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Fluorine dynamics in BaF₂ crystal lattice as an example of complex motion in a simple system

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ABSTRACT

Fluorine relaxation profiles for a BaF₂ single crystal collected at several temperatures have been analyzed in terms of essentially different motional models: free rotational and free translational diffusion. The analysis has been performed to critically review the sensitivity of field dependent relaxation studies to mechanisms of molecular motions. The tested motional models do not realistically describe the fluorine dynamics within the crystal lattice. They have been chosen to attempt to answer quite fundamental questions regarding the feasibility of the field dependent nuclear spin relaxation studies to provide unique information on dynamic processes: 1. Is it possible to get information about the motional mechanisms by analyzing relaxation profiles collected in a broad frequency range? 2. To what extent is it possible to reasonably reproduce relaxation profiles in terms of unrealistic motional models?

It has been concluded from the analysis that the rotational model leading to a single exponential correlation function explains the experimental data much better than the translational one. Validity regimes of the second order perturbation theory have been discussed in the context of the investigated system and the applied models.

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1. Introduction

Nuclear spin relaxation studies are commonly considered as a source of information on mechanisms of motional processes in molecular systems. Within the perturbation regime relaxation rates are given as linear combinations of spectral densities obtained as Fourier transform of time correlation functions. Different motional processes lead to different forms of the correlation functions and, in consequence, the expected relaxation rates vary. In this way, relaxation experiments provide information not only on the timescale of dynamic processes but also, in principle, on the mechanism of motion. This is quite unique and it is worthwhile to put effort extracting such information from relaxation data. Especially helpful are here field dependent relaxation studies. As long as one considers relaxation at one magnetic field (or even at a couple of them) the measured relaxation time can be obtained for various forms of the spectral densities by adjusting the correlation time. Performing such studies at several temperatures one may possibly meet difficulties attempting to analyze the data. If the chosen motional model was incorrect the obtained correlation times might turn out to be

unrealistic or they might change with temperature in a non reasonable way. Such situations arouse our curiosity and encourage us to inquire appropriate motional models. However, it is also likely to obtain a quite consistent interpretation employing a model which does not capture the motional features. Eventually, one might complain that the correlation times obtained for different temperatures do not follow nicely the Arrhenius behavior (for example [1]); however it is rather obvious that the Arrhenius law is a highly idealized picture of real molecular dynamics, because of its single exponential character and the assumption of temperature independent energy barrier. Interpretation of relaxation profiles is much more demanding. The proposed motional models (reflected in the shape of spectral densities) are now compared with experimental data which cover a broad range of frequencies and therefore reveal dynamic processes of different timescales.

This paper is meant as a critical review of the problem of to which extent one can conclude from field dependent relaxation studies on the mechanisms of motional processes. For this purpose we have chosen a rather simple system, namely a single crystal of BaF₂. The crystal exhibits face centered cubic (fcc) structure (space group *Fm* $\bar{3}$ *m*) of cations in which all tetrahedrally coordinated interstices are filled with fluorine ions. Here, each cation is surrounded by eight anions and each anion is tetrahedrally coordinated to four cations [2–4]. The fluorine ions

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jump within available lattice sites and this process causes the fluorine relaxation. However, the focus of the paper is not on a detailed interpretation of fluorine dynamics in BaF₂-type crystals but on the sensitivity of relaxation studies to the nature of investigated motions. This relatively simple system of identical spins 1/2 (¹⁹F nuclei) with only one kind of molecular motion has only been chosen as an example. Since we are interested in major differences in the character of molecular motion, in this paper we attempt to explain fluorine relaxation profiles of BaF₂ collected in a broad frequency range for several temperatures, in terms of essentially different models, namely free rotation and free translation. We consider such an analysis as a possible way to test whether the relaxation studies indeed reflect the most important features of dynamic processes. By applying the free rotation model [5,6] one assumes that the inter-spin distance (in this case, the distance between fluorine ions) does not change in time, while the force free translation diffusion [7,8] allows for unrestricted changes of this distance. None of the models reflect the real character of the fluorine motion. However, by considering the limiting cases we attempt to illustrate the following problems:

- (1) Is it possible to get information about the motional mechanisms by analyzing relaxation profiles collected in a broad frequency range?
- (2) To what extent is it possible to reasonably reproduce relation profiles in terms of unrealistic motional models?

It is very important to point out that most attempts of interpreting and analyzing solid state relaxation data are based on a single exponential correlation function, like the free rotation model, even though it is obvious that the inter-spin distances vary in time. In this context, the illustration given in this paper is very important.

The paper is organized as follows: Section 2 is devoted to the subject of the perturbation description of relaxation, in Section 3 experimental details are given, in Section 4 several motional models are introduced and the data analyses based on these models are presented, while Section 5 contains a discussion of the results of Section 4, Section 6 contains concluding remarks.

2. Relaxation processes

This short section covers basic textbook information [for example 5,6,9,10]. We present it to provide the basic equations, terminology and labeling used in the next sections and underline the limitations of the perturbation treatment of relaxation.

Fluorine nuclear spin relaxation in BaF₂ is caused by dipole-dipole interactions between fluorine spins of the spin quantum number 1/2, mediated by jump diffusion of fluorine ions between available sites within the crystal cubic lattice. In the case of two identical spins $I_1 = I_2 = I = 1/2$, mutually coupled by dipole-dipole interaction, the spin lattice relaxation rate $R_1 = 1/T_1$ (where T_1 is the spin lattice relaxation time), is given by the very well known expression [5,6,9–15]:

$$R_1 = \frac{3}{2} \left(\frac{\mu_0}{4\pi} \gamma_I^2 \hbar \frac{1}{r_{12}^3} \right)^2 [J_1(\omega_0) + 4J_2(2\omega_0)] \quad (1)$$

The quantities $J_1(\omega_0)$ and $J_2(2\omega_0)$ are spectral densities obtained as Fourier transforms of corresponding time correlation functions $C_1(t)$ and $C_2(t)$ (they will be defined later) taken at the nuclear spin Larmor frequency ω_0 and $2\omega_0$, respectively; γ_I is gyromagnetic factor of the nuclear spin and r_{12} is a distance between the two interacting spins, other symbols in Eq. (1) have obvious meanings. Setting up this equation it has been assumed that the

inter-spin distance does not fluctuate in time, i.e. it remains unchanged. Relaxation equations given as combinations of spectral densities stem from the second order perturbation theory and therefore they are valid if the perturbing interaction (in this case the dipole-dipole coupling) fulfills the ‘Redfield condition’ [5,6,9–17], i.e. in this case: $|H_{DD}\tau_c| \ll 1$, where τ_c is a characteristic time constant (correlation time) reflecting the timescale of fluctuations of the dipole-dipole interaction. In BaF₂ crystals, the distance between neighboring fluorine ions can be estimated as 3.1 Å [2–4,18]. This implies that Eq. (1) breaks down and may not be applied if the correlation time becomes of the order of $7 \cdot 10^{-6}$ s or longer.

Being aware of this limitation of perturbation relaxation equations one can turn attention to the form of spectral densities (correlation functions) determining the relaxation rates. Dipole-dipole coupling between spins I_1 and I_2 is a second rank interaction described in the laboratory frame by the Hamiltonian $H_{DD}^{(L)}(I_1, I_2)$ [5,6,9,10,17]:

$$H_{DD}^{(L)}(I_1, I_2) = \sqrt{6} \frac{\mu_0}{4\pi} \gamma_I^2 \hbar \sum_{m=-2}^2 (-1)^m F_{-m}^2(t) T_m^2(I_1, I_2) \quad (2)$$

It has been assumed that $\gamma_{I_1} = \gamma_{I_2} = \gamma_I$. The components $T_m^2(I_1, I_2)$ of the two-spin tensor operator have the form: $T_0^2(I_1, I_2) = 1/\sqrt{6}[2I_{1z}I_{2z} - 1/2(I_{1+}I_{2-} + I_{1-}I_{2+})]$, $T_{\pm 1}^2(I_1, I_2) = \mp 1/2[I_{1z}I_{2\pm} + I_{1\pm}I_{2z}]$, $T_{\pm 2}^2(I_1, I_2) = (1/2)I_{1\pm}I_{2\pm}$. The spatial (time dependent) part of the dipole-dipole Hamiltonian is defined as:

$$F_{-m}^{2(L)}(t) = \left[\frac{D_{0,-m}^2(\Omega)}{r_{12}^3} \right] (t) \quad (3)$$

where the Wigner rotation matrices $D_{0,-m}^2(\Omega)$ with the Euler angle $\Omega \equiv (\alpha, \beta, \gamma)$ describe the orientation of the dipole-dipole axis with respect to the laboratory frame. It should be noted that the term containing the inter-spin distance r_{12} has been included into the spatial tensor components, since in general, both the orientation of the dipole-dipole axis as well as the inter-spin distance fluctuate in time. In the relaxation theory the time correlation functions $C_m(t)$ ($m = 12$ in Eq. (1)) refer to the $F_{-m}^{2(L)}(t)$ quantities and are defined as [5,6,17,19]:

$$C_m(t) = \langle F_{-m}^{2(L)*}(t) F_{-m}^{2(L)}(0) \rangle \\ = \int \int F_{-m}^{2(L)*}(\vec{r}) F_{-m}^{2(L)}(\vec{r}_0) P(\vec{r}, \vec{r}_0, t) P_{eq}(\vec{r}_0) d\vec{r}_0 d\vec{r} \quad (4)$$

In the above equation the vectors $\vec{r} \equiv (\Omega_{DD,L}(t), r_{12}(t))$ and $\vec{r}_0 \equiv (\Omega_{DD,L}(0), r_{12}(0))$ are position vectors (describing the orientation of the dipole-dipole axis as well as the inter-spin distance) at time t and at time 0. The conditional probability density $P(\vec{r}, \vec{r}_0, t)$ that the interacting spins are described by the vector \vec{r} at the time t if they were described by the vector \vec{r}_0 at the initial time can be obtained by solving the diffusion equation. $P_{eq}(\vec{r}_0)$ is the equilibrium distribution of states; in particular it describes the probability of finding the position vector \vec{r}_0 in equilibrium. The diffusion equation assumes a form appropriate for the chosen motional model that leads to the obvious conclusion that the conditional probability $P(\vec{r}, \vec{r}_0, t)$ is determined by the nature of the motion and its timescale.

3. Experimental details and sample preparation

The relaxation experiments have been carried out at a home built electronic field cycling (FC) spectrometer. The spectrometer is equipped with a high temperature probehead which allows for sample temperatures up to 1400 K [20]. The heart of the electronic FC spectrometer [21] is an air-core solenoidal resistive coil system. A field cycle consists of three phases: (a) The sample is polarized

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