NQR Studies of Phase Transitions and Intermolecular Interactions in Crystals*

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Simple methods to analyze the anomalous behavior of NQR parameters are presented. Unusual positive temperature coefficients of antimony resonance frequencies in $(NH_4)_2SbF_5$ below the phase transition at 169 K were interpreted in terms of ordering processes of the ammonium ions. Calculation of the EFG in LaF_3 revealed that the translational diffusion of Li ions brings about an anomalous decrease in η of the ^{139}La NQR at high temperatures. The same kind of an EFG calculation was made to predict the ^{14}N NQR frequency in Li_3N. The calculation of the intermolecular potential energy was used to evaluate the potential barrier to molecular rotation in C_6Cl_6 and *sym*-$C_6Cl_3F_3$. It was shown in the latter that the quadrupolar relaxation, due to a reorientational jump to a metastable site, works in the low temperature phase below 296 K while the molecular three-fold reorientation is the dominant relaxation mechanism in the high temperature phase.

Introduction

NQR parameters such as the resonance frequency and the spin-lattice relaxation time T_1 show in some cases a very peculiar behavior, and close examination leads often to very important new findings. This paper will describe some techniques introduced to analyze or interpret apparently unusual NQR data.

We take up three topics here: The first is an analysis of the anomalous temperature dependence of the antimony NQR frequencies in $(NH_4)_2SbF_5$ in relation to the order-disorder transition associated with the orientation of the NH_4^+ ions. The second topic concerns the NQR parameters in superionic conductors. A model calculation will be introduced to elucidate a possible contribution of the rapidly diffusing ionic species to the electric field gradient (EFG) at the site of the quadrupolar nucleus. The third subject involves a computation of intermolecular interactions in typical molecular crystals. The potential energy calculation will be incorporated in the analyses of the NQR data of C_6Cl_6 and *sym*-$C_6Cl_3F_3$ crystals to extract new or hidden dynamical characteristics in these materials.

Effect of Rotation of NH_4^+ Ion on NQR Frequency

NQR frequencies in some ammonium salts have remarkable positive temperature coefficients in a rather narrow temperature range. We interpreted this phenomenon as the averaging effect on the EFG caused by instantaneous destruction of the hydrogen bond between NH_4^+ and the anion containing the resonance nucleus during the excitation period of the rotation of the NH_4^+ ion [1–3]. When such an effect works, the NQR frequency is given by

$$\nu_Q = \nu_0(T) + (\nu_r \tau_r + \nu_t \tau_t)/(\tau_r + \tau_t) , \qquad (1)$$

where $\nu_0(T)$ represents the usual Bayer effect, ν_r and τ_r are the resonance frequency and residence time when the NH_4^+ ion is in the hydrogen-bonded stable orientation, respectively, and ν_t and τ_t are the frequency and transition time when NH_4^+ is in the rotational state, respectively. This relation holds when $2\pi\nu_Q\tau_r, 2\pi\nu_Q\tau_t \ll 1$.

The results of the analysis of the NQR data using the above equation are summarized in Table 1. They show that the typical transition time τ_t lies around 10^{-12} s.

We recently measured the antimony NQR frequencies in $(NH_4)_2SbF_5$ and $(ND_4)_2SbF_5$ as shown in Figure 1 [4]. The analysis of the data using the above equation gives very long τ_t, 10^{-9} s, which cannot be taken as the normal transition time for the rotation of NH_4^+. Since this compound undergoes phase transitions at 169 and 292 K, the former

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Table 1. Parameters governing the reorientation of ammonium ions and the NQR frequencies in some ammonium salts.

Substance	E_a/kJ mol^{-1}	$\tau_t/10^{-12}$ s	Nucleus	$\Delta\nu$/MHz	Remark Ref.
α-NH_4HgCl_3	9.39	2.8	^{35}Cl	0.12	[1]
NH_4ReO_4	9.14	2.5	^{187}Re	11.1	[1]
NH_4I_3	7.53	~2	^{127}I	29.4	[2, 3]
NH_4Cl		0.18			a
$(NH_4)_2SO_4$		> 50			b
$(NH_4)_2SbF_5$	15.0	$1.0 \cdot 10^3$	^{123}Sb	2.18	[4]

[a] U. Dahlborg, K. E. Larsson, and T. Månsson, Physica **49**, 1 (1970): Neutron scattering data at 295 K.

[b] L. G. Olsson, U. Dahlborg, and T. Månsson, Chem. Phys. Lett. **53**, 413 (1978): Neutron scattering data at 295 K.

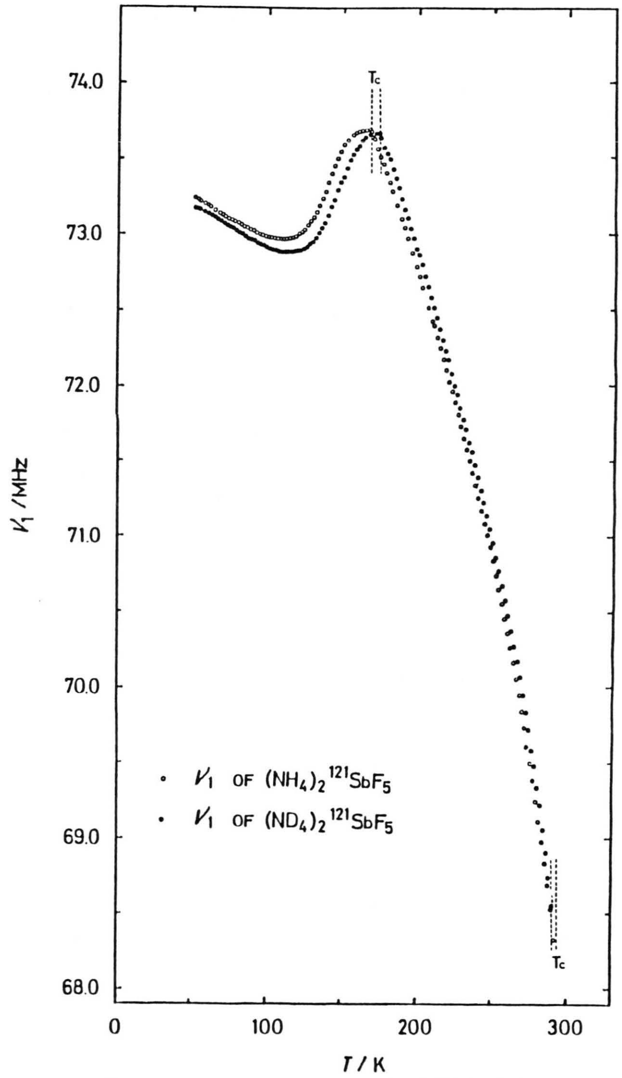

Fig. 1. ^{121}Sb NQR frequencies ν_1 (1/2−3/2) in $(NH_4)_2SbF_5$ and $(ND_4)_2SbF_5$. Phase transitions occur at 169 and 292 K in the NH_4-salt and at 173 and 290 K in the ND_4-salt.

is probably the order-disorder transition with respect to the orientation of the ammonium ions; the ion must spend some finite time $\tau_{r'}$ in its disordered sites below the transition point. So the apparent τ_t obtained above may correspond to this second residence time. In this case we must modify the above equation to

$$\nu_Q = \nu_0(T) + (\nu_r\tau_r + \nu_{r'}\tau_{r'} + \nu_t\tau_t)/(\tau_r + \tau_{r'} + \tau_t) \,, \qquad (2)$$

where $\nu_{r'}$ is the contribution from the NH_4^+ in the disordered orientation to the NQR frequency. As the order of magnitude of τ_t is 10^{-12} s, it may be ignored compared with τ_r and $\tau_{r'}$, and (2) is simplified to

$$\nu_Q = \nu_0(T) + (\nu_r\tau_r + \nu_{t'}\tau_{t'})/(\tau_r + \tau_{t'}) \,. \qquad (3)$$

The order parameter s of the transition is generally given by $s = (\tau_r - \tau_{r'})/(\tau_r + \tau_{r'})$, and the relation $\tau_{r'}/\tau_r = \exp(-\Delta E/RT)$ holds.

The calculated order parameter is shown in Figure 2. The behavior of s just below the transition point seems unreasonable and further exmination will be necessary.

NQR Frequencies in Superionic Conductors

LaF_3 crystallizes in a hexagonal $P6_3cm$ [5] or a trigonal $P\bar{3}c1$ [6] structure and is a superionic conductor in which the vacancy-mediated diffusion of F^- causes its high electric conductivity.

Lee et al. [7] measured the temperature dependence of the ^{139}La NQR frequencies and found that the asymmetry parameter η suddenly begins to decrease above 300 K. Their attempt to interpret the experimental data on the basis of anisotropic

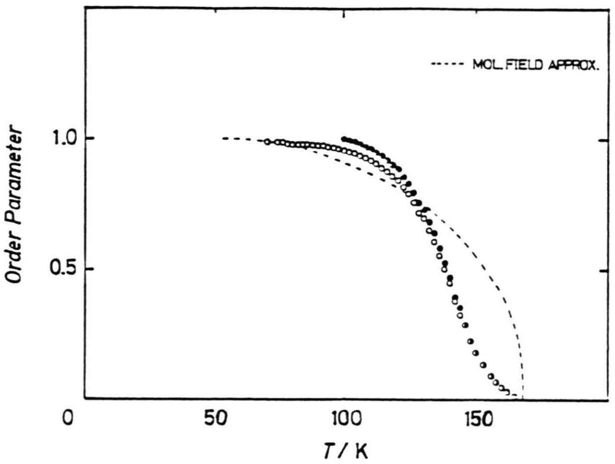

Fig. 2. The order parameter of the order-disorder transition in $(NH_4)_2SbF_5$ deduced from the anomalous part of the ^{121}Sb NQR frequency (ν_1).

lattice vibrational effects led, however, to unreasonable results.

Since LaF_3 is an anionic conductor and the fluorine diffusion is well excited above 300 K [8] it is reasonable to consider that the anomalous behavior of η of the ^{139}La resonance near 300 K is closely connected with the fluorine diffusion. We then examined the effect of the fluorine diffusion on the ^{139}La NQR parameters by a simple model calculation of the EFG [9].

The computation of the EFG was carried out by the Bertaut method [10]. This method takes the lattice sum in the reciprocal lattice space and essentially corresponds to the point charge model but, contrary to the usual point charge model, it assumes a special form of the charge distribution on each ion to attain a very rapid convergency.

The computation was performed under the following conditions:

1) The LaF_3 crystal assumes $P6_3cm$ structure [5] and its unit cell contains 6 formula units. There are four crystallographically different fluorines the numbering of which is the same as in [5].

2) La and F carry formal charges +3 and −1, respectively, with parabolic charge distribution according to Bertaut [10].

3) Among four inequivalent fluorine species only F(1) (there are two F(1)'s in the unit cell) or F(2) (four in the unit cell) can diffuse through channels passing along the c-axis.

4) F(1) or F(2) diffuse via anion vacancies, and the rate of diffusion is higher than the NQR frequencies of ^{139}La so that the F^- ions are homogeneously distributed in their available sites in the time scale of La NQR; each La sees fluorine ions whose charges are reduced to $c_F = (-1) \cdot N_F/(N_F + N_V)$, where N_F and N_V are the numbers of the fluorine atoms engaged in the diffusion and the number of anion vacancies, respectively.

First we calculated the Madelung energy and the EFG at the La site in the perfect crystal. The Madelung constant was calculated to be 27.7461 (with reference to the lattice constant $a = 0.7185$ nm). The $eq \equiv V_{zz}$ and η are listed in Table 2. If we use the literature value of the nuclear quadrupole moment $eQ = 8.01 \times 10^{-48}\,\mathrm{Cm}^2$ [11] for ^{139}La, the experimental $e^2Qq/h = 16.14$ MHz [7] can be reproduced by putting the Sternheimer antishielding factor $(1-\gamma_\infty) = 103$, which is in excellent agreement with a theoretical value, 10 η [12]. The calculated value of η agrees also with the experimental one, 0.8054, at 294 K [7].

Next we applied this method to the case where vacancy-mediated F^- diffusion takes place and first computed the EFG for the decreased amount of the effective charges on two F(1)'s (in other words it corresponds to an increase in the number of vacancies). The result is shown in Figure 3. This figure predicts that the absolute values of both e^2Qq and η decrease when the vacancy concentration increases on heating the specimen, the tendency being consistent with the experimental data above 300 K.

The effective charge c_F at an arbitrary temperature is related to the experimental Schottky defect concentration [8] s/N by $1 - c_F \equiv s/N \equiv N_V/$

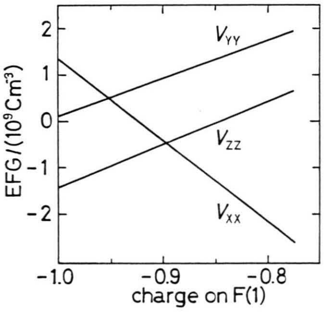

Fig. 3. The variation of the EFG tensor components at the La site in LaF_3 as functions of the effective charges on F(1).

Table 2. Relation between the NQR parameters of ^{139}La and the defect concentration in LaF_3.

T/K	(s/N)/10^{-3}	$\tau_c/10^{-9}$ s	Charges	$eq/10^9$ Cm^{-3}	η	$\Delta\eta$	$\Delta\eta_{exp}$
–[a]	0	–	−1.0	1.438	0.858	–	–
300	1.21[b]	1000[c]	−0.989	1.313	0.721	0.138	–
400	2.35[b]	5.6[c]	−0.979	1.199	0.567	0.291	≅ 0.02

[a] The perfect crystal is assumed.
[b] Ref. [8].
[c] A. V. Chadwick, D. S. Hope, G. Jaroszkiewicz, and J. H. Strange, Fast Ion Transport in Solids (P. Vashishta, J. N. Mundy, and G. K. Shenoy ed.), North-Holland, 1979, p. 683.

($N_F + N_V$), so that η and its shift from that in the perfect crystal, $\Delta\eta$, at that temperature can be estimated. The results are summarized in Table 2. The calculated $\Delta\eta$ is larger than the experimental one by about a factor 10 at 400 K, but it may be stated that the anomaly in η in LaF_3 originates from the vacancy-mediated anion diffusion. If the same kind of calculation is carried out by changing the effective charge on four F(2)'s instead of F(1), η increases with increase in the vacancy concentration, contrary to the experimental result.

A very recent X-ray structure analysis of LaF_3 pointed out that the previous $P6_3cm$ structure is erroneous, without recognizing the twin structure of the specimen. It was proposed that the true structure of this material is $P\bar{3}c1$ [6]. We performed the same calculation as above with these new crystal data and obtained $eq \equiv V_{zz} = -0.9691 \cdot 10^{19}\,\mathrm{JC^{-1}\,m^{-2}}$ and $\eta = 0.3683$. This η cannot explain the experimental value. The discrepancy may come from the inadequate use of the simple point charge model for the EFG calculation, but further close examination of the crystal structure of this compound would be necessary.

The same kind of the EFG calculation was carried out on a lithium conductor, Li_3N, in order to predict the temperature variation of the ^{14}N NQR frequency [13]. The results are that the EFG's at the two crystallographically different lithium sites (Li(1) and Li(2)) do not shown any significant change by changing the amount of charges on either Li(1) or Li(2), being consistent with the experimental finding [14]. On the other hand V_{zz} at the nitrogen site increases dramatically when the vacancy concentration of Li(1) is increased, whereas it decreases rapidly as the Li(2) vacancies are increased. These results show that the measurement of the ^{14}N NQR frequency is of great use to understand the mechanism of the ionic conduction in Li_3N.

Molecular Dynamics in *Sym*-$C_6Cl_3F_3$ and C_6Cl_6

The fact that molecular crystals have usually a large number of degrees of freedom often complicates the analysis of NQR, NMR, or other spectral data. In such cases some computational work concerning the lattice potential energy, lattice dynamics, and so on may be useful to establish the correct picture of the molecular dynamics.

We encountered a rather curious situation in the course of analysis of the ^{35}Cl spin-lattice relaxation time in *sym*-$C_6Cl_3F_3$ [15]. This substance crystallizes in a hexagonal $P6_3/m$ structure and all the chlorine atoms are crystallographically equivalent [16]. The rapid shortening of T_1 above about 170 K as well as the previous high-resolution ^{19}F NMR results on a single crystal of this material [17] suggest strongly the onset of molecular three-fold reorientation above 170 K. An analysis of T_1 according to the strong collision theory [18] gave the activation parameters $\tau_0 = 3.42 \cdot 10^{-7}$ s and $E_a = 18.2$ kJ mol^{-1}. The value of τ_c seems to be too long to take it as the limiting lifetime for the 3-fold reorientation of the molecule.

This material undergoes a phase transition at 296 K [19], but the ^{35}Cl NQR frequency does not show any anomaly at the transition point. Our measurement of T_1 of ^{19}F gave the activation energy 35 kJ mol^{-1} in the high temperature phase (HTP). This value is about twice as large as that obtained in the low temperature phase (LTP) by the ^{35}Cl NQR. In order to establish the correct dynamical picture of this compound we carried out a calculation of the potential barrier for molecular reorientation about its figure axes [20].

The computation essentially takes the lattice sum for individual atomic pair interactions represented by the Buckingham type 6-exponential function.

The potential energy function for the molecular 3-fold rotation is shown in Figure 4. This figure indicates that, in order for each molecule to reorient by 120°, it must overcome a potential barrier of 42.0 kJ mol^{-1}, which obviously corresponds to the activation energy determined by the ^{19}F T_1 in the HTP.

In Fig. 4 another minimum exists at an orientation separated by an angle 25° from the equilibrium orientation. The potential difference between these two minima is $\Delta E = 14.4$ kJ mol^{-1}. A molecule can reach this metastable orientation by overcoming a barrier of 17.4 kJ mol^{-1}, which is nearly equal to the activtion energy obtained by the ^{35}Cl T_1 data in the LTP. We now reanalyzed the ^{35}Cl T_1 data with a scheme that each molecule jumps between asymmetric double minimum potential wells separated from each other by 25°: According to [18] the time evolution of the nuclear polarization P^α at one site of the double minimum potential is given by

$$P^\alpha - \langle P^\alpha \rangle = a_1 \exp(-t/T_1^{\mathrm{I}}) + a_2 \exp(-t/T_1^{\mathrm{II}})$$

where $\langle P^\alpha \rangle$ is the equilibrium polarization, a_i and T_1^{I}, T_1^{II} are functions of the jump angle and the transition probabilities from the equilibrium site to the metastable site, $w_{\alpha'\alpha'}$ and the opposite one, $w_{\alpha\alpha'}$. Here the relations $w_{\alpha\alpha'} = w_{\alpha'\alpha} \exp(\Delta E/\mathrm{RT})$ and $\tau_c \equiv 1/w_{\alpha'\alpha}$ hold. The analysis of T_1 with $\Delta E = 14.4$ kJ mol^{-1} and the jump angle of 25° gives $\tau_0 = 4.97 \cdot 10^{-11}$ s and $\Delta E = 19.7$ kJ mol^{-1}. The value of τ_0 obtained here may be evaluated as the limiting lifetime of the molecular libration about its figure axis.

Hence we now have the dynamical picture of this material that in the LTP only molecular local jumps between two sites are excited while in the HTP the molecues undergo the 3-fold reorientation. We also applied the ^{35}Cl T_1 measurements (Fig. 5) and the model calculation of the intermolecular potential energy to C_6Cl_6 crystal [20]. We then obtained an activation energy of 61 kJ mol^{-1} and a potential barrier to the 6-fold reorientation of 63.0 kJ mol^{-1}. Both agree well with each other.

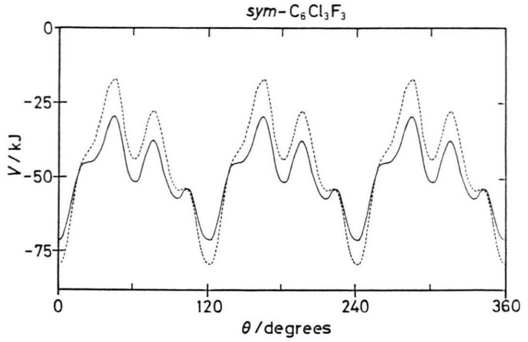

Fig. 4. The potential energy function for the molecular 3-fold rotation of sym-$C_6Cl_3F_3$ at 300 K (solid line) and at 4.2 K (broken lines). Structure data were taken from [16].

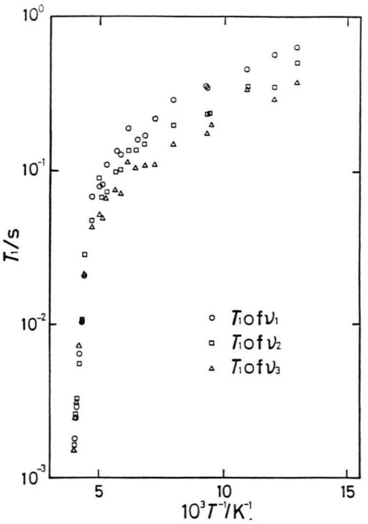

Fig. 5. The spin-lattice relaxation times T_1 of the three ^{35}Cl NQR lines in C_6Cl_6 crystal.

In C_6Cl_6 we looked for a possible metastable molecular orientation by rotating the molecules about its two-fold axes and found a potential minimum at a position rotated by 45° about the axis passing $C_{17}-C_{18}$ in [21] with a height of 8.4 kJ mol^{-1}. This result supports a previous statement that orientational disorder is possible in this material [22].

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