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STUDY OF DOMAIN SIZE IN ORDER- DISORDER NANO-FERROELECTRIC POWDERS FROM NMR RESPONSE OF I=3/2 QUADRUPOLAR SPIN SYSTEMS

AHIRWAL P. K.[1], CHAITANYA P.[2], SHUKLA A.[3] AND *PANDEY L.[1]

[1]Department of Physics & Electronics, Rani Durgavati University, Jabalpur-482001, India
[2]Department of Physics, St. Aloysius College (Autonomous with Potential for Excellence), Jabalpur-482001, India
[3]Department of Physics, National Institute of Technology, Mizoram, Aizawl-796012, India

*Address for correspondence: * Dr .L .Pandey, Professor, Department of Physics & Electronics, Rani Durgavati University, Jabalpur-482001, India,
Email ID: pandeyl@hotmail.com

ABSTRACT

The effect of domain walls on the NMR response of center line transition in I=3/2 quadrupolar spin system has been studied and a method is proposed for the measurement of domain width in order-disorder nano-ferroelectrics. A ferroelectric domain is represented by a one dimensional chain of equidistant nuclear spins having dipolar coupling. Spin populations as function of position, time and ratio of quadrupolar to dipolar transition probabilities are obtained by forming rate equations and solving them for a sample subjected to selective rf pulses by using Laplace Transform. Based on the fact that the electric polarization in an order-disorder ferroelectric undergoes a spiral orientation as one moves from one domain to the adjacent one making the flipping motion of electric dipoles near the domain walls easier due to low activation barrier, it is assumed that at low temperatures the spins near domain walls still undergo relaxation while such a relaxation in the main body of the domain would have almost ceased. The spins present inside the domain undergo relaxation through transfer of magnetization to the domain walls through a spin diffusion process by nearest neighbor interaction. The change produced in central line population by such a process is studied. This is further used to calculate the magnitude of the NMR signal from a powdered sample by summing the contributions from crystallites oriented in all the directions. It is found that the domain width can be estimated by noting the relative amplitude of the pulsed NMR signal at low temperatures provided that relative amplitude of such a signal from a sample of same material with known domain width is also known. The method illustrated by making calculations for ferroelectric $NaNO_2$, is quite general and can be applied to any order disorder ferroelectric with nano sized domains and having spin I=3/2 quadrupolar nuclei.

Keywords: *Spin-lattice relaxation, Spin diffusion, Order-disorder ferroelectrics, Domain width, Nano-ferroelectrics, Spin I=3/2 quadrupolar system.*

INTRODUCTION

Ferroelectrics are a very important class of materials having wide variety of applications in various technological devices such as electro–optic materials, infrared sensors, ultrasonic systems, actuators, electric field and strain sensors, nonvolatile memory devices etc. [10, 25, 28, 29, 35, 36, 38,46]. A material is said to be ferroelectric when it has two or more orientational states of electric polarization and can be reoriented from one state to another by an electric field. If the spontaneous polarization arises due to the ordering of ions or some group of ions, then the ferroelectric is said to be order–disorder ferroelectric. [10, 25, 29]. The thermal motions tend to destroy the ferroelectric order and ferroelectricity usually disappears beyond a certain temperature T_c, called the transition temperature. Below T_c, a ferroelectric material comprises regions of uniform polarization, called domains. Within each domain, the polarization is in the same direction, but in the adjacent

domain it is in different direction. The region joining two adjacent domains is called domain–wall. If the spontaneous polarizations in the adjacent domains are in opposite directions, the domains are called 180° domains and the region joining two 180° domains are called 180°domain-walls. The technological applications of a ferroelectric greatly depend upon its domain structure and behavior and shape of hysteresis loop (polarization vs electric field plot) that in turn is governed by how fast the domains can be switched from one direction to the other. The switching process involves building up of the favorable domains at the expense of the unfavorable ones starting from nucleation and growth at the domain-walls.[29] Also the properties of a ferroelectric tend to change over period of time due to gradual buildup of inhibiting structure at domain walls reducing their mobility.[25,29]

Due to miniaturization trend in device size, many recent research efforts have been focused on the size dependent evolution of ferroelectricity in nano crystalline and thin films samples.[6,11,26,31,38,40, 48,52,53] Single crystalline ferroelectric nano wires and nano tubes having retention time for the induced polarization exceeding several days have been produced.[52] Nano sized nonvolatile polarization domains can be induced on these nanowires indicating that ferroelectric nano wires may be used to fabricate nonvolatile memory devices with an integration density approaching 1 terrabit/cm^2. The potential for application as nonvolatile random access memory has stimulated great interest in the integration of ferroelectric thin films and nano structures.[13,27,39,51] For ultra-high density integration of ferroelectric memories the investigation of size effect and the estimation of domain width has become extremely important.[27]

The ferroelectric properties of thin films samples are studied by using ultra high vacuum Scanned Probe Microscope (SPM). The written polarization is read by using electrostatic force microscopy (EFM) [52] by measuring the shift in the resonance frequency of a SPM cantilever while scanning it with a small tip voltage. The shift is directly proportional to the electrostatic force experienced by the tip and thus to the magnitude of the electric polarization of the nano wire. A plot of the shift as a function of tip position provides a spatial map of electric polarization direction on the nano wire. It has been shown that measured domain size as observed through the EFM is limited by the tip-sample distance (~ few tens of nm) due to long ranged nature of electrostatic interaction. Similarly it has been demonstrated that induced ferroelectric domains as applied through the AFM tip formed information bits with size of 60 nm diameter in PZT. The formed bits were recorded back with high spatial resolution of ~10 nm. Also the polarization retention time is dependent on size of domains.[41] Thus the determination of the size of domains is very crucial for a strategy to achieve maximum integration density.

Study of ferroelectric domains and domain walls including the local dynamics has been drawing considerable attention of research workers in the past as well as in recent years. [12,15,16,17,32,37,38,42,46,50,54] For this various techniques[25] such as optical birefringence, second harmonic generation, electron microscopy, chemical etching, X-ray topography, U.V. photoemission, electrostatic force microscopy, atomic force microscopy etc. have been used for different materials. Nuclear magnetic resonance (NMR) has been a very powerful tool for studying the local environment.[1,8,25,45]

Nuclei with spin $I \geq 1$ possess magnetic dipole moment as well as electric quadrupole moment. Such nuclei respond to the local environment through the interaction of the dipole moments with the local magnetic fields and of the electric quadrupole moments with the electric field gradients. As a result these nuclei can sense subtle changes taking place in the local environment and these changes are recorded through the NMR amplitudes, line widths and relaxation times. The NMR studies of nuclei with $I \geq 1$ have therefore proved to be a very powerful tool for the study of local structure and dynamics including phase transitions. A large number of reports are available on successful use of NMR for such investigations in ferroelectrics; a few illustrative ones are given in the reference. [5, 7, 8, 14, 18, 33] Not much work on the study of effect of domain walls on the spin relaxation is available in literature except those by Kotecha and Pandey [19] and few others [3, 34, 43] for spin I=3/2 systems. In their study the contribution of the domain walls

to the spin lattice relaxation time related to satellite lines and the central line transitions in the NMR spectrum in an order-disorder ferroelectric crystal has been theoretically studied and a method has been proposed for the determination of domain size in nano ferroelectrics. In this paper we present an extension of the work cited above. The NMR signal arising due to population differences in the central line transitions is calculated keeping in mind the nuclear spin relaxation of spin I=3/2 quadrupolar system due to domain walls in order disorder ferroelectrics. The possible application for the determination of domain size in nano ferroelectrics powders possessing spin I=3/2 nuclei is discussed. Wherever necessary the equations and their solutions are reproduced from our earlier paper [43] for completeness. The necessary rate equations for the change of population of various levels in I=3/2 spin system are written as earlier [3, 20, 43] and solved in the next section followed by results and discussions.

CALCULATION OF POPULATION DIFFERENCES FOR SPIN I=3/2 SYSTEM IN AN ORDER-DISORDER NANO FERROEELCTRIC

Let us consider a ferroelectric material of order disorder type having 180^0 domains possessing I=3/2 nuclei. The 180^0 domain–domain wall structure is schematically shown in Fig 1.

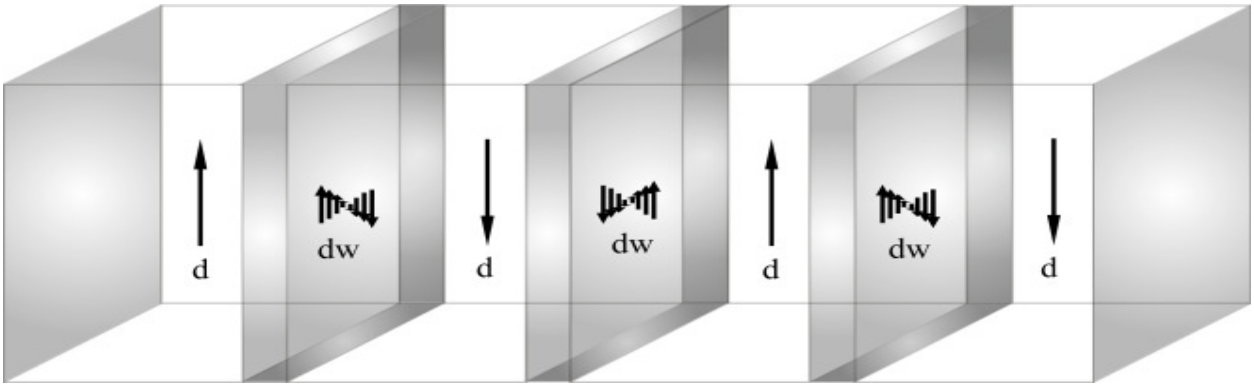

Figure 1: Schematic diagram of 180° domain (d) domain-wall (dw) structure. The arrows indicate the electric polarization. The electric polarization has a spiral orientation as one move from one domain to the adjacent domain.

In order to make the calculations tractable we assume that a 180^0 domain can be represented by a one-dimensional array of equidistant nuclei situated at …x-2*a*, x-*a*, x, x+*a*, x+2*a* ... as shown in Fig 2. The I=3/2 spins would have four Zeeman levels [1,45] with populations $n_{3/}$

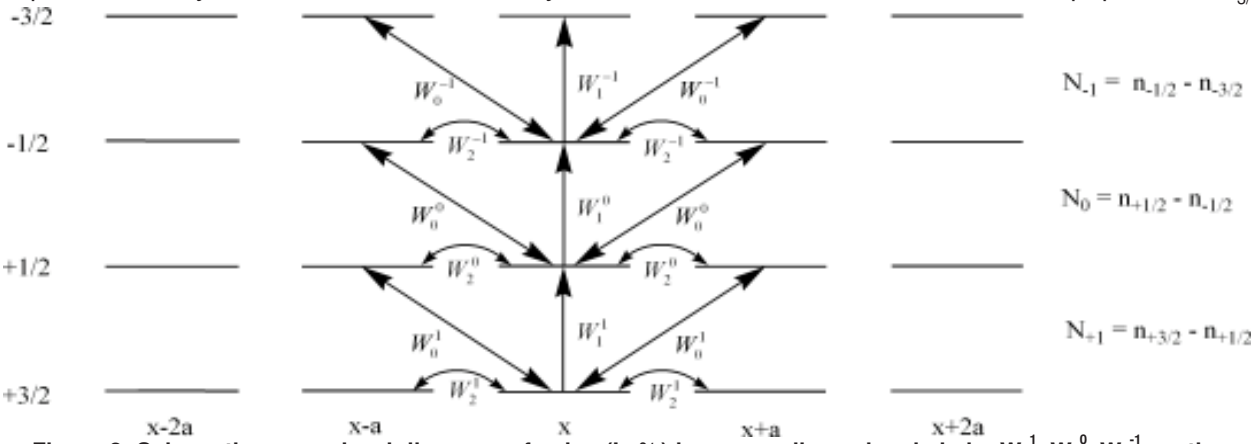

Figure 2: Schematic energy level diagrams of spins (I= $^3/_2$) in a one - dimensional chain. W_0^1, W_0^0, W_0^{-1} are the transition probabilities of $^3/_2 \longleftrightarrow ½$, $½ \longleftrightarrow {}^-½$, $^-½ \longleftrightarrow {}^-3/_2$ levels respectively for the case where one spin undergoing an upward transition while the other spin undergoes downward transition (usually called flip-flop term). W_2^1, W_2^0, W_2^{-1} represent simultaneous upward (or down ward) flip of the pair of spins. W_1^1, W_1^0, W_1^{-1} represent the single spin transition probability for the spin pairs and counted twice for each pair of spins.

$_2$, $n_{1/2}$, $n_{-1/2}$ and $n_{-3/2}$ corresponding to the quantum numbers m=3/2, 1/2, -1/2, -3/2 in an external magnetic field. We further assume that each nucleus interacts with its nearest neighbours only.

The rate of change of deviations of populations from thermal equilibrium values can be written as [1, 4, 19, 23, 24, 43,44]

$$\begin{aligned}
\frac{\partial n_{3/2}(x,t)}{\partial t} = & -2n_{3/2}(x,t)W_1^1 + 2n_{1/2}(x,t)\,W_1^1 - \frac{1}{N}\,n_{3/2}(x,t)\,n_{1/2}(x+a,t)\,W_0^1 \\
& + \frac{1}{N}\,n_{1/2}(x,t)\,n_{3/2}(x+a,t)\,W_0^1 - \frac{1}{N}\,n_{3/2}(x,t)\,n_{1/2}(x-a,t)\,W_0^1 \\
& + \frac{1}{N}\,n_{1/2}(x,t)\,n_{3/2}(x-a,t)\,W_0^1 - \frac{1}{N}\,n_{3/2}(x,t)\,n_{3/2}(x+a,t)\,W_2^1 \\
& + \frac{1}{N}\,n_{1/2}(x,t)\,n_{1/2}(x+a,t)\,W_2^1 - \frac{1}{N}\,n_{3/2}(x,t)\,n_{3/2}(x-a,t)\,W_2^1 \\
& + \frac{1}{N}\,n_{1/2}(x,t)\,n_{1/2}(x-a,t)\,W_2^1
\end{aligned}$$

$$\begin{aligned}
\frac{\partial n_{1/2}(x,t)}{\partial t} = & \; 2n_{3/2}(x,t)W_1^1 - 2n_{1/2}(x,t)\,W_1^1 - 2n_{1/2}(x,t)W_1^0 + 2n_{-1/2}(x,t)\,W_1^0 \\
& - \frac{1}{N}\,n_{3/2}(x-a,t)\,n_{1/2}(x,t)\,W_0^1 - \frac{1}{N}\,n_{1/2}(x,t)\,n_{3/2}(x+a,t)\,W_0^1 \\
& + \frac{1}{N}\,n_{3/2}(x,t)\,n_{1/2}(x-a,t)\,W_0^1 + \frac{1}{N}\,n_{3/2}(x,t)\,n_{1/2}(x+a,t)\,W_0^1 \\
& + \frac{1}{N}\,n_{-1/2}(x,t)\,n_{1/2}(x+a,t)\,W_0^0 - \frac{1}{N}\,n_{1/2}(x,t)\,n_{-1/2}(x-a,t)\,W_0^0 \\
& + \frac{1}{N}\,n_{-1/2}(x,t)\,n_{1/2}(x-a,t)\,W_0^0 - \frac{1}{N}\,n_{1/2}(x,t)\,n_{-1/2}(x+a,t)\,W_0^0 \\
& + \frac{1}{N}\,n_{3/2}(x,t)\,n_{3/2}(x+a,t)\,W_2^1 - \frac{1}{N}\,n_{1/2}(x,t)\,n_{1/2}(x+a,t)\,W_2^1 \\
& + \frac{1}{N}\,n_{3/2}(x,t)\,n_{3/2}(x-a,t)\,W_2^1 - \frac{1}{N}\,n_{1/2}(x,t)\,n_{1/2}(x-a,t)\,W_2^1 \\
& - \frac{1}{N}\,n_{1/2}(x,t)\,n_{1/2}(x+a,t)\,W_2^0 + \frac{1}{N}\,n_{-1/2}(x,t)\,n_{-1/2}(x+a,t)\,W_2^0 \\
& - \frac{1}{N}\,n_{1/2}(x,t)\,n_{1/2}(x-a,t)\,W_2^0 + \frac{1}{N}\,n_{-1/2}(x,t)\,n_{-1/2}(x-a,t)\,W_2^0
\end{aligned}$$

$$\begin{aligned}
\frac{\partial n_{-1/2}(x,t)}{\partial t} = & \; 2n_{1/2}(x,t)W_1^0 - 2n_{-1/2}(x,t)\,W_1^0 - 2n_{-1/2}(x,t)W_1^{-1} + 2n_{-3/2}(x,t)\,W_1^{-1} \\
& - \frac{1}{N}\,n_{1/2}(x-a,t)\,n_{-1/2}(x,t)\,W_0^0 - \frac{1}{N}\,n_{-1/2}(x,t)\,n_{1/2}(x+a,t)\,W_0^0 \\
& + \frac{1}{N}\,n_{1/2}(x,t)\,n_{-1/2}(x-a,t)\,W_0^0 + \frac{1}{N}\,n_{1/2}(x,t)\,n_{-1/2}(x+a,t)\,W_0^0 \\
& + \frac{1}{N}\,n_{-3/2}(x,t)\,n_{-1/2}(x+a,t)\,W_0^{-1} - \frac{1}{N}\,n_{-1/2}(x,t)\,n_{-3/2}(x-a,t)\,W_0^{-1} \\
& + \frac{1}{N}\,n_{-3/2}(x,t)\,n_{-1/2}(x-a,t)\,W_0^{-1} - \frac{1}{N}\,n_{-1/2}(x,t)\,n_{-3/2}(x+a,t)\,W_0^{-1} \\
& + \frac{1}{N}\,n_{1/2}(x,t)n_{1/2}(x+a,t)\,W_2^0 - \frac{1}{N}\,n_{-1/2}(x,t)\,n_{-1/2}(x+a,t)\,W_2^0 \\
& + \frac{1}{N}\,n_{1/2}(x,t)\,n_{1/2}(x-a,t)\,W_2^0 - \frac{1}{N}\,n_{-1/2}(x,t)\,n_{-1/2}(x-a,t)\,W_2^0 \\
& + \frac{1}{N}\,n_{1/2}(x,t)\,n_{1/2}(x-a,t)\,W_2^0 - \frac{1}{N}\,n_{-1/2}(x,t)\,n_{-1/2}(x-a,t)\,W_2^0 \\
& - \frac{1}{N}\,n_{-1/2}(x,t)\,n_{-1/2}(x+a,t)\,W_2^{-1} + \frac{1}{N}\,n_{-3/2}(x,t)\,n_{-3/2}(x+a,t)\,W_2^{-1} \\
& - \frac{1}{N}\,n_{-1/2}(x,t)\,n_{-1/2}(x-a,t)\,W_2^{-1} + \frac{1}{N}\,n_{-3/2}(x,t)\,n_{-3/2}(x-a,t)\,W_2^{-1}
\end{aligned}$$

$$\begin{aligned}
\frac{\partial n_{-3/2}(x,t)}{\partial t} = & \; 2n_{-1/2}(x,t)\,W_1^{-1} - 2n_{-3/2}(x,t)\,W_1^{-1} \\
& + \frac{1}{N}\,n_{-1/2}(x,t)n_{-3/2}(x+a,t)\,W_0^{-1} - \frac{1}{N}\,n_{-3/2}(x,t)n_{-1/2}(x+a,t)\,W_0^{-1} \\
& + \frac{1}{N}\,n_{-1/2}(x,t)n_{-3/2}(x-a,t)\,W_0^{-1} - \frac{1}{N}\,n_{-3/2}(x,t)n_{-1/2}(x-a,t)\,W_0^{-1} \\
& + \frac{1}{N}\,n_{-1/2}(x,t)n_{-1/2}(x+a,t)\,W_2^{-1} - \frac{1}{N}\,n_{-3/2}(x,t)n_{-3/2}(x+a,t)\,W_2^{-1} \\
& + \frac{1}{N}\,n_{-1/2}(x,t)n_{-1/2}(x-a,t)\,W_2^{-1} - \frac{1}{N}\,n_{-3/2}(x,t)n_{-3/2}(x-a,t)\,W_2^{-1}
\end{aligned}$$

Eq. (1)

Where $N = n_{3/2} + n_{1/2} + n_{-1/2} + n_{-3/2,}$ and W^1_0, W^0_0, W^{-1}_0 are the transition probabilities of 3/2 ⟷ 1/2, 1/2 ⟷ -1/2, -1/2 ⟷ -3/2 levels respectively for the case where one spin is undergoing an upward transitions while the other spin undergoes downward transition (usually called flip-flop term).[1,45] The probabilities W^1_2, W^0_2, W^{-1}_2 represent simultaneous upward (or down ward) flip of the pair of spins. Similarly W^1_1, W^0_1, W^{-1}_1 represent the single spin transition probability for the spin-pairs and counted twice for each pair of spins. Here we have used the same symbols and notations as used earlier in Ref.[20, 43]

Defining the polulation differences as

$N_{+1} = n_{3/2} - n_{1/2}$

$N_0 = n_{+1/2} - n_{-1/2}$

$N_{-1} = n_{-1/2} - n_{-3/2}$

And assuming that

W^i_0 ≅ $W^i_0(x, x+a)$ ≅ $W^i_0(x, x-a)$ (for i = 1, 0, -1)

W^i_2 ≅ $W^i_2(x, x+a)$ ≅ $W^i_2(x, x-a)$

As adjacent neighbors have identical interactions, we can rewrite Eq. (1) as

$$\begin{aligned}
\frac{\partial N_{+1}}{\partial t}(x,t) = & -2\rho N_{+1}(x,t) - 2\sigma N_{+1}(x+a,t) - 2\sigma N_{+1}(x-a,t) \\
& + \rho' N_0(x,t) + \sigma' N_0(x+a,t) + \sigma' N_0(x-a,t)
\end{aligned}$$

$$\begin{aligned}
\frac{\partial N_0}{\partial t}(x,t) = & \; \rho N_{+1}(x,t) + \sigma N_{+1}(x+a,t) + \sigma N_{+1}(x-a,t) \\
& - 2\rho' N_0(x,t) - 2\sigma' N_0(x+a,t) - 2\sigma' N_0(x-a,t) \\
& + \rho'' N_{-1}(x,t) + \sigma'' N_{-1}(x+a,t) + \sigma'' N_{-1}(x-a,t)
\end{aligned}$$

$$\begin{aligned}
\frac{\partial N_{-1}}{\partial t}(x,t) = & \; \rho' N_0(x,t) + \sigma' N_0(x+a,t) + \sigma' N_0(x-a,t) \\
& - 2\rho'' N_{-1}(x,t) - 2\sigma'' N_{-1}(x+a,t) - 2\sigma'' N_{-1}(x-a,t)
\end{aligned}$$

Eq. (2)

where

$$\rho = 2W_1^1 + \frac{W_0^1}{2} + \frac{W_2^1}{2}, \qquad \sigma = \frac{W_2^1 - W_0^1}{4}$$

$$\rho' = 2W_1^0 + \frac{W_0^0}{2} + \frac{W_2^0}{2}, \qquad \sigma' = \frac{W_2^0 - W_0^0}{4}$$

$$\rho'' = 2W_1^{-1} + \frac{W_0^{-1}}{2} + \frac{W_2^{-1}}{2}, \qquad \sigma'' = \frac{W_2^{-1} - W_0^{-1}}{4}$$

After Taylor series expansion of the terms $N_{+1}(x+a, t)$, $N_{-1}(x+a, t)$, $N_0(x+a, t)$, $N_0(x-a,t)$, $N_{-1}(x-a, t)$, $N_{+1}(x-a, t)$ about x and retaining the terms up

to the second order the set of Eq. (2) reduces to

$$\frac{\partial N_{+1}}{\partial t}(x,t) = -2a_1 N_{+1}(x,t) + 2D_1 \frac{\partial^2}{\partial x^2} N_{+1}(x,t) + a_2 N_0(x,t) - D_2 \frac{\partial^2}{\partial x^2} N_0(x,t)$$

$$\frac{\partial N_0}{\partial t}(x,t) = a_1 N_{+1}(x,t) - D_1 \frac{\partial^2}{\partial x^2} N_{+1}(x,t) - 2a_2 N_0(x,t) + 2D_2 \frac{\partial^2}{\partial x^2} N_0(x,t) + a_2 N_{-1}(x,t) - D_2 \frac{\partial^2}{\partial x^2} N_{-1}(x,t)$$

$$\frac{\partial N_{-1}}{\partial t}(x,t) = a_2 N_0(x,t) - D_2 \frac{\partial^2}{\partial x^2} N_0(x,t) - 2a_3 N_{-1}(x,t) + 2D_3 \frac{\partial^2}{\partial x^2} N_{-1}(x,t) \quad \text{Eq. (3)}$$

Where

$$a_1 = \rho + 2\sigma \qquad a_2 = \rho' + 2\sigma' \qquad a_3 = \rho'' + 2\sigma''$$

$$D_1 = -\sigma a^2 \qquad D_2 = -\sigma' a^2 \qquad D_3 = -\sigma'' a^2$$

Now these coupled simultaneous partial differential equations representing spin diffusion are solved by using Laplace Transform. [22, 2, 21, 43] Taking the Laplace Transform of Eq. (3) over the variable *t* and denoting the transforms as

$Z_{+1} = \Lambda\{N_{+1}(x, t)\}$, $Z_0 = \{N_0(x, t)\}$, $Z_{-1} = \{N_{-1}(x, t)\}$, Eq. (3) yields

$$4C_2 \frac{\partial^2 Z_{+1}}{\partial x^2} + (4C_1 + 3s) Z_{+1} + 2sZ_0 + sZ_{-1} = k_1$$

$$2C_4 \frac{\partial^2 Z_0}{\partial x^2} + sZ_{+1} + (2s + 2C_3) Z_0 + sZ_{-1} = k_2$$

$$4C_6 \frac{\partial^2 Z_{-1}}{\partial x^2} + sZ_{+1} + 2sZ_0 + (4C_5 + 3s) Z_{-1} = k_3 \quad \text{Eq. (4)}$$

With

$k_1 = 3N_{+1}(x, 0) + N_{-1}(x, 0) + 2N_0(x, 0)$
$k_2 = N_{+1}(x, 0) + N_{-1}(x, 0) + 2N_0(x, 0)$
$k_3 = N_{+1}(x, 0) + 3N_{-1}(x, 0) + 2N_0(x, 0)$

and $C_1 = 2W_1^1 + W_2^1$, $C_2 = -\frac{a^2}{4}(W_0^1 - W_2^1)$

$C_3 = 2W_1^0 + W_2^0$, $C_4 = -\frac{a^2}{4}(W_0^0 - W_2^0)$

$C_5 = 2W_1^{-1} + W_2^{-1}$, $C_6 = -\frac{a^2}{4}(W_0^{-1} - W_2^{-1})$

For the given I = 3/2 system, the value of the probabilities can be written as [43, 45]

$$W_0^1 = \frac{9}{8}\frac{A_0^2}{\hbar^2}(1 - 3\cos^2\theta)^2 \tau_c$$

$$W_0^0 = 2\frac{A_0^2}{\hbar^2}(1 - 3\cos^2\theta)^2 \tau_c$$

$$W_0^{-1} = \frac{9}{8}\frac{A_0^2}{\hbar^2}(1 - 3\cos^2\theta)^2 \tau_c$$

$$W_1^1 = \frac{27}{8}\frac{A_0^2}{\hbar^2}\sin^2\theta\cos^2\theta\,\tau_c$$

$$W_1^0 = \frac{9}{2}\frac{A_0^2}{\hbar^2}\sin^2\theta\cos^2\theta\,\tau_c$$

$$W_1^{-1} = \frac{243}{8}\frac{A_0^2}{\hbar^2}\sin^2\theta\cos^2\theta\,\tau_c$$

$$W_2^1 = \frac{81}{8}\frac{A_0^2}{\hbar^2}\sin^4\theta\,\tau_c$$

$$W_2^0 = 18\frac{A_0^2}{\hbar^2}\sin^4\theta\,\tau_c$$

$$W_2^{-1} = \frac{81}{8}\frac{A_0^2}{\hbar^2}\sin^4\theta\,\tau_c$$

where $A_0 = \gamma_I \gamma_I \hbar^2 / r^3$, q is the polar angle of the radius vector joining two nuclei with respect to the external magnetic field and τ_c is the correlation time. The internuclear spacing is denoted by r and γ_1 is the gyromagnetic ratio.

The Eq. (4) are coupled partial differential equations and were difficult to solve analytically for the general case. So we made a simplifying assumption that only those transitions where

one spin is undergoing an upward transitions while the other spin undergoes downward transition (the so-called flip-flop terms) [1, 43, 45] are important. We therefore set C_1, C_3 and C_5 in Eq. (4) equal to zero. The Eq. (4) can then be written as

The Eq. (4) can then be written as

$$Z''_{+1} = -\frac{1}{9|b|}\left[k_1 - 3s\,Z_{+1} - 2sZ_0 - sZ_{-1}\right]$$

$$Z''_{0} = -\frac{1}{8|b|}\left[k_2 - s\,Z_{+1} - 2sZ_0 - sZ_{-1}\right]$$

$$|b| = \frac{a^2 W_{00}}{16},\ W_{00} = W_0^0 = \left(\frac{2A_0^2}{\hbar^2}\right)\left(1 - 3\cos^2\theta\right)$$

$$Z''_{-1} = -\frac{1}{9|b|}\left[k_3 - s\,Z_{+1} - 2sZ_0 - 3sZ_{-1}\right]$$

Eq. (5)

Where

$$|b| = \frac{a^2 W_{00}}{16},\ W_{00} = W_0^0 = \left(\frac{2A_0^2}{\hbar^2}\right)\left(1 - 3\cos^2\theta\right)$$

's' being the Laplace variable.

The set of Eq. (5) can be solved for different initial and boundary conditions. For an easy comparison of the results with the generally performed pulsed NMR relaxation measurements or devising new experiments and also to study the domain-wall effects, we consider the following situations.

An intense radio frequency pulse is applied to the sample at a frequency that would be equal to the central line frequency in a crystal of same material. We make a crude assumption to begin with that it causes a fraction a of spins flip from the lower state I = 1/2 to the higher state I = -1/2 and the population differences become

$$N_0(x, 0) = -2a,\quad N_{-1}(x, 0) = a,\quad N_{+1}(x, 0) = a$$

Eq. (6)

The time t = 0 corresponds to the end of the pulse. To demonstrate the procedure of calculations the value of a is chosen to be 0.5 which corresponds to a $\pi/2$ pulse for crystals. A single 180° domain with the domain-wall at its end is considered. The origin of the coordinates, x = 0, is taken at the domain-wall and the wall is taken to be thin.

Quadrupolar nuclei such as ^{23}Na in $NaNO_2$ possess both magnetic moment and electric field gradient. It is known that spin lattice relaxation of quadrupolar nuclei in ferroelectrics usually occurs predominantly through interaction of quadrupole moment with the fluctuating electric field gradients that are created by local motions of ions or group of ions. For example, it has been shown that ^{23}Na nuclei in $NaNO_2$, which is an order-disorder ferroelectric, undergo spin-lattice relaxation due to flipping motions of NO_2 [33]. Also it was shown by Hughes and Pandey[14,33] that in order-disorder ferroelectrics the electric polarization undergoes a spiral orientation as one move from one domain to the other. If we visualize the whole sample to be made up of thin slices, then it means that the polarization in adjacent slices in the larger body of the domains are almost parallel to each other, whereas the polarization in the slices close to the domain wall have progressive relative tilts so that it gets completely reversed in the adjacent domain. As a result, the activation barrier E_a for the flipping motion of group of ions in the regions close to the domain-wall would most likely be lower as compared to that for the regions deep inside the domain. As the flip probability at any temperature T would vary as $\exp(-E_a/kT)$,it is implied that at lower temperatures, when the flips in the interior body of domain would have almost ceased the groups near or inside the wall may still be executing some flipping motions. This in turn, implies that nuclei near the walls would be still experiencing relaxation whereas those deep inside the domain would not be relaxing. Further, it has been recently found by Blinc and coworkers [49] that ^{23}Na spin-lattice relaxation rate in micro confined $NaNO_2$ in the ferroelectric is similar to that in the bulk. Therefore, we liberally assume that the nature of quadrupolar relaxation for nuclei at the domain-wall is similar to that for those deep inside the domain for order-disorder ferroelectrics in general. Therefore we further assume that the populations at the domain-wall follow the time dependence [4, 30, 43]

$$N_{\pm1}(0, t) = a\,e^{-2W_1 t}$$

$$N_0(0, t) = a\,[e^{-2W_1 t} + e^{-2W_2 t}]$$

Eq. (7)

Where W_1 and W_2 are the quadrupolar relaxation probabilities corresponding to the transition m = ±3/2 ⟷±1/2 and m = ± 3/2 ⟷ +1/2 respectively. It should be noted in deciding the location of the origin, i.e. x = 0, that the NMR of nuclei lying inside the wall would not be usually observable due to structural disorders. So, x = 0 would correspond to the region near the wall. At present we are assuming that the wall thickness is negligible.

Using the above boundary conditions, Eq. (5) were solved to yield

$$Z_{+1}(x,s) = - a_3\left(1-\frac{\varphi_1^2}{18}\right)e^{-m_1 x} - a_4\left(1-\frac{\varphi_2^2}{18}\right)e^{-m_2 x} - \frac{A_2}{2}e^{-x\sqrt{\mu s}} + \frac{-k_2+k_3}{2s}$$

$$Z_0(x,s) = a_3 e^{-m_1 x} + a_4 e^{-m_2 x} - \frac{k_1-4k_2+k_3}{4s}$$

$$Z_{-1}(x,s) = - a_3\left(1-\frac{\varphi_1^2}{18}\right)e^{-m_1 x} - a_4\left(1-\frac{\varphi_2^2}{18}\right)e^{-m_2 x} + \frac{A_2}{2}e^{-x\sqrt{\mu s}} + \frac{k_1-k_2}{2s}$$

Eq. (8)

Where

$$\varphi_1^2 = 25+\sqrt{337}, \qquad \varphi_2^2 = 25-\sqrt{337}$$

$$m_1 = \varphi_1\sqrt{\frac{s}{72|b|}}, \qquad m_2 = \varphi_2\sqrt{\frac{s}{72|b|}}$$

$$\mu = \frac{2}{9|b|}$$

$$A_2 = -\frac{k_1-k_3}{2s}$$

$$a_3 = -\frac{18}{\varphi_2^2-\varphi_1^2}\left\{\begin{array}{l} -\frac{k_1-2k_2+k_3}{4s} - \left(\frac{\varphi_1^2}{18}-1\right)\left(\frac{k_1-4k_2+k_3}{4s}\right) \\ +\frac{\varphi_1^2}{18}\frac{\alpha}{s+2W_1} + \left(\frac{\varphi_1^2}{18}-1\right)\frac{\alpha}{s+2W_2}\end{array}\right\} + \frac{k_1-4k_2+k_3}{4s} - \frac{\alpha}{s+2W_1} - \frac{\alpha}{s+2W_2}$$

$$a_4 = \frac{18}{\varphi_2^2-\varphi_1^2}\left\{\begin{array}{l} -\frac{k_1-2k_2+k_3}{4s} - \left(\frac{\varphi_1^2}{18}-1\right)\left(\frac{k_1-4k_2+k_3}{4s}\right) \\ +\frac{\varphi_1^2}{18}\frac{\alpha}{s+2W_1} + \left(\frac{\varphi_1^2}{18}-1\right)\frac{\alpha}{s+2W_2}\end{array}\right\}$$

By taking the inverse Laplace Transform [2] of Eq. (8) the values of $N_{\pm1}(x, t)$ and $N_0(x, t)$ can be written as

$$N_{+1}(x,t) = C_{11}\phi_1(x,t) + C_{12}\phi_2(x,t) + C_{13}\phi_3(x,t) + C_{14}\phi_4(x,t) + C_{15}\phi_5(x,t) + C_{16}\phi_6(x,t) + C_{17}\phi_7(x,t) + C_{18}$$

$$N_{-1}(x,t) = C_{21}\phi_1(x,t) + C_{22}\phi_2(x,t) + C_{23}\phi_3(x,t) + C_{24}\phi_4(x,t) + C_{25}\phi_5(x,t) + C_{26}\phi_6(x,t) + C_{27}\phi_7(x,t) + C_{28}$$

$$N_0(x,t) = C_{31}\phi_1(x,t) + C_{32}\phi_2(x,t) + C_{33}\phi_3(x,t) + C_{34}\phi_4(x,t) + C_{35}\phi_5(x,t) + C_{36}\phi_6(x,t) + C_{38}$$

Eq. (9)

Where

$$C_{11} = C_{21} = -\left(1-\frac{\varphi_1^2}{18}\right)C_{31} = -\left(1-\frac{\varphi_1^2}{18}\right)\left[\begin{array}{l}\frac{\frac{18}{4}(k_1-2k_2+k_3)}{\varphi_2^2-\varphi_1^2} + \frac{18}{\varphi_2^2-\varphi_1^2}\times\left(\frac{\varphi_1^2}{18}-1\right) \\ \frac{(k_1-4k_2+k_3)}{4} + \frac{(k_1-4k_2+k_3)}{4}\end{array}\right]$$

$$C_{12} = C_{22} = -\left(1-\frac{\varphi_1^2}{18}\right)C_{32} = \left(1-\frac{\varphi_1^2}{18}\right)\left(\frac{\varphi_2^2}{\varphi_2^2-\varphi_1^2}\right)$$

$$C_{13} = C_{23} = -\left(1-\frac{\varphi_1^2}{18}\right)C_{33} = \left(1-\frac{\varphi_1^2}{18}\right)\left[\left(\frac{\varphi_1^2}{18}-1\right)\frac{18}{\varphi_2^2-\varphi_1^2}+1\right]$$

$$C_{14} = C_{24} = -\left(1-\frac{\varphi_2^2}{18}\right)C_{34} = -\left(1-\frac{\varphi_2^2}{18}\right)\left[\begin{array}{l}\frac{-\frac{18}{4}(k_1-2k_2+k_3)}{\varphi_2^2-\varphi_1^2} - \frac{18}{\varphi_2^2-\varphi_1^2}\times \\ \left(\frac{\varphi_1^2}{18}-1\right)\left(\frac{(k_1-4k_2+k_3)}{4}\right)\end{array}\right]$$

$$C_{15} = C_{25} = -\left(1-\frac{\varphi_2^2}{18}\right)C_{35} = \left(1-\frac{\varphi_2^2}{18}\right)\left(\frac{\varphi_1^2}{\varphi_2^2-\varphi_1^2}\right)$$

$$C_{16} = C_{26} = -\left(1-\frac{\varphi_2^2}{18}\right)C_{36} = \left(1-\frac{\varphi_2^2}{18}\right)\left[\left(\frac{\varphi_1^2}{18}-1\right)\frac{18}{\varphi_2^2-\varphi_2^2}\right]$$

$$C_{17} = -\frac{k_1-k_3}{4}, \quad C_{27} = \frac{k_1-k_3}{4}, \quad C_{18} = \frac{k_1-k_2}{4}, \quad C_{28} = \frac{k_3-k_2}{4}, \quad C_{38} = -\frac{k_1-4k_2+k_3}{4}$$

And $f_1(x, t)$, $f_2(x, t)$ etc. are complicated functions involving error functions as given below

$$\phi_1(x,t) = erfc\left(\frac{x\varphi_1}{\sqrt{72|b|}}\frac{1}{2\sqrt{t}}\right)$$

$$\phi_2(x,t) = \frac{\alpha}{2}e^{-2W_1 t}\left\{\begin{array}{l} e^{\sqrt{-2W_1}\frac{x\varphi_1}{\sqrt{72|b|}}}erfc\left(-\sqrt{-2W_1 t}+\frac{x\varphi_1}{\sqrt{72|b|}}\frac{1}{2\sqrt{t}}\right) \\ + e^{\sqrt{2W_1}\frac{x\varphi_1}{\sqrt{72|b|}}}erfc\left(\sqrt{-2W_1 t}+\frac{x\varphi_1}{\sqrt{72|b|}}\frac{1}{2\sqrt{t}}\right)\end{array}\right\}$$

$$\phi_3(x,t) = \frac{\alpha}{2} e^{-2W_2 t} \left\{ \begin{array}{l} e^{-\sqrt{-2W_2}\frac{x\varphi_1}{\sqrt{72|b|}}} erfc\left(-\sqrt{-2W_2 t} + \frac{x\varphi_1}{\sqrt{72|b|}}\frac{1}{2\sqrt{t}}\right) \\ + e^{\sqrt{-2W_2}\frac{x\varphi_1}{\sqrt{72|b|}}} erfc\left(\sqrt{-2W_2 t} + \frac{x\varphi_1}{\sqrt{72|b|}}\frac{1}{2\sqrt{t}}\right) \end{array} \right\}$$

$$\phi_4(x,t) = erfc\left(\frac{x\varphi_2}{\sqrt{72|b|}}\frac{1}{2\sqrt{t}}\right)$$

$$\phi_5(x,t) = \frac{\alpha}{2} e^{-2W_1 t} \left\{ \begin{array}{l} e^{-\sqrt{-2W_1}\frac{x\varphi_2}{\sqrt{72|b|}}} erfc\left(-\sqrt{-2W_1 t} + \frac{x\varphi_2}{\sqrt{72|b|}}\frac{1}{2\sqrt{t}}\right) \\ + e^{\sqrt{-2W_1}\frac{x\varphi_2}{\sqrt{72|b|}}} erfc\left(\sqrt{-2W_1 t} + \frac{x\varphi_2}{\sqrt{72|b|}}\frac{1}{2\sqrt{t}}\right) \end{array} \right\}$$

$$\phi_6(x,t) = \frac{\alpha}{2} e^{-2W_2 t} \left\{ \begin{array}{l} e^{-\sqrt{-2W_2}\frac{x\varphi_2}{\sqrt{72|b|}}} erfc\left(-\sqrt{-2W_2 t} + \frac{x\varphi_2}{\sqrt{72|b|}}\frac{1}{2\sqrt{t}}\right) \\ + e^{\sqrt{-2W_2}\frac{x\varphi_2}{\sqrt{72|b|}}} erfc\left(\sqrt{-2W_2 t} + \frac{x\varphi_2}{\sqrt{72|b|}}\frac{1}{2\sqrt{t}}\right) \end{array} \right\}$$

$$\phi_7(x,t) = erfc\left(x\sqrt{\frac{2}{9|b|}}\frac{1}{2\sqrt{t}}\right)$$

The functions $\phi_2(x, t)$, $\phi_3(x, t)$, $\phi_5(x, t)$ and $\phi_6(x, t)$ can be simplified using the numerical expansion of complex error function.

The average values of the population differences for the entire domain would then be given by

$$N_i(t) = \frac{1}{L}\int_0^L N_i(x,t)\,dx$$

Eq. (10)

Where i =1, 0 or –1 and L is the thickness of the domain. In our treatment domain-wall thickness has been ignored. For clarity and ready reference the symbols and useful expressions have been kept same as taken in the Ref.[19, 43]

RESULTS AND DISCUSSION

The time dependence of the population differences $N_{+1}(t)$, $N_{-1}(t)$ and $N_0(t)$ as given by Eq.(9) and (10) were evaluated numerically using 32 point Gaussian quadrature [Abramowitz 1972] for different values of the ratios W_1/W_{00} taking W_2/W_1 = 1 and various values of L/a by Shukla et al.[43] and Pandey et al.[34].The necessary computer programs were developed in BASIC language. Wherever needed relevant data for ferroelectric $NaNO_2$ were used just to see the behavior. It was found that $N_{\pm1}(t)$ and $N_0(t)$ are in general non exponential. Treating the quantity $(W_{00}a^2)^{1/2}$ as the diffusion coefficient D, the function $(W_{00}a^2t)^{1/2}$ becomes the diffusion length and provides an estimate of the distance up to which the magnetization would have diffused from the domain-walls (x = 0) into the domain in time t. The quantity $(\sqrt{W_{00}}a^2t)/L$ then gives an estimate of the portion of the domain of length L getting affected in time t due to relaxation occurring in the domain wall. Values of the population differences $N_{\pm1}(t)$ and $N_0(t)$ were calculated for various values of L/a and were plotted (L ranging approximately from 1 nm to 20 nm, a = 3.56 A^0 for $NaNO_2$). These plots can be found in references [34, 43]. It was further found that $N_{\pm1,0}(t)$ follow a power law dependence on 't' given by

$$N_{\pm1,0}(t) = C_1\left(\frac{L}{a}\right)^p\left(\frac{1}{W_{00}}\right)^{\frac{p}{2}} t^{-\frac{p}{2}}$$

Eq. (11)

The values of C_1 and p would depend upon the ratios W_2/W_1 and W_1/W_{00}. Relaxation time was chosen to be equal to the duration in which $N_{\pm1,0}(t)$ has decayed to e^{-1} of some initial value [43].

Based on the theoretical studies it was proposed that, if the spin lattice relaxation time for a ferroelectric of usual domain size is known, then the domain width of an unknown sample of the same ferroelectric having nano-sized domains can be estimated by measuring the value of relaxation time for that sample at low temperatures. This was further proposed that these results were quite general and can be applied to any ferroelectric system having 180° domains. For applying these results to powders an averaging over various orientations has to be carried out.

A crystalline powder is an assembly of single crystals randomly oriented in different directions. The satellite signals would not be clearly visible in the spectrum. However a calculation can be done to get an approximate behavior of the time dependence of the NMR signal arising due to domain wall effects after radiating the sample by a radio frequency pulse applied close to the centre line frequency of spin I=3/2 system and

calculating $N_0(t)$. The calculations can be simplified by treating the powder as made up of single crystals possessing domains of length L having one dimensional array of spin I=3/2 nuclei as shown in Fig 2. And obtaining the sum over all orientations θ (0 to 180^0) and ϕ (0 to 360^0). The signal is approximated by the population difference $N_0(t)$ as given by Eq (9). However, Eq (10) is modified to

$$N_i(t) = \int_{\theta=0}^{\pi}\int_{\varphi=0}^{2\pi}\left[\frac{1}{L}\int_0^L N_i(x,t,\theta,\varphi)\,dx\right]\sin\theta\,d\theta\,d\varphi$$

Eq. (12)

The numerical calculations were performed by utilizing trapezoidal rule for integration over the angles θ (0 to 180^0) and ϕ (0 to 360^0) and using the 32 - point Gaussian Quadrature program employed for single crystal calculations described in the previous section as a subroutine. The computer program was developed in house in BASIC.

It was observed that the time dependence of $N_0(t)$ is non-exponential. An attempt was made to get an empirical relation representing this time dependence. Since, now we are treating the powder as an assembly of one dimensional arrays oriented in various directions, the quantity $(4\pi/3)(\sqrt{W_{00}a^2t})/L)^3$,which is nothing but the volume fraction, would then give an estimate of the portion getting affected in time t due to relaxation occurring in the domain wall.The variation of $N_0(t)$ as function of$(4\pi/3)(\sqrt{W_{00}a^2t})/L)^3$, is shown in Fig. 3 in logarithmic plots for various values of the ratio of domain width to internuclear spacing a denoted by L/a . For plotting value of W_{00} is chosen as 0.005[47] and the values of N_0 at various times (denoted by N_0 (T) (II) where T= W_{00} (t) have been normalized by dividing by the value, N_0 (T) (1), just after the pulse.

It is noted that the plots in Fig 3 are almost linear and N_0 (t) can be empirically represented

$$\frac{N_0(t)}{N_0(1)} = C\left[\left(\frac{4\pi}{3}\right)\left(\frac{\sqrt{W_{00}a^2t}}{L}\right)^3\right]^m$$

Eq. (13)

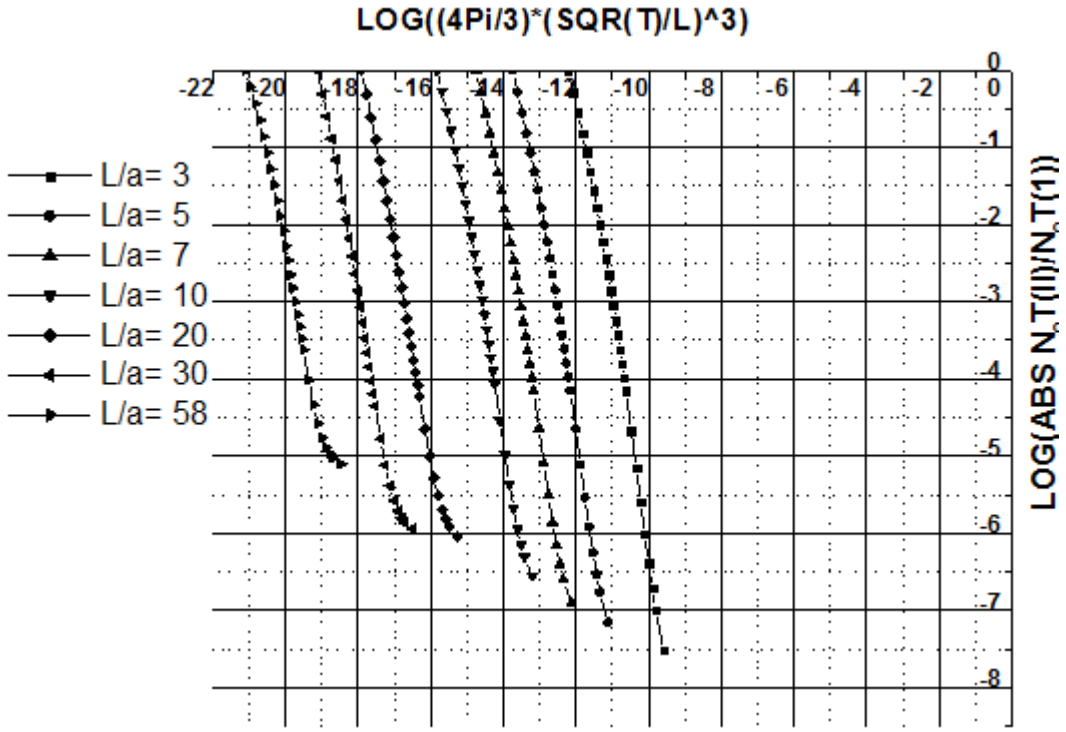

Figure 3. Variation of Log(Abs $(N_0(T)(II)/N_0(T)(1))$ as function of $(4\pi/3)[\sqrt{(W_{00}t)}/(L/a)]^3$ for various values of the ratio of domain width to inter nuclear spacing , L/a (ie L= 1.068 nm to 20.648 nm) using a= 3.56 A^0 for $NaNO_2$. T=0.005 t.

Where C is a constant and m is the slope that depend upon the domain width. $N_0(1)$ is the value of $N_0(t)$ just after the pulse and has been used to normalize the values for easy comparison. It is clear from Eq. (13) that it can be used to compare the domain widths in samples of same material since values of W_{00} and the interatomic spacing 'a' would be the same. Also, using this equation domain width in a sample of unknown domain width can be estimated by noting the signal amplitude after the NMR pulse provided that corresponding signal amplitude in a sample of known domain width is available.

It may be mentioned that these results are quite general and can be applied to any ferroelectric system having 180^o domains. It is worth mentioning here that spin lattice relaxation for I=3/2 system in a ferroelectric would get contributions from various mechanisms. However as mentioned earlier, in most of the ferroelectrics the relaxation is usually quadrupolar and proceeds through the interaction between nuclear electric quadrupole moment and the fluctuating electric field gradient which generally arises due to flipping/tumbling motions of ionic groups (for example NO_2 group in $NaNO_2$). As these flipping/tumbling motions almost cease at low temperatures the relaxation rate becomes very small at low temperatures in a quadrupolar system. Thus the method that we propose here involves two steps: first the pulsed NMR signal amplitude of I=3/2 nuclei in the ferroelectric material of known domain width should be measured at low temperatures, second the corresponding value is measured again at same temperature for the same nuclei but in the sample with unknown nano sized domains. Then the width of the nano domains is obtained from the Fig. 3 just by comparison and Eq. (13). The values of constants appearing in eq. (13) would be constant for a given material and would in general be different for different materials. Therefore we would have specific graph such as fig.3 for different materials. These results are general and are expected to prompt experimentalists to verify them.

CONCLUSIONS

The pulsed NMR signal of I=3/2 quadrupolar spin system due to domain-walls in order-disorder ferroelectric was theoretically studied by representing the 180^0 domain by a chain of equidistant I=3/2 spins. The electric polarization undergoes spiral orientation as one moves from one domain to the adjacent one. This implies that if we treat the domain to be made up of thin slices, then the polarization in the slices deep inside the domain would be almost parallel to each other whereas the polarization in slices near the domain-wall would undergo larger relative tilts. Therefore owing to the lower activation barrier near the walls the probability of activated reorientational flipping motions of group of ions near the wall would be more. As a result at a given temperature, the nuclei near the walls would be experiencing quadrupolar relaxation whereas those inside the domain would not do so. This would lead to spin diffusion from the domain-walls. Rate equations are formed for the population difference for I=3/2 quadrupolar nuclei and are solved analytically using Laplace Transform. Expression for signal amplitude taking into account relaxation due to domain-walls is derived in terms of domain width. A general method is proposed for estimation of domain width of a nano-ferroelectric powder by measuring the NMR signal at low temperatures and using the corresponding value for the same ferroelectric having domains of known width. This may also be used for estimating the extent of poling of a powder sample of order-disorder nano-ferroelectrics.

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