

## $^{23}\text{Na}$ quadrupolar relaxation study of disorder effects in $\text{KTaO}_3:\text{Na}$

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$^{23}\text{Na}$  NMR spectra and spin-lattice relaxation measurements in  $\text{K}_{1-x}\text{TaO}_3:\text{Na}_x$  single crystals, in the temperature range 4–400 K, at frequencies ranging from 7 to 80 MHz and for Na concentration  $x$  of 5, 12, and 18 at. %, are presented. An analysis of the data is carried out by taking into account theoretical pictures for systems with disorder in the interactions, yielding insights on the local disorder dynamics of the Na ions. In particular, it is discussed how disorder effects, in the absence of a real ferroelectric transition, cause the occurrence of a "pretransitional" central peak in the spectral density for the vibrational motion of Na ions. The associated correlation times, namely the inverse width of the central peak, appear widely distributed. The time dependence of the recovery law for the nuclear magnetization after a sudden temperature jump points out metastability effects bearing resemblance to glass systems. Results on the strength and distribution of the local potential barriers are derived from the temperature and the frequency dependence of the relaxation rates. On cooling below 10 K, the Na dynamics displays a changeover from relaxational character to a resonant one. It is argued how this effect can result from the tunneling of Na ions between the minima of the local potential, for a number of barriers whose height diverges for  $T \rightarrow 0$  K. Finally, the NMR results indicate that a possible structural phase transition of the  $\text{KTaO}_3$  matrix cannot imply a displacement of the Na ion larger than 0.1 Å or a rotation of the  $\text{TaO}_6$  octahedra larger than  $10^{-2}$  rad, and that the interaction among the Na disordered units is probably of elastic character rather than electric dipolar one.

### I. INTRODUCTION

Amorphous glasses and their magnetic analog, spin-glasses, have recently triggered a great deal of theoretical and experimental work.<sup>1,2</sup> Less attention has been devoted to disordered crystals, namely the "structural" glasses. Alkali halides with substitutional polar groups, such as  $\text{KCl}:\text{OH}$ ,<sup>3</sup> perovskites with impurities, such as  $\text{KTaO}_3:\text{Li}$ ,<sup>4,5</sup> and structurally frustrated ferroelectric-antiferroelectric mixed crystals<sup>6</sup> have been considered, sometimes with controversial interpretations, as the equivalent of spin-glasses.

For "ordered" crystals, characterized by translational invariance in the critical variables, one has rather well-established theoretical descriptions for the critical dynamics and for the ordering process.<sup>7</sup> When substitutional disorder and/or disorder in the interactions is introduced in an ordered crystal, the theoretical picture is no longer straightforward. By extending theoretical and experimental results<sup>1,2</sup> that mostly pertain to amorphous glasses and to spin-glasses, a variety of complex phenomena can be expected in disordered crystals. The cooperative slow-down involving the critical variables  $\mathbf{S}_i(t)$  results in the onset of a "frozen" state with no long-range order parameter. Thus, if  $\langle \mathbf{S}_i \rangle_{t_m}$  indicates an average over the time  $t_m$  characteristic of an experiment, one has

$$\lim_{|r_i - r_j| \rightarrow \infty} \langle \langle \mathbf{S}_i \rangle_{t_m} \cdot \langle \mathbf{S}_j \rangle_{t_m} \rangle_{\text{av}} = 0, \quad (1)$$

where  $\langle \rangle_{\text{av}}$  refers to a spatial average. This condition does not hold if  $i$  and  $j$  are chosen within a short-range region of correlated motions (cluster); this would give a

value different from zero for the double average. When  $\langle \mathbf{S}_i \rangle_{t_m} \neq 0$ , the critical variables appear frozen over the time of the experiment. The freezing is not, in itself, proof of the occurrence of a glasslike state resulting from frustration,<sup>8</sup> namely the existence of a large number of degenerate energy states. A possible distinction between a frozen state and a glass state can be given<sup>9</sup> in terms of the correlation function  $g(t) = \langle \mathbf{S}_i(0) \cdot \mathbf{S}_i(t) \rangle$ : while simple freezing implies  $g(t)$  flat over the time scale  $t_m$ , the system is in a glass state when  $g_{\text{flat}} > \langle S_{\text{eq}}^2 \rangle$ , where  $\langle S_{\text{eq}}^2 \rangle$  is the statistical equilibrium average taken over all configurations. In such a condensed phase some nonergodic behavior and history-dependent effects can be expected. If  $g(t)$  is still flat for  $t_m \rightarrow \infty$ , a real phase transition, in a thermodynamical sense, has occurred.

As regards the critical dynamics driving the cooperative freezing, a widely accepted picture, based on phenomenological models and computer simulations, involves a large distribution of disorder modes of relaxational character. Such a distribution often can be embedded in a correlation function of the form  $\exp[-(t/\tau)^\beta]$ , with  $\tau$  fitting the empirical relation

$$\tau = \tau_0 \exp[E/k(T - T_0)], \quad (2)$$

i.e., an apparent activation energy for the relaxation which increases with decreasing temperature. The progressive freezing induces a divergent behavior of the average correlation time and of the second moment of the distribution.<sup>10</sup> Thus a number of local effective barriers should diverge for  $T \rightarrow 0$  K.

When thermal hopping is practically inhibited, alternative dynamics can be promoted by quantum tunneling.

For an asymmetric local potential the order-disorder units can undergo Anderson tunneling, equivalent to phonon-assisted transitions between two nonequivalent minima, with spectral density of relaxational character. For a symmetric double-well potential, it has been recently suggested,<sup>11</sup> on the basis of thermal and dielectric measurements in  $\text{KBr}_{1-x}(\text{CN})_x$  and in  $\text{KCl}$  with Li impurities,<sup>12</sup> that the disorder units undergo quantum tunneling, somewhat equivalent to a resonant motion.

Thus, a complex picture describes a disordered crystal when it approaches a temperature range where an ordered crystal would become structurally unstable. NMR and NQR spectra and spin-lattice relaxation, in principle, should provide enlightening information in that respect. In fact, in view of their local character, the spectra should reflect the spatial distribution of some order parameters, while the nuclear relaxation is sensitive to the insurgence of local modes and to their temperature dependence.<sup>13</sup> A suitable system is a crystal where only a slight disorder in the interactions is introduced with respect to the ordered crystal, where the phase transitions and critical dynamics are rather well understood. This is the case of  $\text{KTaO}_3$  with random Na substitution of K for Na concentration  $x$  below a value around 20 at. %, which is a percolation-type limit<sup>14</sup> for the occurrence of the usual phase transitions in the mixed crystals  $(\text{KTaO}_3)_{1-x}(\text{NaTaO}_3)_x$ . As we will see, the substitution of K with Na results in a slight modification of the local potential at the Na sites and the crystal displays the features outlined above.

This paper deals with a thorough presentation and analysis of <sup>23</sup>Na spin-lattice relaxation measurements in  $\text{K}_{1-x}\text{TaO}_3:\text{Na}_x$ , for  $x = 5, 12,$  and  $18$  at. %, and for measuring frequency  $\nu_L$  ranging from 8 to 60 MHz in the temperature range 4–400 K. Some spin-lattice relaxation data in  $\text{KTaO}_3:\text{Na}$  have already been published in preliminary reports.<sup>15–17</sup> Other authors<sup>18</sup> have also reported relaxation results at high frequency ( $\nu_L = 88$  MHz), in particular suggesting the possible occurrence of sizable anharmonic effects in the Na dynamics.

In Sec. II the major experimental results, namely the onset of the local disorder dynamics below a certain temperature  $T_g$  around 150 K, the metastability effects following a sudden temperature jump below  $T_g$ , and the changeover from relaxational to a resonant dynamics, for  $T \leq 10$  K, are presented.

Section III is devoted to a theoretical analysis of the relevant results. This analysis is carried out mainly on the basis of a picture of frustrated transition accompanied by the raising of a central peak in the spectral density for the Na motions.

## II. EXPERIMENTAL RESULTS

$\text{K}_{1-x}\text{TaO}_3:\text{Na}_x$  single crystals have been grown by Rytz using a slow-cooling method already described in Ref. 19. The Na content was derived from the concentration dependence of dielectric and NMR data. For  $x \leq 0.20$  at. %, clustering phenomena should not cause sizable concentration gradients. In fact, the behavior of our crystals at  $x = 5, 12,$  and  $18$  at. % is remarkably

different, thus supporting the estimates that the concentration inhomogeneities are within a few percent.<sup>20</sup>

<sup>23</sup>Na NMR spectra and spin-lattice relaxation times  $T_1$  have been obtained by means of standard pulse techniques, with Fourier transformation (FT) of the free-induction decay (FID). In the study of the recovery law, a saturating sequence of about ten  $\pi/2$  pulses has been used to induce complete equalization in the populations of the Zeeman levels. Then, the growth of the magnetization was monitored from the FID signal  $s(t)$  a time  $t$  later. The static magnetic field  $H_0$  has been varied from 7 to about 56 kG, while the amplitude of the radio-frequency field  $H_1$  was around 45 G. In the measurements at variable temperature, the temperature stabilization was around 0.1 K. For the investigation of metastability effects and for the  $\nu_L$  dependence of the relaxation rate at 77 and at 4.2 K, the crystal was kept in a cryogenic bath. The experimental and instrumental details can be found in Ref. 21.

### A. <sup>23</sup>Na NMR spectra and static effects

The <sup>23</sup>Na spectra have been analyzed in the light of their dependence from the length of the rf pulse and from the orientation of the crystal, for different temperatures and frequencies.

The dependence on the pulse length was used to check if only the central transition  $\pm\frac{1}{2} \leftrightarrow \mp\frac{1}{2}$  was detected, the satellite lines being possibly spread over a wide frequency range. At all temperatures the <sup>23</sup>Na signal was maximized by a pulse length corresponding to the irradiation of all lines and equal to the value  $\tau_{\pi/2}$  maximizing the signal in a NaCl solution. The signal would be maximized by a pulse length  $\tau_{\pi/2}/2$  if only the central line is irradiated.<sup>22</sup> One should observe that for a quadrupole coupling constant less than  $H_1/\gamma \simeq 50$  kHz the satellite transitions would also be irradiated. However, in this present case, the satellite lines would be shifted with respect to  $\nu_L$  and detected as a broadening of the single NMR line.

The <sup>23</sup>Na linewidth (full width at half-intensity  $\delta\nu_{\text{FWHI}}$ ) and its angular dependence are in agreement with the theoretical evaluations based on the dipolar contribution to the Van Vleck second moment. In fact, by taking into account the contributions from <sup>39</sup>K, <sup>23</sup>Na, and <sup>181</sup>Ta, one derives, for a rotation of the crystal around the cubic axis **a**,

$$\begin{aligned} \delta\nu_{\text{FWHI}} = & [(1-x)^{1/2}0.26 + (x)^{1/2}2.45] \\ & \times [0.813 - 0.5 \sin^2(2\phi)]^{1/2} \\ & + 1.08 |\sin(2\phi)| + 0.12 \text{ KHz}, \end{aligned} \quad (3)$$

where  $\phi$  is the angle between **H**<sub>0</sub> and the cubic axis **b**. The angle-independent term in Eq. (3) refers to the contribution from Ta nuclei, other than the first-nearest neighbors, for which the small angular dependence has not been detailed.

In Fig. 1 the spectra are shown and compared with the theoretical behavior predicted by Eq. (3). In Fig. 2 the temperature dependence of  $\delta\nu$  is reported for  $\phi = 45^\circ$ .

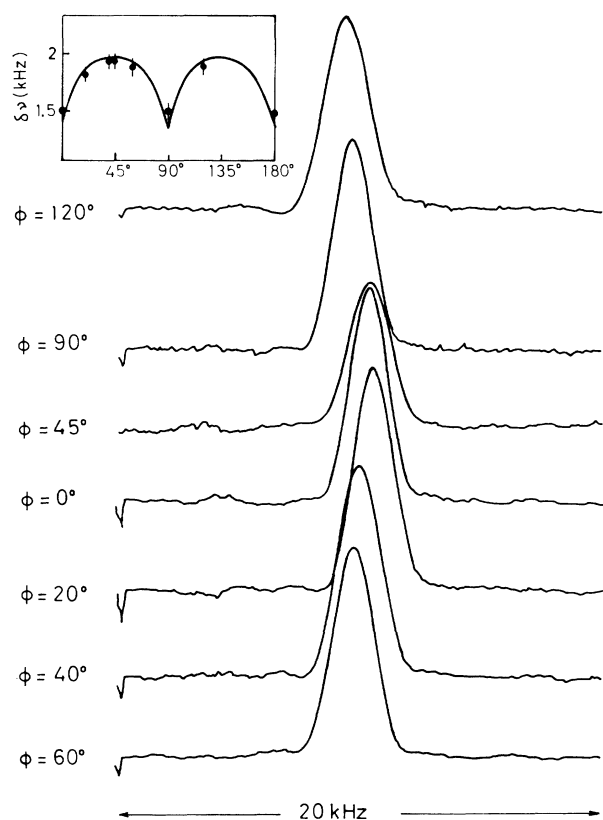


FIG. 1.  $^{23}\text{Na}$  NMR spectra in a single crystal of  $\text{K}_{0.82}\text{TaO}_3:\text{Na}_{0.18}$  at  $T=11$  K and  $\nu_L=24$  MHz, as a function of the angle  $\phi$  between  $\mathbf{H}_0$  and a cubic axis ( $\mathbf{H}_0$  in the  $a$ - $b$  plane). In the inset the full width at half-intensity (FWHI)  $\delta\nu$  vs  $\phi$  is compared with the theoretical behavior predicted by Eq. (3) in the text.

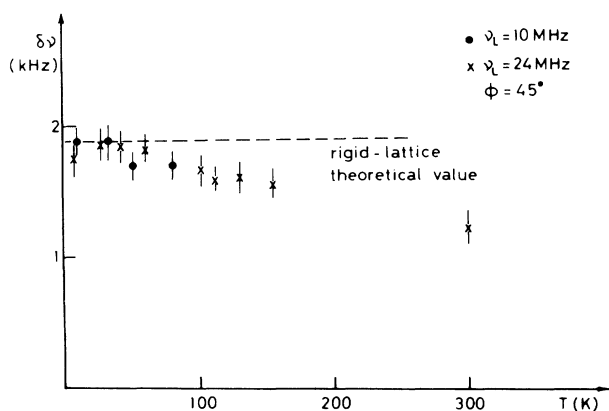


FIG. 2. Temperature dependence of the FWHI linewidth  $\delta\nu$  for  $\text{K}_{0.82}\text{TaO}_3:\text{Na}_{0.18}$ , for angle  $\phi=45^\circ$  between  $\mathbf{H}_0$  and a cubic axis and comparison with the theoretical estimate [see Eq. (3) in the text]. The rather large error bar is mostly due to the uncertainty in the subtraction of the contribution to the second moment from the magnetic field inhomogeneity.

On the basis of the linewidths and their angular dependence, one can conclude that there are no detectable electric field gradients (EFG's) present at the Na site, at any temperature. This result sets a limit for the tetragonal distortion and/or rotation of the  $\text{TaO}_6$  octahedra accompanying possible ferroelectric or antiferroelectric structural transition in the  $\text{KTaO}_3$  matrix.<sup>23,24</sup> By setting a detectability limit for the first-order broadening of the satellite transitions of the order of  $\delta\nu/2$ , a direct calculation using a point-charge approximation yields an upper limit of  $\langle\theta^2\rangle^{1/2} \leq 10^{-2}$  rad for the local rotation of the octahedra. For a deformation of the cell, as resulting from a ferroelectric-type transition, the upper limit for the displacement of Na is around 0.1 Å.

### B. Spin-lattice relaxation

In the temperature range  $4 \leq T \leq 450$  K the recovery of the nuclear magnetization was always described by an exponential law (with the exclusion of the metastability effects for the samples at  $x=5$  and 12 at. % discussed later on). The nuclear relaxation is driven by the time-dependent part of the EFG's at the  $^{23}\text{Na}$  site, through the  $\Delta m = 1, 2$  relaxation transition probabilities  $W_1$  and  $W_2$  due to the quadrupole Hamiltonian  $\mathcal{H}_Q(t)$ ,<sup>25</sup> yielding for the relaxation rate

$$T_1^{-1} = 2(W_1 + 4W_2)/5. \quad (4)$$

In Fig. 3 the relaxation rates at two typical frequencies, for the samples at  $x=12$  and 18 at. %, are shown

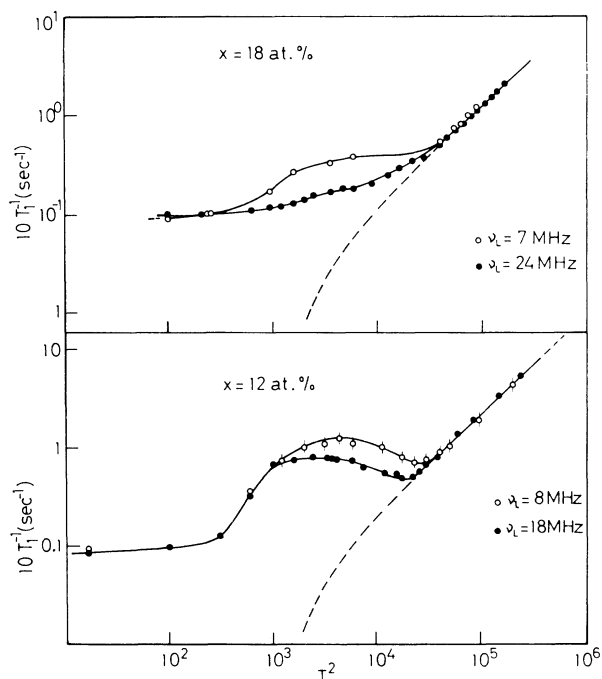


FIG. 3. Temperature behavior of the  $^{23}\text{Na}$  spin-lattice relaxation rate in  $\text{K}_{1-x}\text{TaO}_3:\text{Na}_x$  for  $x=12$  and 18 at. %, for two measuring frequencies. The solid lines are a guide for the eye. The dashed line is the sketchy behavior of the data for the  $^{23}\text{Na}$  relaxation rates in NaCl.

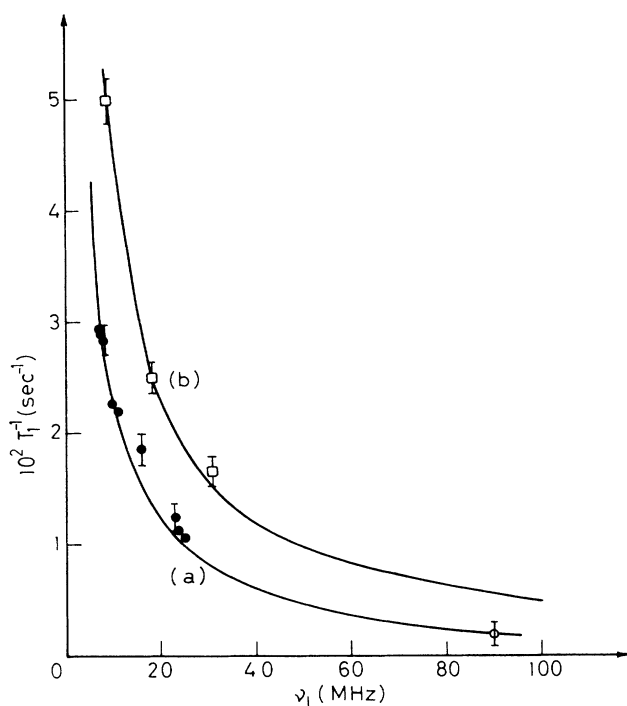


FIG. 4. Dependence from the measuring frequency of the  $^{23}\text{Na}$  relaxation rate for (a)  $\text{K}_{0.82}\text{TaO}_3:\text{Na}_{0.18}$  at  $T=77$  K and for (b)  $\text{K}_{0.95}\text{TaO}_3:\text{Na}_{0.05}$  at  $T=114$  K. The point at  $\nu_L=88$  MHz is from Ref. 18, for a crystal with  $x=21$  at. % (the conclusions about the frequency dependence of  $T_1$  are not affected by this difference in view of the small value of the relaxation rate at high frequencies). The lines are the theoretical behaviors according Eq. (15) in the text in the limit  $b \rightarrow \infty$ .

as a function of temperature. As it appears from the figures, in the high-temperature range  $T_1^{-1}$  is frequency independent and it is proportional to  $T^2$ , with absolute values close to the ones measured in NaCl. Below a temperature  $T_g \simeq 150$  K a  $\nu_L$ -dependent contribution to the relaxation rate is observed. This contribution has a broad maximum around 50–60 K for  $x=18$  at. % and around 40–50 K for  $x=12$  at. %. In Fig. 4 the  $\nu_L$  dependence of the relaxation rates at two representative temperatures is shown. The solid lines in Fig. 4 are the theoretical best fits, as discussed in Sec. III [Eq. (15)]. For  $T < 30$  K the frequency dependence of  $T_1$  is progressively changing, as shown schematically in Fig. 5 for three different measuring frequencies. For the crystal at  $x=18$  at. % a complete analysis of the frequency dependence of the relaxation rate has been carried out at  $T \simeq 4.2$  K. The results are shown in Fig. 6. A few other data obtained at  $T \simeq 2$  K (for  $x=18$  at. %) and at  $T \simeq 4.2$  K for  $x=5$  at. % will be given in the analysis of the results (Sec. III).

### C. History-dependent effects

History-dependent effects involve the recovery law  $R(t_m) = [s(\infty) - s(t_m)] / s(\infty)$  for the  $^{23}\text{Na}$  nuclear magnetization, as derived from the FID amplitude  $s(t_m)$  following a train of saturating pulses. In the crystal at

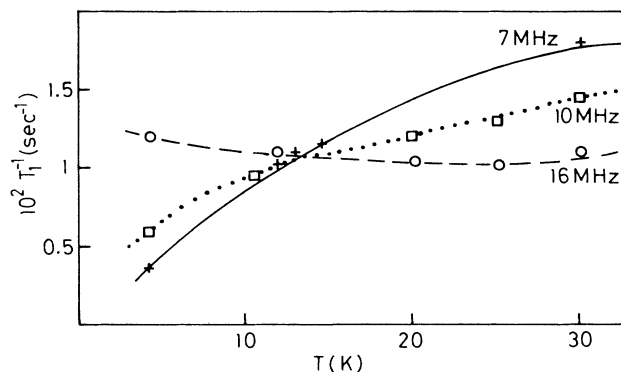


FIG. 5. Illustration of the changeover in the  $\nu_L$  dependence of the  $^{23}\text{Na}$  relaxation rate for  $T \lesssim 30$  K in  $\text{K}_{0.82}\text{TaO}_3:\text{Na}_{0.18}$  (the lines are only guides to the eye).

$x=5$  at. % (and partially for the one at  $x=12$  at. %), one observes that, after a temperature jump  $\Delta T$  from above to below  $T_g$ ,  $R(t_m)$  depends on the time  $t$  elapsed from  $\Delta T$ . After the temperature jump  $\Delta T$  [typically from room temperature (RT) down to 77 K] the recovery is described by an exponential law, i.e.,  $R(t_m) = \exp(-t_m/T_1^i)$ . After a time  $t \simeq 200$  h the recovery is again exponential with a time constant  $T_1^{(t \rightarrow \infty)} \equiv T_1^f$  different from  $T_1^i$ .

As shown in Fig. 7, in an intermediate  $t$  range the recovery is not described by an exponential law. In the crystal at  $x=12$  at. % the difference between  $T_1^i$  and  $T_1^f$  is smaller than the one for  $x=5$  at. % and the nonexponentiality of the recovery is more difficult to detect.

The metastability effects are angle independent (at least for rotation of the crystal around a cubic axis perpendicular to  $\mathbf{H}_0$ ), but they do depend on the measuring frequency  $\nu_L$  (at 8 MHz the effect was hardly detectable). For a temperature jump from room temperature (RT) to  $T > T_g$  the recovery of the magnetization was always exponential, at several  $\nu_L$  frequencies ranging from 9 to about 60 MHz.

It is appropriate to observe that a nonexponential

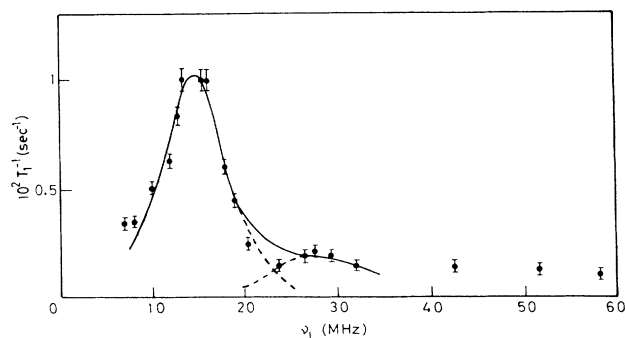


FIG. 6. Dependence of the  $^{23}\text{Na}$  relaxation rate in  $\text{K}_{0.82}\text{TaO}_3:\text{Na}_{0.18}$  from the measuring frequency  $\nu_L$ , at liquid-helium temperature. The solid line is the best-fit theoretical behavior of the data according to Eq. (18) or (20) in the text (the dashed lines represent the behaviors of the individual components at  $\omega_L$  and  $2\omega_L$  which add up to yield the solid line).

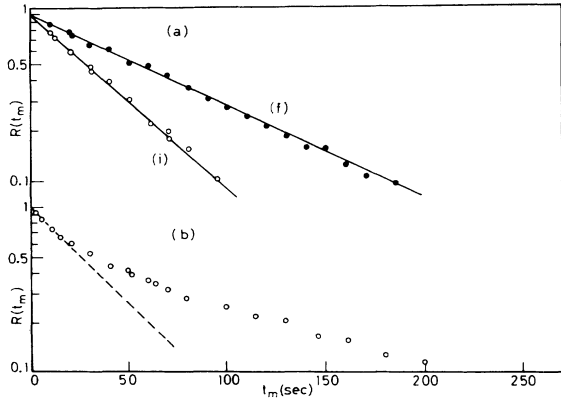


FIG. 7. Illustration of the metastability effects on the recovery law for the  $^{23}\text{Na}$  nuclear magnetization in  $\text{K}_{0.95}\text{TaO}_3:\text{Na}_{0.05}$  crystal, following a temperature jump from RT down to liquid-nitrogen temperature. In (a) the initial ( $t=0$ ) and final ( $t \rightarrow \infty$ ) recovery are shown. (b) refers to the intermediate ( $t=25$  h) nonexponential recovery.

recovery can occur, for equally spaced Zeeman levels, only when the spin diffusion does not induce a common spin temperature in parts of the system having different  $T_1$ 's.<sup>26</sup> When the spin-diffusion process, namely the transport of spin temperature through energy-conserving spin flips, is fast enough to induce a common spin temperature within a time shorter than  $t_m \simeq T_1$ , then  $R(t_m)$  is exponential, with an average time constant. On the basis of the spin-diffusion equation<sup>26</sup> one can estimate the length  $\lambda$  over which the spin temperature diffuses in a time  $t_m$ :

$$\lambda = d(t_m/GT_2)^{1/2} \simeq 65a(t_m/G)^{1/2}/x^{1/12}. \quad (5)$$

In Eq. (5),  $T_2$  is the rigid-lattice spin-spin relaxation time that from the evaluation of the dipole-dipole second moment for a crystal with cubic axis along  $\mathbf{H}_0$  (see Sec. II A) is  $T_2^{-1} = 4.16 \times 10^3 \sqrt{x}$  rad sec<sup>-1</sup>;  $d = (a/x^{1/3})$  ( $a$  being the cubic lattice constant) is the nearest-neighbor distance between Na nuclei and  $G$  is a constant depending on the particular lattice, roughly varying between 10 and 50. By using  $G \simeq 25$  and  $t_m \simeq 10$  sec, Eq. (5) yields  $\lambda \simeq 220$  Å for  $x = 5$  at. %. One can conclude that there are regions which do not immediately attain thermal equilibrium, yielding to a distribution of  $T_1$ 's in the metastable state.

### III. ANALYSIS OF THE RESULTS AND LOCAL DISORDER DYNAMICS

The  $^{23}\text{Na}$  spin-lattice relaxation is driven by the time-dependent part of the EFG functions  $V_{1,2}(t)$  involving the  $V_{jk}$  components in the laboratory frame of reference  $\Sigma^H$ .<sup>25</sup> In order to derive  $W_1$  and  $W_2$  one can expand  $V_{1,2}$  in terms of the displacement of the Na ion. By referring for simplicity of presentation to the case of the motion along one direction, one writes

$$V_{1,2}(t) = 0 + \left. \frac{\partial V_{1,2}}{\partial x} \right|_0 x(t) + \frac{1}{2} \left. \frac{\partial^2 V_{1,2}}{\partial x^2} \right|_0 x^2(t). \quad (6)$$

For quasiharmonic local potentials, with well-defined phonon states, the effective relaxation mechanism is associated to the quadratic term through a two-phonon second-order process. For a qualitative discussion of the  $T_1$  data in the high-temperature region ( $T \gtrsim 200$  K) one can disregard the details of the phonon spectrum. Thus, we will schematically describe the spectrum of the excitations with a Lorentzian density of states  $g(\omega)$ , centered at an effective frequency  $\omega_{\text{eff}}$ , with a width  $\Gamma$  taking into account the broadenings due to the dispersion and/or to lifetime of the phonons. Under such an assumption, by using Eq. (4) and the quadratic term in Eq. (6) and by integrating over  $\omega$ , one can obtain<sup>27</sup>

$$T_1^{-1} = \frac{e^2 Q^2}{2m \hbar^2} (1 - \gamma_\infty)^2 \left( \frac{160e}{a^5} \right)^2 \frac{k^2 T^2}{\Gamma \omega_{\text{eff}}^4}. \quad (7)$$

In the derivatives for  $V_{1,2}$  we have assumed the isotropy conditions

$$\langle |V_1(t=0)|^2 \rangle = 2 \langle |V_{zz}(t=0)|^2 \rangle = \frac{8}{7} \langle |V_2(t=0)|^2 \rangle,$$

while for  $V_{zz}$  the results of a numerical calculation<sup>28</sup> in the  $\text{KTaO}_3$  lattice have been used. Equation (7), with the  $T^2$  dependence and its  $\nu_L$  independence (two characteristic features of the second-order two-phonon relaxation process), describes the  $T_1$  results in Fig. 3 for  $T \gtrsim 200$  K.

The  $T_1$  data for  $T \lesssim 200$  K require a rather different description. In fact, one observes a progressive departure with respect to the behavior in NaCl, with a marked  $\nu_L$  dependence and a broad maximum in the relaxation rate which depends on  $\nu_L$  and  $x$ . The frequency dependence indicates that the relaxation mechanism taking place below  $T_g \simeq 150$  K is a direct process,<sup>29</sup> related to the first-order term in Eq. (6). Since for quasiharmonic phonon modes one has a low number of excitations in the radio-frequency range, one can conclude that below  $T_g$  the relaxation rates reflect the insurgence of an alternative dynamics implying modifications in the effective local potential.

The changeover in the local potential can be described, according to two basic pictures, as somewhat equivalent: (a) mean-field-approximation (MFA) dynamics of the Na impurity in the soft paraelectric matrix  $\text{KTaO}_3$ , and (b) a "frustrated" transition, with pretransitional clusters and raising of a central peak. Case (a) refers to the evaluation<sup>30</sup> of the correlation function for impurities in perovskite crystals, predicting a local freezing. Instead of a strictly static order parameter, which is an artifact of the MFA, a slow hopping mode of relaxational character between the off-center positions substitutes the resonant soft-lattice modes.

Case (b) is more directly related to the effect of the disorder. By considering the  $\text{KTaO}_3:\text{Na}$  crystals as resulting from the dilution of  $\text{NaTaO}_3$  with the paraelectric  $\text{KTaO}_3$  (with  $T_c \rightarrow 0$ ), one expects that, below a threshold concentration, the disorder is capable of frustrating the ferroelectric transition. Therefore, in a rather wide temperature range the mixed crystal is in a "pretransitional" situation and develops short-range clusters of correlated fluctuations. The short-range order im-

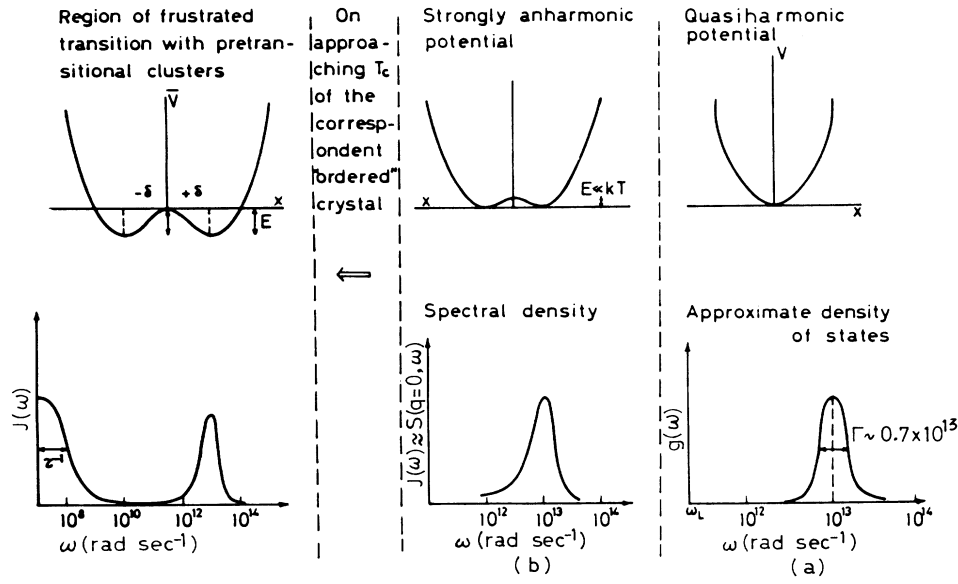


FIG. 8. Schematic illustration of the local potentials for the Na ion in the high-temperature range ( $T \gg T_g$ ) and for  $T < T_g$ , with the corresponding spectral densities for the spin-lattice relaxation process (see text).

plies, on cooling, a crossover from a displacive to an order-disorder regime, yielding a local strongly anharmonic potential, as shown by computer simulations<sup>31</sup> and by one-dimensional analytic treatments.<sup>32,33</sup> Thus, on approaching  $T_c$  one observes the onset of a central peak (CP) in the dynamical structure factor  $S(\mathbf{q}, \omega)$ , in addition to the soft modes of resonant character.

The above picture is illustrated in Fig. 8. Figure 8(a) refers to the model of a quasiharmonic potential and the density of states  $g(\omega)$  involved in the two-phonon relaxation mechanism (quantum lattice) which has been derived from Eq. (7), in the assumption  $\Gamma \sim \omega_{\text{eff}}$ ; Fig. 8(b) is the high-temperature region for a double-well local potential with the condition  $kT \gg E$  and the correspondent spectral density is the schematic representation of the result for the dynamical structure factor  $S(\mathbf{q}, \omega)$  for  $\mathbf{q}=0$ .<sup>33</sup> For the derivation of  $J(\omega)$  we have used the results for  $E$  and  $\delta$  obtained in the analysis of the relaxation rate as a function of temperature and of the measuring frequency (see below). One should note the basic equivalence in the case of Figs. 8(a) and 8(b) with regard to the spectrum of the excitations. In Fig. 8(c) the situation arising in presence of a frustrated transition, and pretransitional short-range clusters of correlated motion, is described. The data reported for illustration of the spectral density have been derived from the experimental results (see below). To describe the relaxation process in the pretransitional situation let us refer to the one-dimensional potential of the form considered by Aubry:<sup>33</sup>

$$V = \sum_i (-ax_i^2 + bx_i^4 + \bar{c}x_i x_{i+1}), \quad (8)$$

namely a double-well potential with minima at  $\delta = \pm(a/2b)^{1/2}$  and barrier height  $E = (a\delta^2/2)$ . The coefficient  $\bar{c}$  describing the bilinear coupling in Eq. (8)

takes into account a cluster average over the possible configurations:

$$\sum_{i,j} cp_i p_j x_i x_j = \bar{c} \sum_{i,j} x_i x_j$$

( $p_i = 1$  when the site is occupied by Na; 0 otherwise).

For a direct relaxation mechanism, one can refer to a model of a "classical lattice" and write  $W_{1,2}$  in terms of the correlation function  $g(t) = \langle x(t)x(0) \rangle$ .<sup>29</sup>  $W_{1,2}$  involves the Fourier transform of  $g(t)$  in the low-frequency region. We can derive the correlation function for the motion of the Na ions by referring to the results of Aubry<sup>33</sup> in the asymptotic limit and integrating over  $\mathbf{q}$ . We obtain

$$g(t) = \delta^2 \exp(-t/\tau) \quad (9)$$

with an effective correlation time  $\tau = \xi/v$ , where  $\xi$  is the static correlation length and  $v$  an average velocity of propagation of the solitonlike excitation, of the order of the sound velocity.

The correlation length results,

$$\xi = -2d \left[ \frac{\bar{c}}{a} \right]^{1/2} [\ln \tanh(E_{\text{eff}}/kT)]^{-1} \quad (10)$$

with  $E_{\text{eff}} \approx 1.75E(2\bar{c}/a)^{1/2}$ , which, for  $kT < E_{\text{eff}}$ , yields to

$$\tau = \tau_0 \exp(E_{\text{eff}}/kT) \quad (11)$$

with  $\tau_0 = d(\bar{c}/a)^{1/2}/v$ , of the order of the time required for the excitation to proceed over the average Na-Na distance  $d$ .

Starting from the standard expressions<sup>25</sup> for  $W_{1,2}$  in terms of the Fourier transform of the correlation function, one has

$$W_{1,2} = \frac{1}{12} \frac{e^2 Q^2}{\hbar^2} \left[ \frac{\partial V_{1,2}}{\partial x} \right]_0^2 \delta^2 \frac{2\tau}{1 + \omega_{1,2}^2 \tau^2} \quad (12)$$

with  $\omega_1 = \omega_L$  and  $\omega_2 = 2\omega_L$ . Taking into account the symmetry conditions for a crystal with a cubic axis perpendicular to  $\mathbf{H}_0$ , the correlation functions for the  $V_{jk}$  components can be related to each other. From Eq. (4), by using Eq. (12), the relaxation rate becomes

$$T_1^{-1} = \frac{1}{5} \omega_Q^2 \left[ \chi \frac{2\tau}{1 + \omega_L^2 \tau^2} + 2(1 + \chi) \frac{2\tau}{1 + 4\omega_L^2 \tau^2} \right], \quad (13)$$

where  $\chi = \frac{4}{3} \langle V_{xy}^2 \rangle / \langle V_{zz}^2 \rangle$  is a constant of the order of unity. In Eq. (13),  $\omega_Q$  is an effective quadrupole coupling constant,

$$\omega_Q = \frac{eQ}{2\hbar} \left[ \frac{\partial V_{zz}}{\partial x} \right] \delta = \frac{eQ}{2\hbar} (\langle V_{zz}^2 \rangle)^{1/2}, \quad (14)$$

$$T_1^{-1} = \frac{\omega_Q^2}{5} \frac{1}{\omega_L \ln b} \{ \arctan(\omega_L \tau_g b) - \arctan(\omega_L \tau_g / b) + 2[ \arctan(2\omega_L \tau_g b) - \arctan(2\omega_L \tau_g / b) ] \}, \quad (15)$$

where  $\tau_g$  is the geometrical average. One can note from Eq. (15) that for  $b \gg 1$  one has  $T_1^{-1} \propto \omega_L^{-1}$ .

In spite of the crudeness of the assumptions leading to Eq. (15), this relation fits rather well the experimental results for the  $\nu_L$  dependence (see Fig. 4) as well as the temperature behavior at constant  $\nu_L$ , for  $T \gtrsim 20$  K (see Fig. 9). One should stress that in order to reduce the number of adjustable parameters we have assumed that the effective activation energy for  $\tau$  [see Eq. (11)] is temperature independent. The departure of the theoretical behavior from the experimental data for  $T \lesssim 20$  K is a consequence of this assumption and it will be discussed later.

From the fitting of the relaxation rates as a function of  $T$  and  $\nu_L$  on the basis of Eq. (15), one derives for the effective activation energy  $E_{\text{eff}} = 1.75(2\bar{c}/a)^{1/2} E \simeq 200 \pm 20$  K; the distribution of  $E_{\text{eff}}$ , given by  $\Delta = T \ln b$ ,

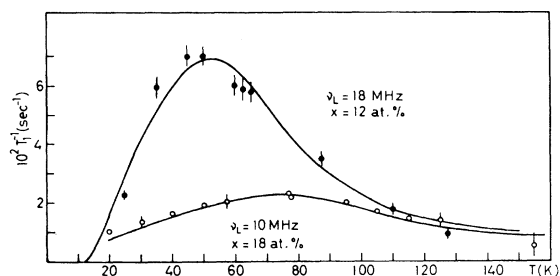


FIG. 9. Comparison between the experimental results for the first-order contribution to the  $^{23}\text{Na}$  relaxation rate (as obtained from the data in Fig. 3 with the subtraction of the background due to the second-order term) and the theoretical behaviors predicted by Eq. (15) in the text.

that the Na-nucleus experiments in one of the off-center positions given by the minima in  $V(x)$  [see Eq. (8)].

One can note, from Eq. (13), that the relaxation mechanism is equivalent to the one associated to the rotation of a static EFG moving the frame of reference of its principal axes with respect to  $\mathbf{H}_0$ , as occurs for the quadrupolar spin-lattice relaxation in liquids.

In view of Eq. (11) and of the meaning of  $\bar{c}$ , one has to consider a possible distribution of effective correlation times  $\tau$ , a feature typical of disordered systems. The common distributions are of Gaussian type. In this case, only numerical evaluations would be possible. We prefer to assume a simple rectangular distribution of  $\tau$  in logarithmic scale, which allows a derivation of  $T_1$  in close form and leads to conclusions analogous to the ones obtained by means of a numerical evaluation with a Gaussian distribution.

By integrating Eq. (13) over the distribution of  $\tau$ 's ranging from  $\tau_g/b$  to  $\tau_g b$ , and by assuming  $\chi=1$ , one has

is around 150 K, while the quadrupole coupling constant is

$$\nu_Q = 1.0 \pm 0.1 \text{ kHz}. \quad (16)$$

From this estimate, in light of Eq. (14), by using for  $V_{zz}$  a numerical evaluation in the point-charge approximation and taking into account up to five nearest neighbors, one obtains the distance where the local potential has the minima:

$$\delta \simeq 0.04 \text{ \AA}. \quad (17)$$

As already observed, for  $T \lesssim 20$  K the temperature and frequency dependencies of the relaxation rates no longer follow the theoretical predictions based on the assumption of a central peak of diffusive character. This low-temperature departure could be somewhat expected and indirectly supports the hypothesis that in disordered systems the height of a number of local barriers critically diverges for  $T \rightarrow 0$  K. In particular, the frequency dependence of the spin-lattice relaxation rate (see Fig. 6), for  $x = 18$  at. %, indicates that for  $T = 4.2$  K the dominant relaxation mechanism must be associated with a spectral density of resonant character.

Possible extrinsic sources for resonant relaxation mechanisms, such as paramagnetic impurities and cross relaxation with other nuclei at short  $T_1$ 's, have been considered. However, the temperature and concentration dependences seem to rule out the occurrence of spurious, nonintrinsic effects. It is worthwhile to discuss in some detail the possibility of cross relaxation with the Zeeman NQR  $^{181}\text{Ta}$  levels, in view of the experimental observation<sup>34</sup> of a wide distribution of  $^{181}\text{Ta}$  quadrupole coupling constants. The possibility of a fortuitous cross-

ing of <sup>23</sup>Na Zeeman levels with mixed quadrupole and magnetic levels of <sup>181</sup>Ta at  $H = 13$  kG (where the resonance spectrum of <sup>181</sup>Ta is not observable) cannot be completely excluded. However, it appears unlikely, in view of the following experimental findings:

(i) the relative sharpness of the effect (a magnetic-field range of about 6 kG) compared to the width<sup>34</sup> of the distribution of the mixed NMR-NQR <sup>181</sup>Ta levels;

(ii) the resonant peak in the relaxation rate disappears for  $T \cong 10$  K, where  $T_1$  is practically independent on  $\nu_L$  (see Fig. 5); and

(iii) the resonant peak in  $J(\omega)$  around 14 MHz has not been observed for concentration  $x = 5$  at.%, while a cross-relaxation mechanism should involve the nearest-neighbors Ta nuclei, thus being practically independent of the Na concentration.

The shape of the local potential and the occurrence of analogous phenomena in glasslike systems<sup>11</sup> leads to the hypothesis of quantum tunneling involving the minima of  $V(x)$ . The large mass of Na ions does not prevent quantum tunneling, mostly because of the small separation of the minima. Moreover, heavy-ion tunneling effects on spin-lattice relaxation have already been indirectly observed, e.g., for  $\text{Ag}^+$  in RbCl, from Cl and Rb NMR.<sup>35</sup>

The description of the spin-lattice relaxation driven by the quantum tunneling, in the presence of phonons, is a rather delicate matter and there are still unsettled questions.<sup>36</sup> When the excitations of the thermal bath are tunneling related, a quantum-lattice model can be more appropriate. Level crossing, between the Zeeman nuclear levels and the tunneling-split lattice ones, have to be considered in principle. This approach would imply an elaborate theoretical description, preventing an immediate comparison with the Na relaxation rates in the high-temperature regime, where a classical lattice is appropriate. Therefore we will first analyze  $T_1$  data at 4 K within a classical-lattice model, by assuming a resonant motion at the tunneling frequency  $\omega_T$  and a broadening over a frequency range  $\omega_c \sim \tau_c^{-1}$ , with  $\tau_c$  a characteristic time of coherence.<sup>37</sup> Further on, by referring to the tunneling along one of the cubic directions, we also show that equivalent results are obtained in the quantum-lattice scheme.

For an oscillatory motion at frequency  $\omega_T$ , the correlation function can be written as

$$g(t) = \delta^2 \exp(-\omega_c t \pm i\omega_T t),$$

and starting from Eq. (4) and by expressing  $W_{1,2}$  in the straightforward procedure, the analog of Eq. (13) is derived:

$$T_1^{-1} = \frac{1}{5} \omega_Q^2 \left[ \chi \frac{\tau_c}{1 + (\omega_L - \omega_T)^2 \tau_c^2} + \frac{2(1 + \chi)\tau_c}{1 + (2\omega_L - \omega_T)^2 \tau_c^2} \right]. \quad (18)$$

In the quantum-lattice scheme, the  $\Delta m = 1$  relaxation transition probability can be written as

$$W_1 = \frac{2\pi}{\hbar} \int |\langle \frac{1}{2}, g | \mathcal{H}_Q | \frac{1}{2}, u \rangle|^2 p(E_g) [1 - p(E_u)] \times \rho(E_u) \rho(E_g) \delta(E_u - E_g - \hbar\omega_T) dE_u dE_g. \quad (19)$$

An analogous expression holds for  $W_2$ . In Eq. (19)  $g$  and  $u$  label the *gerade* and *ungerade* lattice states with separation energy  $\hbar\omega_T$ , and the  $\rho(E_{u,g})$  are the respective densities of states with their occupation probabilities  $p$ . The underlying assumption is that two-phonon relaxation and/or phonon-phonon interactions are effective enough to maintain a thermal equilibrium distribution over the  $g$  and  $u$  states. This should be true in our case, in view of the very long  $T_1$ 's which circumvent phonon bottleneck.<sup>38</sup> In order to take into account the expected distribution in the barriers, and/or a possible broadening related to coherence effects, one can consider a distribution for the  $E_{u,g}$  energies, for which we assume a Lorentzian function of width  $\Delta$ . By expanding  $\mathcal{H}_Q$  in Eq. (19) similarly to Eq. (6), by evaluating the matrix elements of the quadrupole operators, and by using the same simplifying assumptions which lead from  $\partial V_{1,2}/\partial x$  to  $\partial V_{zz}/\partial x$  [see Eqs. (12) and (13)], one finally derives, for the relaxation rate,

$$T_1^{-1} = \frac{\omega_Q^2}{5} \left[ \chi \frac{\hbar/\Delta}{1 + (\omega_L - \omega_T)^2 \hbar^2/\Delta^2} + 2(1 + \chi) \frac{\hbar/\Delta}{1 + (2\omega_L - \omega_T)^2 \hbar^2/\Delta^2} \right]. \quad (20)$$

The equivalence of the classical-lattice and quantum-lattice descriptions is apparent from the comparison between Eqs. (20) and (18), under the condition  $\tau_c = \hbar/\Delta$ .

Equations (18) and (20) predict maxima in the relaxation rates for  $\nu_L = \omega_T/2\pi$  and  $\omega_T/4\hbar$  whose widths and amplitudes depend on  $\tau_c$ . The experimental results are compared with the theoretical behaviors in Fig. 6 for  $\chi = \frac{1}{3}$  and  $\tau_c = 3.9/\omega_T$ .

One can observe that the agreement between the theoretical expressions and the experimental data at  $T = 4.2$  K for  $x = 18$  at.% does not imply that all the Na ions tunnel in the local potential. In fact, the spin diffusion can transfer a fast-relaxation mechanism, thus yielding an exponential recovery with an average relaxation rate, even though the majority of the nuclei should not undergo the quantum tunneling. A crude estimate of the fraction of tunneling ions can be obtained by evaluating the value of  $T_1^{-1}$  at the peak in Fig. 6, expected on the basis of Eqs. (18) or (20). One has  $(T_1^{-1})_{\text{peak}} \cong 2\omega_Q^2/\omega_T$ . Thus by using for  $\omega_Q$  the value in Eq. (16), one observes that in order to obtain the experimental result  $(T_1^{-1})_{\text{peak}} = 10^{-2} \text{ sec}^{-1}$  one has to assume that only a few percent of the Na ions are actually tunneling.

A quantitative discussion of  $\omega_T$  requires the evaluation of tunneling matrix elements and uncertain results are often obtained, particularly when phonons are disregarded. To allow for the phonon modes there are basi-



cally two approaches. In the dressed-mass approach,<sup>39</sup> an approximate expression for  $\omega_T$  can be derived<sup>40</sup> in the form

$$\omega_T = \frac{8\sqrt{3}}{\pi\sqrt{\hbar}} m^{-1/4} (2\delta)^{-1/2} c^{1/4} E_{\text{eff}}^{3/4} \times \exp[-(mc)^{1/2} E_{\text{eff}}^{1/2} 2\delta/\hbar], \quad (21)$$

$c$  being the dressing factor of the mass  $m$  of the tunneling unit. In the renormalization-truncation approximation, the effective tunneling rate is given by<sup>41</sup>

$$\omega_T = \omega_T^0 \exp(-W_0/2), \quad (22)$$

where  $W_0$  is a kind of Debye-Waller factor related to the phonon spectrum and to constants characteristic of the matrix embedding the tunneling impurity.

By assuming for the barrier at  $T=4.2$  K an indicative value  $E_{\text{eff}}=500$  K, and keeping for  $\delta$  the value in Eq. (17), one derives  $\omega_T$  in the radio-frequency range for  $c \approx 40$  or, equivalently, for a factor  $W_0 \approx 30$ . These numerical estimates do not appear unrealistic in light of other results<sup>41,42</sup> for similar systems.

As already mentioned, in the crystal at  $x=5$  at. % a search for a peak in the relaxation rate as a function of  $\nu_L$ , carried out in the range 8–20 MHz, was negative. A very long  $T_1$ , of the order of hours, was measured at  $\sim 4$  K, practically independent of the frequency. This very long  $T_1$  rules out the hypothesis of “extrinsic” sources for the resonant peak in  $J(\omega)$  observed in the crystal with  $x=18$  at. %. Furthermore, a decrease by a factor of around 100 of the relaxation rate on reducing  $x$  from 18 to 5 at. % suggests a remarkable role of the concentration: the dynamics driving the relaxation appears related to the interaction among the Na impurities and is drastically reduced and/or shifted in frequency when the Na concentration is lowered.

Finally, we would like to discuss the metastability effects. The major conclusion is that, in the metastable condition, there is a spatial distribution of “local”  $T_1^{(i)}$ s which is not mediated by spin diffusion. In view of the fluctuation-dissipation theorem, we can conveniently discuss the distribution of the cluster-dependent relaxation rates in terms of the local dielectric susceptibility  $\chi_i''(\omega)$ . For simplicity of discussion, one can consider  $\chi_i''(\omega)$  to be equivalent to the homogeneous  $q=0$  dielectric susceptibility, even though, in general, one has a more complicated relationship between  $T_1$  and  $\chi''(\omega)$ .<sup>29</sup> It should be remarked that metastability effects on the magnetic susceptibility have been observed, below  $T_g$ , in Cu(Mn) spin-glass.<sup>43</sup> Following a temperature step, while the thermal equilibrium is achieved within few seconds,  $\chi''(\omega \rightarrow 0, T)$  shows a time dependence, reaching the equilibrium value  $\chi_{\text{eq}}''(\omega \rightarrow 0, T)$  in times of the order of 200 sec. By taking into account that local dielectric responses are of relaxational character (as indicated by the  $\nu_L$  dependence of the spectral densities) and that below  $T_g$  one has the onset of local order, one can write

$$(T_1^i)^{-1} \propto \frac{\chi_i''(\omega_L)}{\omega_L} = \frac{\chi_i(0)\tau_i}{1 + \omega_L^2 \tau_i^2}, \quad (23)$$

where  $\tau_i$  is an average relaxation time which, during the metastability, is different from cluster to cluster. A possible model supporting different  $\tau$ 's can rely on the consideration that the local short-range order induced below  $T_g$  in a cluster affects  $\tau_i$  in a way similar to the case of ordered crystals below  $T_c$ . Then, by referring, for example, to the dynamical Ising model, one has

$$\tau_i = \tau_0 \chi_i(0) \left( \frac{e^2 \langle x^2 \rangle}{kT} (1-p^2) \right)^{-1}, \quad (24)$$

where  $\tau_0$  is the relaxation time in the absence of the interactions,  $e \langle x^2 \rangle^{1/2}$  is the equivalent of a single-particle dipole, and  $p$  is a local order parameter within the cluster. One can observe that the distribution of cluster-dependent  $\tau_i$ 's occurs only during the metastability, the susceptibility at the thermal equilibrium being homogeneous over the whole crystal, with a common local dynamics and “order parameter”  $p$ .

One should mention that an analogous distribution of magnetic susceptibilities, in the configurational space, has been used<sup>44</sup> to explain the nonexponential form of the nuclear magnetization recovery in the dilute Cu(Mn) spin-glass. One can observe that the lack of the metastability effect for the crystal at  $x=18$  at. % indicates that the condition of homogeneous dynamics is achieved shortly after the temperature jump. This is not surprising in view of the observation that, for  $x \approx 16$  at. %, each Na ion always has another Na ion as its nearest neighbor (for homogeneous concentration).

History-dependent effects analogous to the ones showing up in the recovery law for the nuclear magnetization should be detectable in dielectric measurements. If no correlation is assumed, the extra contribution of  $n$  ions to the susceptibility, of the order of  $\chi_{\text{extra}} = ne^2 \langle x^2 \rangle / 3kT$ , with  $\langle x^2 \rangle = \delta^2$  and given by 0.04 Å, is smaller than the lattice susceptibility of the pure KTaO<sub>3</sub> by a factor of around 10<sup>4</sup>. The correlation of  $s$  ions within a cluster yields to an increase by a factor  $s$ . A time dependence of  $\epsilon'$  measured at 20 MHz after the temperature jump from RT to 77 K has actually been observed,<sup>45</sup> with a maximum variation of about a few percent after about 33 h. The interpretative model outlined above for the spin-lattice relaxation data also qualitatively explains the effects observed in the dielectric measurements.<sup>45</sup>

We would like to conclude with a few remarks on the character of the interactions among the Na<sup>+</sup> disordered units. An analysis of susceptibility data has been recently<sup>46</sup> carried out in order to elucidate the nature of the low-temperature phase in  $\text{K}_{1-x}\text{TaO}_3:\text{Na}_x$ . The analysis<sup>46</sup> seems to conclude in favor of a dipolar glass phase, analogous to the magnetic spin-glasses, associated with the off-center positions of the Na<sup>+</sup> ions.

As discussed in Sec. II A, the NMR spectra cannot rule out the occurrence of a small lattice distortion of ferroelectric type. However, the <sup>23</sup>Na NMR spectra do prove that the Na ions are not frozen out off center, on a time scale less than  $\nu_Q^{-1} \sim 10^{-3}$  sec. Furthermore, the experimental findings do not support the assumption of dipolar interactions among the Na units. In fact, the

minima in the local potential are so close, less than 0.1 Å, that the vibrational dynamics involves both the minima, yielding the on-center average position. Moreover, the order of magnitude of the interaction constant  $\bar{c}$  can be estimated from the assumption  $\bar{c}\delta^2 \simeq E_{\text{eff}}$  and from  $\nu_Q$  and the experimental activation energy one has  $\bar{c} \approx 10^{21}$  K/cm<sup>2</sup>. In the crude assumption of dipolar interaction of the form  $\bar{c}x_1x_2 = (e\delta\alpha)^2/ed^3$ , where  $\alpha$  is the enhancement factor of the dipole due to the polarizability of the matrix,<sup>28</sup> one has  $\bar{c} = 10^{19}(\alpha^2/\epsilon)$  K/cm<sup>2</sup>; to justify our estimate of  $\bar{c}$ , it would require, for  $\epsilon = 1000$ , an enhancement factor of  $\alpha \approx 100$ , unrealistic if compared with  $\alpha \approx 10$  evaluated<sup>28</sup> for the Li ion in KTaO<sub>3</sub>. Also, the measurements of the saturation polarization, yielding<sup>47</sup>  $P_s = 12$  mC/m<sup>2</sup>, would imply a maximum for  $\alpha$  around 5, even neglecting the large contribution to the polarization coming from the lattice.

Thus one is brought to the conclusion that the interaction among the disordered units should not be of long-

range dipolar character. The strong dependence of the metastable effects on the concentration  $x$  also does not support the hypothesis of dipolar interactions. In conclusion, the KTaO<sub>3</sub>:Na crystals are examples of crystals with disorder in the interactions and peculiar local dynamics which appear more similar to the structural glasses.

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