Journal of Magnetic Resonance 231 (2013) 54–60

Contents lists available at SciVerse ScienceDirect

Journal of Magnetic Resonance

journal homepage: www.elsevier.com/locate/jmr

Proton dynamics at low and high temperatures in a novel ferroelectric diammonium hypodiphosphate $(NH_4)_2H_2P_2O_6$ (ADhP) as studied by ^1H spin–lattice relaxation time and second moment of NMR line

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ARTICLE INFO

Article history:
Received 9 January 2013
Revised 2 March 2013
Available online 21 March 2013

Keywords:
Solid state
Paraelectric and ferroelectric phases
Internal dynamics
Proton spin–lattice relaxation time
Proton second moment of NMR line
Complex motion
Schrödinger equation
Tunnelling splitting
Tunnelling jump

ABSTRACT

Proton spin–lattice relaxation times T_1 at 24.7 MHz and 15 MHz and second moment of NMR line have been applied to study molecular dynamics of a novel ferroelectric $(NH_4)_2H_2P_2O_6$ (T_c = 178 K) in the temperature range 10–290 K. Low-temperature T_1 behaviour below T_c is interpreted in terms of Haupt's theory and Schrödinger correlation time of tunnelling jumps. A shallow T_1 minimum observed around 39 K is attributed to the C_3 classical motion of "intra" proton–proton vectors of NH_3 (ammonium groups NH_4^+ may perform stochastic jumps about any of the four C_3 symmetry axes). The tunnelling splitting of the ground state vibrational level, $(\nu_T)_{v0}$, of the same frequency for both ammonium groups was estimated as high as 900 MHz ($(\hbar\omega_T)_{v0} = 3.7$ μeV). This tunnelling splitting exists only in the ferroelectric phase. Magnetisation recovery is found to be non-exponential in the temperature regime 63–48 K. The temperature of 63 K is the discovered T^{tun} above which the probability of stochastic tunnelling jumps equals zero. The T_1 relaxation time is temperature independent below 25 K, which is related to a constant value of the correlation time characterising tunnelling jumps according to Schrödinger. The T_1 minima observed in the paraelectric phase (204 K at 15 MHz and 213 K at 24.7 MHz) as well as second moment reduction at about 130 K are attributed to isotropic motion of all protons.

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1. Introduction

Diammonium dihydrogen hypophosphate, $(NH_4)_2H_2P_2O_6$ (ADhP), belongs to an important family of hydrogen bonded ferroelectrics (KDP type). The crystal structure of KDP is characterised by a three dimensional hydrogen bond network. Ferroelectric crystals are particularly attractive because of their wide range of applications, from electronics to optics. Recent prototype applications include ultrafast switching, cheap room-temperature magnetic-field detectors, piezoelectric nanotubes for microfluidic systems, electrocaloric coolers for computers, phased-array radar, and three-dimensional trenched capacitors for dynamic random access memories [1]. New ferroelectric materials with enhanced properties have been continually searched for. The ferroelectric properties of ADhP have been recently reported by Szklarz et al. [2,3]. The crystal is built up of discrete hypophosphate anions $H_2P_2O_6^{-2}$ and ammonium cations NH_4^+. The hypophosphate anions are involved in two types of hydrogen bonds: (i) strong O–H···O bonds (~0.254 nm) connecting the neighbouring moieties into infinite folded ribbons along the *c* direction and (ii) the N–H···O bonds (from 0.277 nm to 0.322 nm) between hypodiphosphate anions and ammonium cations linking anionic ribbons into three-dimensional network. The paraelectric–ferroelectric phase transition in this crystal occurs at about 178 K. The mechanism of this phase transition has been discussed in detail in Ref. [4]. The phase transition has been studied also by specific heat measurements (ac-calorimetry) in Ref. [3]. However, to the best of our knowledge ^1H NMR studies as a function of temperature have not been reported.

The details of the order–disorder phase transition are still not understood, and a particularly interesting question is that concerning the motion of the NH_4^+ ions. The complex molecular dynamics of ND_4 group has been studied by us in paper [5].

Probably NH_4^+ groups are ordered in the ferroelectric low temperature phase and randomly oriented in the unit cells in the paraelectric, high temperature phase. Such an order–disorder transition has been recognised in ammonium halides by Gutowsky et al. [6].

In this article we report the measurements of ^1H NMR spin–lattice relaxation time T_1 at two Larmor frequencies carried for $(NH_4)_2H_2P_2O_6$. The relaxation time T_1 (24.7 MHz) was measured

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http://dx.doi.org/10.1016/j.jmr.2013.03.005

in the wide temperature regime 290–10 K and T_1 (15 MHz) above liquid nitrogen temperature in the range 290–77 K. Results of the second moment of ^{1}H NMR line in the temperature range from 108 K to *RT* support the conclusions following from T_1 measurements. The results are analysed using appropriate theoretical models pertaining to the dynamics of the cations and anions of ADhP at high and low temperatures.

The low temperature T_1 behaviour (63–10 K) is interpreted in terms of NH$_4$ groups undergoing classical and tunnel jumps over and through the triple potential barrier and tunnel splitting of vibrational levels. It is known that the tunnel splitting of NH$_4$ group in a number of solids is large [7].

Ammonium groups NH$_4$ (or ND$_4$) are able to perform hindered rotation about any of the C$_3$ axes which makes their reorientation similar to that of the methyl group. Such anisotropy of reorientation follows from the shape of the three-welled potential experienced by the CH$_4$ group of protons upon their reorientation.

The proton or deuteron spin–lattice relaxation time, T_1, in methyl bearing solids exhibits full flattening at lowest temperatures. In contrast to the other tunnelling correlation times known in literature, that proposed by Schrodinger implies such a property of the temperature dependence of T_1. A constant value of T_1 for ADhP protons was observed in the temperature range (25–10) K.

The T_1 relaxation in higher temperatures (290–96) K can be attributed to the isotropic motion of ADhP protons. The T_1 minimum due to isotropic motion can be well correlated with the second moment reduction occurring in the temperature range (130–178) K (178 K is the phase transition temperature).

2. Experimental

Diammonium hypodiphosphate was prepared by addition of stoichiometric amounts of ammonium carbonate to an aqueous solution of hypodiphosphoric acid, H$_4$P$_2$O$_6$. Single crystals of (NH$_4$)$_2$H$_2$P$_2$)$_6$ were grown by a slow evaporation of the solution at a constant room temperature. The pulverized single crystals of ADHP were degassed under pressure of 10^{-5} Torr and sealed under vacuum in glass ampoules.

The proton spin–lattice relaxation (T_1) measurements at a Larmor frequency 24.7 MHz were carried out on an SXP 4/100 Bruker pulse NMR spectrometer. Proton T_1 relaxation times were measured employing the (180°–τ–90°) pulse (IR) sequence for times shorter than 1 s and by the conventional saturation-recovery (SR) sequence, $[(90°–\tau_1–90°)_n–\tau–90°]$ where $n = 15$. Delay τ_1 was typically of 4 ms. The measurements at 15 MHz were performed on a laboratory made pulse spectrometer.

The temperature of the sample was automatically controlled by means of a gas-flow CF1200 Oxford cryostat to an accuracy of about 1 K, during each measurement.

The NMR measurements were made using an ELLAB TEL-Atomic CWS 12-50 spectrometer. The second moment of ^{1}H NMR line was measured in temperature range from 108 K to room temperature by a continuous wave spectrometer working on protons at the frequency of 26.8 MHz. The second moment values were found by numerical integration of the absorption curve derivatives. The temperature of the sample was controlled by a UNIPAN 660 temperature controller employing a Pt 100 sensor providing long time temperature stability better than 1 K.

3. Theory

Particular contributions to the relaxation rate ($1/T_1$) and the second moment of ^{1}H NMR line are brought by functions of spectral densities depending on the model of motion. The spectral densities depend on the correlation times which characterise the frequency of molecular motions.

The three stochastic motions of the ADHP protons modulate the dipolar interaction Hamiltonian independently of one another. It is the case for the complex motion of R_{is} vector. Each component motion has its own correlation function determined by a different correlation time. The τ_3^H is the correlation time of the jumps over the barrier (C$_3$ motion of the three protons of NH$_4$ group undergoing C$_3$ rotation around the N–H symmetry axis linking N atom with the fourth proton), τ_3^T is the correlation time of the tunnelling jumps of NH$_3$ protons in a triple potential and τ^{iso} (or τ^2) is an additional motion which can be isotropic motion of whole protons or jumps between two equilibrium sites.

The correlation times of C$_3$ jumps over the barrier as well as isotropic motion follow the Arrhenius dependence

$$\tau_3^H = \tau_{03}^H \exp(E_H/RT) \tag{1}$$

$$\tau^{iso(or\,2)} = \tau_0^{iso(or\,2)} \exp\left(E_{iso(or\,2)}/RT\right) \tag{2}$$

where the motional parameters are preexponential factors τ_{03}^H, $\tau_0^{iso(or\,2)}$ and activation energies E_H and $E_{iso(or\,2)}$.

The expression for the tunnelling correlation time has been derived in Refs. [8,9]. This expression follows from the Schrödinger equation [5,8–15]:

$$\tau_3^T = \tau_{03}^T e^{B\sqrt{(E_H - C_pT)}} \tag{3}$$

where

$$B = \frac{2L}{\hbar}\sqrt{\frac{2m}{N_{Av}}} \tag{4}$$

The value of B depends on the mass "m" of the tunnelling particle and on the width of the potential barrier "L". If the mass of the tunnelling proton equals $m = 1.67 \times 10^{-27}$ kg and the barrier width $L = 0.144$ nm (proton–proton distance), then the value of B is $0.2(\sqrt{\text{Joul}})^{-1}$. The average thermal energy equals C_pT, where C_p is the molar specific heat, E_H is the molar activation energy and T is temperature in the Kelvin scale. When $C_pT \ll E_H$, then the tunnelling correlation time assumes a constant value $\tau_3^T = \tau_{03}^T e^{B\sqrt{E_H}}$. The Arrhenius correlation time is long at low temperatures and therefore, T_1 due to tunnelling correlation time becomes temperature independent. Such an effect – the constant value of T_1 has been detected at low temperatures for tunnelling solids [5,8–17]. The tunnelling jumps begin at a low temperature T^{tun} at which the thermal energy of the particle becomes lower than the activation energy ($C_pT \leqslant E_H$). To calculate the tunnelling correlation time, the value of molar heat capacity C_p should be known. This parameter is not constant [3]. Therefore the temperature dependence of C_p should be known.

Because of a significant activation energy of the isotropic motion (or jumps between two equilibrium sites) it usually reveals at high temperatures on the T_1 temperature dependence as a T_1 minimum.

The correlation function and spectral density of this complex motion of R_{is} relaxation vector can be derived in a simple way (Eqs. (18) and (19) in Ref. [15]).

The vibrational relaxation is much faster than the spin–lattice NMR relaxation. Therefore, it can be assumed that at any time the molecules are distributed between the vibrational levels. The fractions of molecules n_{v0} and n_{v1}, in separate vibrational levels can be assumed to be Boltzmann fractions of molecules associated with the average energies of the ground and first excited levels. Because the population of molecules in the second excited vibrational level is very low, it seems reasonable to take into account only two vibrational levels and the relaxation rate is

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