Crossover from relaxational to resonant tunneling dynamics for random-site interacting dipoles in $(K_{1-x}Na_x)TaO_3$

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The low-frequency spectral density of the motion of Na ions substituting for K in the paraelectric crystal KTaO₃ has been obtained through the dependence of the [23]Na spin-lattice relaxation upon the measuring frequency in the range 5–80 MHz. A dramatic changeover has been found: At 77 K the motion is a thermally activated hopping, with a spectral density of relaxational character and a distribution of correlation times, whereas at $T \simeq 4$ K it has a resonant character centered around 28 MHz. We discuss how Na tunneling between the minima of the local potential can be responsible for this effect.

INTRODUCTION

The dynamics of Na or Li ions substituting for K in the paraelectric $(T_c \rightarrow 0)$ crystal KTaO₃ is presently attracting strong interest in view of the similarity between these dipolar systems and magnetic spin glasses. In particular, NMR relaxation and dielectric measurements for [23]Na (Ref. 1) as well as [7]Li (Ref. 2) have shown that below a certain temperature the ions have a low-frequency hopping dynamics related to the transformation[3] of the local potential from quasiharmonic to a double-well one, with off-center minima along the cubic directions. The correlation times for the off-center dipoles are widely distributed and no evidence of a real ferroelectric phase is obtained down to 4 K.

A suitable way to obtain the spectral density $J(\omega)$ of the Na motion is offered by the dependence of the NMR spin-lattice relaxation rate T_1^{-1} upon the measuring frequency ω_L. The relaxation process, in fact, is driven by the time-dependent part of the electric field gradients V_{jk} experienced in the off-center positions and the relaxation rate is directly related to the spectral density of the motion. This paper deals with the observation of an interesting changeover in the local dynamics of the Na dipoles. At $T = 77$ K the measurements show that $J(\omega)$ is of relaxational character, typical of thermally activated motions with a distribution of correlation times, whereas at $T \simeq 4$ K a quite different behavior of T_1 vs ω_L points out that the Na motion has changed to a resonant character. It is argued that the quantum tunneling of Na between the equivalent minima in the local potential can be responsible for the changeover.

EXPERIMENTAL RESULTS AND ANALYSIS

The [23]Na relaxation rate driven by the electric quadrupole interaction can be written[4]

$$T_1^{-1} = \tfrac{1}{5}\omega_Q^2[\chi J(\omega_L) + 2(1+\chi)J(2\omega_L)] \ , \qquad (1)$$

where $\omega_Q = (eQ/2\hbar)(\langle V_z^2 \rangle)^{1/2}$ is an effective quadrupole coupling constant (involving the average value of the electric-field-gradient components V_{jk} experienced by the Na nucleus in the off-center positions), $J(\omega)$ is a common reduced correlation function for the motions of the dipoles, and $\chi = \tfrac{4}{3}(\langle V_{xy}^2 \rangle / \langle V_z^2 \rangle)$ is a constant of the order of unity.

The experimental measurements have been carried out in the crystals $K_{1-x}Na_xTaO_3$ with $x = 0.05$, 0.12, and 0.18, at different measuring frequencies ranging from 6 to 80 MHz and in the temperature range from 4 to 300 K. The [23]Na T_1 have been evaluated by studying the recovery of the nuclear magnetization with standard pulse techniques: The four $(m = \pm\tfrac{3}{2}, \pm\tfrac{1}{2})$ Zeeman levels were saturated with a number of $\sim \pi/2$ in-resonance rf pulses, and the growth of the magnetization was then monitored from the height of the free-induction signal following a $\pi/2$ pulse at a time t later. In the whole temperature range investigated no static quadrupole effects are present, as inferred from the length of the pulse maximizing the free precession signal and from the width of the resonance line.

In the temperature range 10–150 K the analysis of the data in the following shows that the motion of the dipoles has relaxational character, with a distribution of correlation times τ. The complete experimental results will be published elsewhere.[5] For the sake of illustration, we report in Fig. 1 the behavior of the relaxation rate as a function of ω_L at 77 K. For a monodispersive hopping motion with a single correlation time the spectral density is $J(\omega) = (2\tau/1+\omega^2\tau^2)$. Thus, in the slow-motion regime, i.e.,
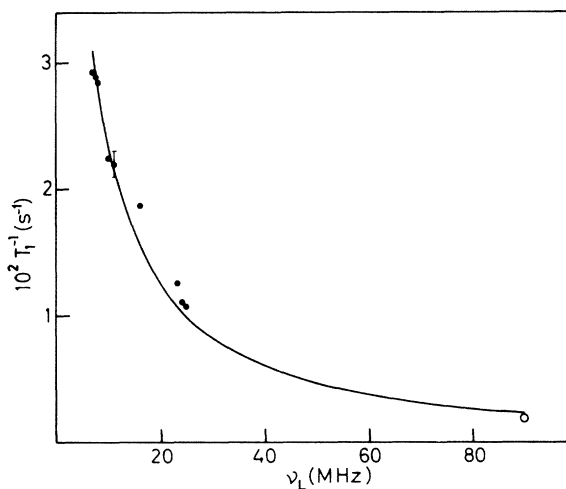

FIG. 1. [23]Na relaxation rates for $K_{0.82}Na_{0.18}TaO_3$ as a function of the measuring frequency ν_L, at $T = 77$ K ($\bullet$, present work; O, from Ref. 6). The solid line is the best-fit theoretical behavior according to Eq. (2) in the text, for $\tau_g = 5 \times 10^{-9}$ s and $b = 7$.

$\omega_L \tau > 1$, the frequency dependence of the relaxation rate would be of the form $T_1^{-1} \propto \omega_L^{-2}$. However, a distribution of correlation times, typical of glass-type systems, has to be taken into account, and this is expected to reduce the ω_L dependence of the relaxation rate, in qualitative agreement with the data shown in Fig. 1. For a more quantitative analysis, one can consider a simple distribution of activation energies of the form

$$P(E) = \frac{1}{2\Delta} , \quad \text{for } E_g - \Delta \leq E \leq E_g + \Delta ,$$

$$P(E) = 0, \quad \text{elsewhere} ,$$

corresponding to a rectangular distribution of correlation times (in logarithmic scale) with geometrical average $\tau_g = \tau_0 \exp(E_g/k_B T)$ and width $2\ln b = 2\Delta/k_B T$.

The integration of Eq. (1), assuming for simplicity $\langle V_{xy}^2 \rangle = \langle v_{zz}^2 \rangle$, yields

$$T_1^{-1} = \frac{\omega_Q^2}{5} \frac{1}{3\omega_L} \frac{1}{\ln b} [4(\arctan\omega_L\tau_g b - \arctan\omega_L\tau_g/b)$$

$$+ 7(\arctan 2\omega_L\tau_g b - \arctan 2\omega_L\tau_g/b)] .$$

$$(2)$$

It can be noted that for $\Delta \to \infty$ one has $T_1^{-1} \propto \omega_L^{-1}$.

By fitting the data in Fig. 1 on the basis of Eq. (2) one gets $\tau_g = 5 \times 10^{-9}$ s and $b = 7$.

A more realistic Gaussian distribution $P(E)$ does not allow one to derive an expression equivalent to Eq. (2) in a close form. However, a numerical evaluation of the relaxation rate in terms of such a Gaussian distribution leads to conclusions analogous to those obtained with the rectangular distribution.[1]

We point out that the T_1 results as a function of temperature, for different x, can also be consistently fitted by Eq. (2) for $T \gtrsim 15$ K. Thus one derives $E_g \simeq 200$ K, while the quadrupole coupling constant turns out to be

$$\nu_Q = 0.8 \text{ KHz} .$$

$$(3)$$

We turn now to the analysis of the data for $T < 15$ K where the frequency and temperature dependences of the relaxation rate change progressively on cooling. The results obtained for $x = 0.18$ at 4.2 K are reported in Fig. 2. The behavior of T_1^{-1} vs ω_L, and also an order of magnitude estimate on the basis of Eq. (2), indicate that around 4 K the hopping motion is practically ineffective to induce the ^{23}Na relaxation process. We argue in the following that the relaxation is driven by a quite different dynamics, of resonant character.
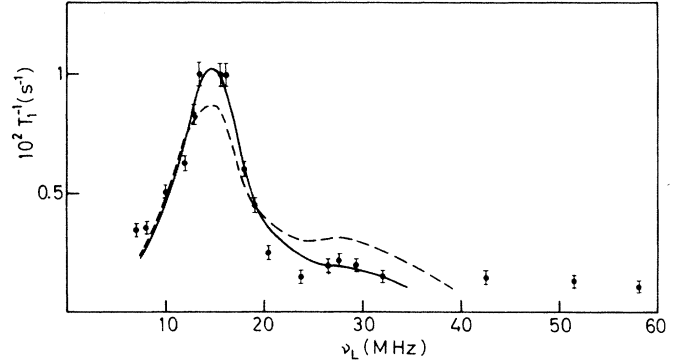

FIG. 2. Frequency dependence of the ^{23}Na relaxation rate in $K_{0.82}Na_{0.18}TaO_3$ at 4.2 K. The solid and dashed lines are the theoretical behaviors predicted by Eq. (5) for a spectral density as in Eq. (4), with $\omega_t = 2\pi \times 28.5$ MHz and $\omega_t\tau_c = 3.9$ for $X = \frac{1}{3}$ and $X = \frac{4}{3}$.

The shape of the local potential and the occurrence of analogous phenomena in glasslike systems[7] suggest the possibility of tunneling involving equivalent minima along the cubic directions. The effect on nuclear spin-lattice relaxation of low-temperature tunneling, in the presence of phonons, is a rather delicate matter. Suitable theories have been developed[8-10] only for proton relaxation in NH_4^+, CH_3, and similar groups. The role of the phonons, in particular, is still an unsettled question.[8] An analysis of the data in Fig. 2, however, can be carried out with a simple model of "classical lattice" for the time-dependent V_{jk} functions, with a deterministic tunneling "motion" of the Na ion at a frequency ω_t and a time of coherence τ_c.[11,8] The "broadening" of the tunneling frequency over a frequency range of the order of $\omega_c \simeq \tau_c^{-1}$ justifies the assumption of a classical thermal bath for the nuclear relaxation. We remark that, in principle, another possible source of broadening is the statistical distribution of tunneling rates, related to a distribution of local barrier heights.[7] In this case ω_c measures the width of such a distribution. When considering the tunneling motion, we will not detail the correlation function in terms of probability amplitudes for the six equivalent positions of Na along the cubic axes, and no distinction will be made between 180° and 90° tunneling. Thus the reduced correlation function leads to the spectral density

$$J(\omega) = \frac{\tau_c}{1 + (\omega + \omega_t)^2\tau_c^2} + \frac{\tau_c}{1 + (\omega - \omega_t)^2\tau_c^2} .$$

$$(4)$$

From Eq. (4) we obtain for the relaxation rate

$$T_1^{-1} \propto \frac{\tau_c}{1 + (\omega_L + \omega_t)^2\tau_c^2} + \frac{\tau_c}{1 + (\omega_L - \omega_t)^2\tau_c^2} + 2[(1+X)/X]\left[\frac{\tau_c}{1 + (2\omega_L + \omega_t)^2\tau_c^2} + \frac{\tau_c}{1 + (2\omega_L - \omega_t)^2\tau_c^2} \right]$$

$$\simeq \left[\frac{\tau_c}{1 + (\omega_L - \omega_t)^2\tau_c^2} + [2(1+X)/X] \frac{\tau_c}{1 + (2\omega_L - \omega_t)^2\tau_c^2} \right] .$$

$$(5)$$

This equation predicts maxima in the relaxation rates for $\nu_L = \omega_t/4\pi$ and $\nu_L = \omega_t/2\pi$, whose widths and amplitudes depend on τ_c. In Fig. 2 the experimental results are compared with the theoretical behaviors predicted by Eq. (5) for $\omega_t = 2\pi \times 28.5$ MHz and $\omega_t\tau_t = 3.9$, for $X = \frac{4}{3}$ and $X = \frac{1}{3}$.

A quantitative discussion of the tunneling frequency requires the evaluation of the tunneling matrix element, and uncertain results are often obtained, particularly when phonons are disregarded. A usual approach to allow for the phonon modes is to introduce a dressed mass Mc for the

tunneling particle, where c is a factor related to the inverse phonon frequencies and to the shape of the local potential.[12] We will use an approximate expression of this type given by[13]

$$\omega_t = \frac{8\sqrt{3}}{\sqrt{\hbar}\,\pi} M^{-1/4} Q_0^{-1/2} c^{1/4} E_g^{3/4} \exp(-M^{1/2} c^{1/2} E_g^{1/2} Q_0/\hbar) \, , \quad (6)$$

where Q_0 is the distance between the two minima. Equation (6) is in agreement with the tunneling transition probability derived long ago[14] for molecular rotations in periodic potentials and is often used to describe the proton tunneling in ammonium compounds.[8,9,11]

For an estimate of the tunneling frequency from Eq. (6) we use $Q_0 \sim 0.1$ Å, as indicated by the value (3) for ν_Q (see also Ref. 1), and $E_g = 0.05$ eV. One should observe that since ν_Q and E_g have been evaluated from data at higher temperatures, the above values are probably smaller than the real ones at 4 K. With the above-mentioned data, Eq. (6) leads to ν_t of the order of 100 MHz if a value $c \simeq 40$ is assumed for the dressing coefficient. This assumption for c would correspond to a dressing exponent $2R_0 \simeq 14$, as discussed by Tonks and Dick[15] for the phonon-assisted orientational tunneling of Ag^+ ions in RbCl, studied by Cl and Rb NMR.[16]

In conclusion, we stress that the experimental results of ^{23}Na NMR T_1 clearly evidence the crossover from relaxational to resonant dynamics in the glasslike dipolar crystals $K_{1-x}Na_xTaO_3$ on cooling down to 4 K. Finally, we mention that preliminary measurements performed at $T \simeq 2$ K seem to indicate a narrowing of the peak in T_1^{-1} at $\nu_L \simeq 14.5$ MHz, thus in favor of a phonon-induced broadening. Further work is in progress, also in order to investigate the transformation of the tunneling mode in thermal hopping on increasing temperature.

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