data above the ferroelastic transition temperature support the existence of two types of ferroelastic domain structures in the ferroelastic phase.

This work was supported by the Korea Science and Engineering Foundation through the RCDAMP at Pusan National University, and by the Ministry of Education (Grants No. BSRI-94-2410 and No. BSRI-94-2411). Thanks are due to K. S. Hong at the Korea Basic Science Institute for technical assistance.

---

*To whom all correspondence should be addressed.

[1] R. Blinc and B. Zeks, Ferroelectrics **72**, 193 (1987), and references therein.

[2] K. S. Lee and D. H. Ha, Phys. Rev. B **48**, 73 (1993).

[3] K. Irokawa, M. Komukae, T. Osaka, and Y. Makita, J. Phys. Soc. Jpn. **63**, 1162 (1994).

[4] A. Matsuo, K. Irokawa, M. Kokumae, T. Osaka, and Y. Makita, J. Phys. Soc. Jpn. **63**, 1626 (1994).

[5] R. J. Nelms, Solid State Commun. **39**, 741 (1981).

[6] K. S. Lee, S. M. Ju, K. L. Kim, S. K. Lee, J. H. Kim, J. B. Kim, B. C. Choi, and J. N. Kim, Ferroelectrics **137**, 123 (1992).

[7] K. S. Lee and K. L. Kim, J. Phys. Soc. Jpn. **60**, 3207 (1991).

[8] J. Seliger, V. Zagar, and R. Blinc, Phys. Rev. B **48**, 52 (1993).

[9] R. Blinc, M. Rozmarin, F. Milia, and M. Melisaropoulou, Solid State Commun. **27**, 999 (1978).

[10] R. H. Nelmes and R. N. P. Choudhary, Solid State Commun. **38**, 321 (1981).

[11] J. Seliger, V. Zagar, R. Blinc, and V. H. Schmidt, J. Chem. Phys. **88**, 3260 (1988).

[12] R. J. Nelmes, G. M. Meyer, and J. E. Tibballs, J. Phys. C **15**, 59 (1982).

[13] J. L. Bjorkstam and E. A. Uehling, Phys. Rev. **114**, 961 (1959).

[14] V. H. Schmidt and E. A. Uehling, Phys. Rev. **126**, 446 (1962).

[15] N. Nakamura, Ferroelectrics **78**, 191 (1988).

[16] H. Yoshida, M. Endo, T. Kaneko, T. Osaka, and Y. Makita, J. Phys. Soc. Jpn. **53**, 910 (1984).

[17] T. Matsuo and H. Suga, Solid State Commun. **21**, 923 (1977).

[18] W. T. Sobol, I. G. Cameron, M. M. Pintar, and R. Blinc, Phys. Rev. B **35**, 7299 (1987); I. A. Campbell, J.-M. Flesselles, R. Jullien, and R. Botet, Phys. Rev. B **37**, 3825 (1988); R. Blinc, D. C. Ailion, B. Gunther, and S. Zumer, Phys. Rev. Lett. **57**, 2826 (1986).