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## Ultrasonic dispersion and quadrupolar moments in $K_{0.95}Li_{0.05}TaO_3$

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**Abstract.** Ultrasonic measurements are reported on  $K_{0.95}Li_{0.05}TaO_3$  in a frequency range from  $10^7$  to  $10^9$  Hz and in a temperature range from 4 K to 200 K. The data for  $T \geq 75$  K are discussed in terms of a relaxation process associated with  $\pi/2$  reorientations and quadrupole moments induced by off-centre Li impurities. Relaxation is slightly polydispersive and follows an Arrhenius law with an excitation energy of 1070 K; there is no critical retardation. The Arrhenius parameters are similar to those found for nuclear magnetic relaxation. Below 70 K the data are indicative of scattering of acoustic waves by macroscopic domains.

### 1. Introduction

The mixed crystal  $K_{1-x}Li_xTaO_3$  consists of a host lattice  $KTaO_3$  with a cubic perovskite structure and also Li impurities which replace K at positions displaced by  $1.2 \text{ \AA}$  with respect to the centrosymmetric site [1, 2]. Accordingly, Li carries a dipole moment  $D = e\delta$  and a quadrupole moment  $e\delta^2$ , where  $\delta$  is the off-centre displacement. Numerous investigations have dealt with the properties of interacting dipole moments. The consensus is now that they dominate at low concentration and that they are at the origin of glass formation when  $x$  is less than about 0.04 [3, 4]. Several investigations suggest that this might not be the case at larger concentrations: evidence of long-range order has been provided by birefringence investigations [3–7], by x-ray [8] and neutron diffraction [9, 10], by Brillouin spectroscopy [5] and on theoretical grounds [4, 11, 12].

The attribution of experimental results to dipolar and quadrupolar properties has often been ambiguous in early investigations. A clear distinction was first made by Chase *et al* [5] who suggested that anisotropy seen by Raman scattering and hypersound was a sign of long-range quadrupolar order on at least a micrometre scale, whereas dipolar correlation was probably at a microscopic length scale, thus explaining the frustrated dipolar response. This view has, however, been disputed until recently; in particular some authors believe that crossover from glass formation to more or less long-range order can be attributed entirely to a change of dipolar interaction with concentration [4].

With the intention of shedding light on this controversy, we wish to report data on the *dynamic* elastic response of a sample with  $x = 0.05$ . To this end we present results for the complex elastic susceptibility at various frequencies  $\omega/2\pi$  and temperatures  $T$ . In contrast to most work on acoustic spectroscopy we want to express the frequency-dependent elastic constant in terms of a reduced dispersion curve  $\delta c(\omega)/c_0$  for fixed  $T$ . The dispersion curves are then parametrized in terms of generalized Debye relaxation functions. Their parameters will be given as a function of temperature and compared to analogous parameters gained from dielectric relaxation measurements. This will help us settle the question as to the origin of the relaxation modes in  $\text{KTaO}_3:\text{Li}$ . In addition, rapid variations of  $c$  with  $T$  are observed below 70 K. These observations which depend on sample history give information on symmetry changes of a macroscopic scale at low  $T$ .

## 2. Experiment

Single crystals were grown from a top-seeded solution [13] and shaped into parallelepipeds  $7 \times 3 \times 3$  mm in dimension with faces normal to [100] directions. The optical polish and parallelism of the sample faces allowed for ultrasonic propagation at high frequency and its detection by the pulse echo method [14]. From the transit time and from the ultrasonic attenuation we obtain the real and imaginary parts of the complex elastic constant  $c_1^*$  simply denoted  $c$ . We have measured the change of sound velocity with respect to a given calibration value at a fixed temperature and the ultrasonic attenuation, both as a function of frequency and temperature. To the best of our knowledge no such data have been reported in the literature. Therefore we describe in some detail how these data have been evaluated. Rather than plotting  $c$  versus  $T$  at some fixed  $\omega$  we chose to plot  $\delta c/c_0 = -c_1 + jc_2$  versus frequency,  $\omega/2\pi$ , at fixed  $T$ . The reference value is  $c_0 = 4.2 \times 10^{11} \text{ N m}^{-2}$ . With this convention,  $c_1 > 0$  and  $c_2 > 0$  denote a slowing down and an attenuation of the ultrasonic wave, respectively. We have subtracted a constant background from  $c_2$  and a background linear in  $T$  from  $c_1$  and plotted the results in figure 1.

At first sight it appears that a fit to

$$\delta c/c_0 = \Delta c/(1 + j\omega\tau) \quad (1)$$

is reasonable. A numerical fit of the data to (1) shows, however, that the ultrasonic response is broader than that predicted by the Debye model for a single relaxation. In dielectric spectroscopy [15, 16] it is standard to replace the relaxation time  $\tau$  by a distribution of relaxation times [17]. If we derive the relaxation times from a Debye model we may interpret them as arising from a reorientation between equivalent states over a barrier  $E_b$  [18]. A Gaussian distribution of barriers leads to a Gaussian distribution in  $\ln \tau$  and, in view of superposition, to the Debye–Wagner function [17] defined as

$$\delta c/c_0 = \Delta c \int (1 + j\omega\tau)^{-1} g(\ln \tau) d \ln \tau \quad (2a)$$

where

$$g(\ln \tau) = \pi^{-1/2} \Delta^{-1} \exp(-(\ln \tau - \ln \tau_0)^2/\Delta^2) \quad (2b)$$

is a log-normal distribution of relaxation times centred at  $\ln \tau_0$ . In the limit of vanishing width,  $\Delta = 0$ , (2a) and (2b) reduce to the expression for Debye relaxation, (1).

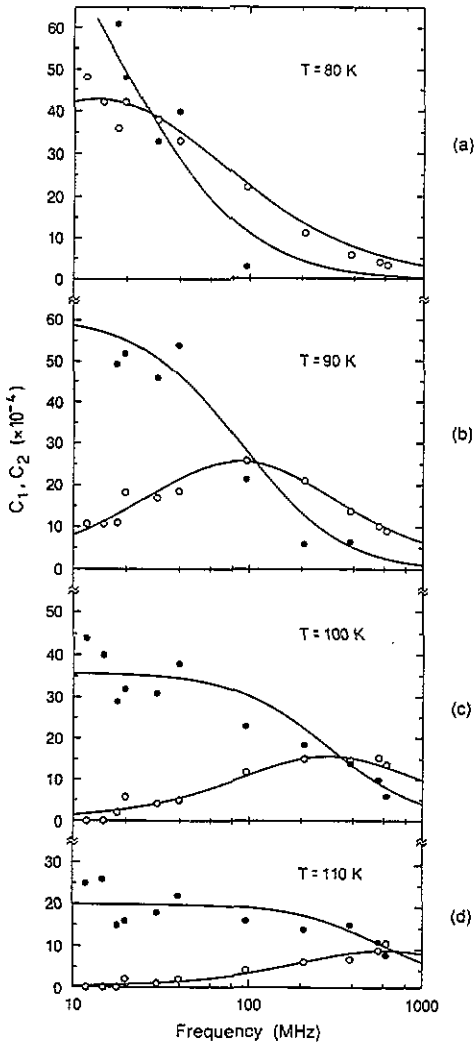
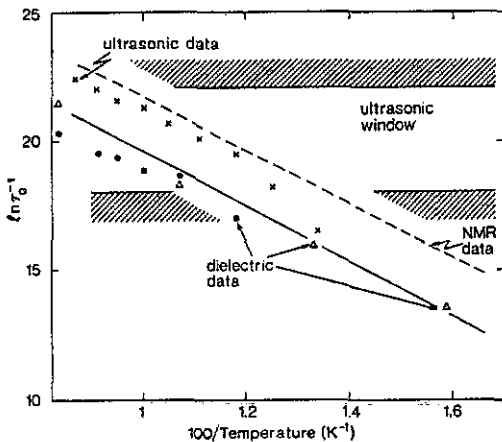


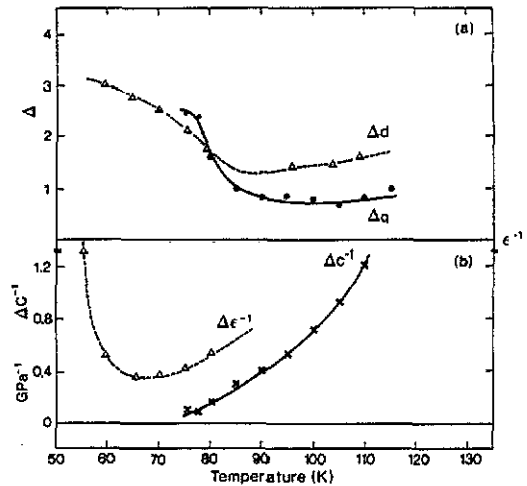
Figure 1. Real (●) and imaginary (○) parts of quadrupolar susceptibility  $c_1$  and  $c_2$  versus  $\ln \omega$  and fit to Debye-Wagner functions (see (2) in text). A constant background is subtracted from  $c_2$  and a background linear in  $T$  from  $c_1$ . For the fit, the weight of  $c_2$  is three times that of  $c_1$ .

There are three parameters, namely  $\Delta c$ ,  $\tau_0$  and  $\Delta$  to be determined from the numerical fit of  $\delta c(\omega)$  versus (2). These fits are presented in figure 1 for several temperatures. We note that the scatter of the real part is larger than that of the imaginary part. This reflects two contributions to the experimental uncertainty, one arising from the temperature-dependent (rather than constant) background of  $c_1$ , the other due to propagation problems in small samples, especially at low frequency. We have chosen to reduce the weight of  $c_1$  data by a factor of three, thus balancing the relative contribution of the data for  $c_1$  and  $c_2$  to the error function  $\chi^2$  [19]. We note that for relaxation rates within the window for ultrasonic experimentation, i.e. between 12 and 600 MHz (see figure 1), the results do not depend critically upon the weight function. A fit of  $c_2$  only to (2) gives very similar results. Such a fit does not, however, take into account causality as expressed by the Kramers-Kronig relation between  $c_1$  and  $c_2$ .

In figure 2 we present the relaxation rate  $\tau_0^{-1}$  versus  $1/T$  on semilog scales. A straight line fits the data in this Arrhenius plot. The relevant parameters are the attempt rate



**Figure 2.** Relaxation rate  $\tau_0^{-1}$  versus  $1/T$  on a semilog scale:  $x$  elastic data (this work);  $\bullet$  dielectric data  $x = 0.06$ ;  $\Delta$  dielectric data,  $x = 0.04$  (from [16]); solid line: fit to elastic data; broken line: NMR data equation (27) of [2].



**Figure 3.** (a) Width of relaxation time distribution  $\Delta_q$  for quadrupoles and  $\Delta_d$  for dipoles [26]. (b) Inverse of quadrupolar and dipolar [26] dispersion steps versus temperature. Full curves indicate elastic dispersion step, broken curves indicate dielectric dispersion step. Curves are guides to the eye.

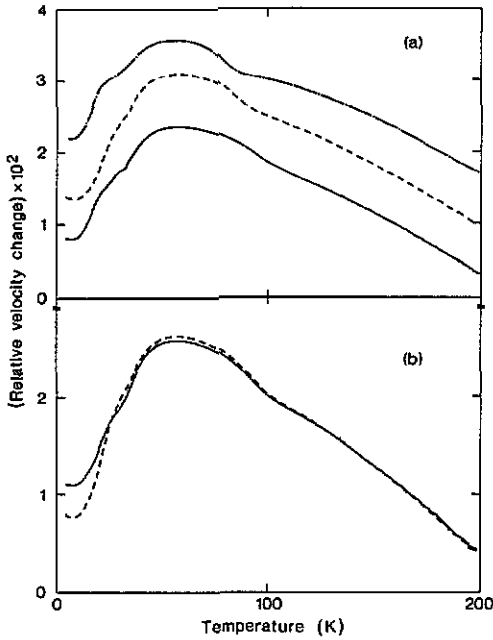
$\tau_x^{-1} = 7 \times 10^{13} \text{ s}^{-1}$  and the energy barrier hindering quadrupolar reorientation  $E_b = 1070 \text{ K}$ . The data are very similar to those taken by nuclear magnetic resonance, also shown in figure 2. It appears that quadrupolar relaxation is systematically more rapid than dielectric relaxation, by about a factor of six. The data for the distribution width are given in figure 3(a). We note a slight increase in  $\Delta$  if  $T$  drops. The values are somewhat below the corresponding values obtained from dielectric relaxation [16]. The elastic dispersion step varies much more rapidly with  $T$  than the Curie law (figure 3(b)). It is a maximum at 75 K, the lowest temperature where meaningful ultrasound data were taken.

Below 70 K we observe a sound propagation which varies in an irregular way with frequency and temperature. The found velocity decreases by about 1.5% from 60 K to 10 K with only a weak dependence on the frequency and the cooling rate (figure 4(a)). On the other hand the sound attenuation shows a behaviour which strongly depends on the frequency and on the cooling rate. It presents for the higher frequencies a rather complicated aspect with narrow peaks and dips (figure 5).

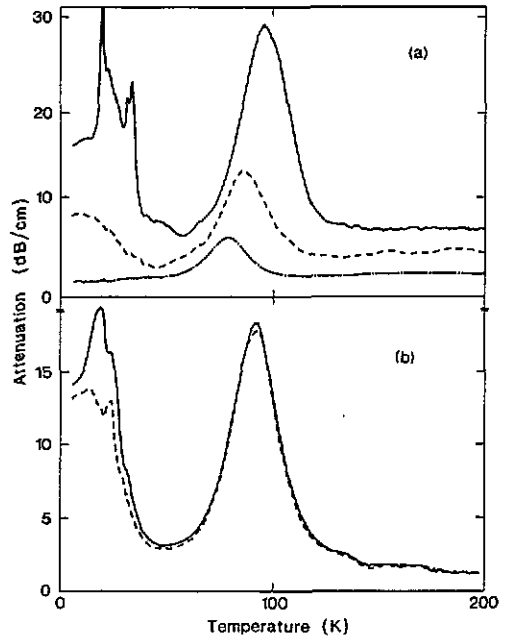
We found thus that the response of Li-associated quadrupoles to a strain becomes progressively slower as  $T$  drops towards 75 K and that the average relaxation rate was described by an Arrhenius function. Relaxation becomes stronger and the relaxation-time distribution wider as  $T$  drops. Below 75 K the spectra are irregular in many respects. We shall compare these findings with analogous and complementary results and attempt to explain these facts in the next section.

### 3. Interpretation

We start by evaluating the temperature dependence of the relaxation parameters  $\tau_0$ ,  $\Delta$  and  $\Delta c$  and by comparing it to analogous values obtained by other methods. From figure



**Figure 4.** (a) Relative sound velocity change as a function of temperature for longitudinal waves in the [100] direction of a  $K_{0.95}Li_{0.05}TaO_3$  sample at various frequencies: chain curve: 30 MHz; broken curve: 90 MHz; full curve: 627 MHz. (b) Same as in (a) but at 210 MHz for both sets of data taken at different cooling rates.



**Figure 5.** (a) Sound attenuation as a function of temperature for longitudinal waves in the [100] direction of a  $K_{0.95}Li_{0.05}TaO_3$  sample at various frequencies: chain curve: 30 MHz; broken curve: 90 MHz; full curve: 627 MHz. (b) Same as in (a) but at 210 MHz for both sets of data taken at different cooling rates.

2, it is evident that the average relaxation rate follows an Arrhenius law  $\tau_q = \tau_\infty \exp(E_b/kT)$  where  $\tau_\infty = 0.14 \times 10^{-13}$  s;  $E_b = 1070$  K. This behaviour is very nearly identical with the relaxation rate obtained by nuclear magnetic resonance experiments [2]. This indicates that, at least above 80 K, the elastic quadrupole moments are tied to the nuclear quadrupole moments and that these moments behave nearly as independent entities. At and below 80 K the elastic quadrupoles relax more slowly than the nuclear quadrupoles and, in addition, relaxation becomes non-exponential. This is evidenced by a rapid broadening [14] of the log-normal distribution of relaxation times as shown in figure 3(a). Finally, we remark that the relaxation strength  $\Delta c$  increases more rapidly than with  $T^{-1}$ . We have plotted  $\Delta c^{-1}$  versus  $T$  in an attempt to determine a critical temperature at which  $\Delta c^{-1} = 0$ , i.e. where the elastic susceptibility diverges. Inspection of figure 3(b) shows that such a critical point cannot be given since  $\Delta c^{-1}$  reaches 0 asymptotically. This statement is reinforced by the observation of a strong elastic dispersion in a torsion pendulum experiment at  $\sim 0.1$  Hz [20]. We first attempt to account for these findings in terms of spin-glass terminology: the relation between the magnetic susceptibility and the acoustic response has been considered recently [21] on the basis of the Sherrington-Kirkpatrick [22] model of a spin glass. Translated into dipole-glass terminology the findings imply that the static acoustic susceptibility varies as a monotonic function  $\gamma^2/T$  where  $\gamma = [\text{Var}(J)]^{-1} \times \partial \text{Var}(J)/\partial S$ ,  $S$  being the strain, and  $J$  the interaction between dipoles assumed to have zero average and non-zero variance  $\text{Var}(J)$ ,

whereas  $\varepsilon \sim c/T\{1 + \text{constant}/(T - T_0)\}$  tends to diverge at  $T_0$ . Quantitative differences between  $\varepsilon$  and  $\delta c$  are also revealed by Monte-Carlo calculations [23]. The dynamics, as described by  $\tau_0$  and the width of the distribution should, however, be the same for  $\varepsilon$  as for  $\delta c$ .

Inspection of figures 2 and 3 supports these findings: dielectric and ultrasonic relaxation are attributed to the same barrier and the actual rates are the same within a numerical factor. We believe that the single-particle relaxation rates should be identical for quadrupoles and for dipoles and that the observed difference is a consequence of interaction between particles. Another hint at interactions is provided by the relaxation distribution, whose widths are nearly the same at all temperatures. The dielectric relaxation steps shows a maximum near 70 K whereas there is insufficient evidence for a maximum on the basis of ultrasonic spectroscopy. The 70 K anomaly was, however, observed in piezoelectric-resonance investigations at low frequency [24].

For temperatures  $T \leq 70$  K we have observed the time-dependent effects of hysteresis and cooling-rate dependence. They were also seen in x-ray [8] and birefringence [7] experiments. In addition, we have observed a marked decrease of the sound velocity when the temperature is decreased and a complicated scattering of the ultrasonic waves in the 100 MHz range. On the other hand, Andrews [8] has shown that the tetragonality measured with x-rays steadily increases when the temperature goes to zero. It is likely that an increasing elastic anisotropy is associated with that tetragonality.

These features are reminiscent of the scattering of an elastic wave in an inhomogeneous medium. We know that in this case the velocity is less sensitive to inhomogeneities than the attenuation [25]. The inhomogeneities could be domains of tetragonal symmetry, as observed by Andrews [8], with their fourfold axis directed along one of the three parent cubic axes. Considering that the measured attenuation is negligible at 30 MHz and rather strong at 300 MHz we may infer that the domain size is of the order of the magnitude of the wavelength in the 300 MHz range, i.e. a few micrometres. The sample is thus made up of a compact array of three mutually perpendicular types of domains. In this heterogeneous medium an elastic wave suffers a Rayleigh scattering which is strong when the wavelength is of the order of the scatterers' size. The sound velocity results from an averaging over the sample: if two-thirds of the domains decreases the velocity (as compared to the velocity in the cubic phase) while the other third increases it, averaging may lead to a net decrease as observed. Obviously the distribution of the domains depends on the quenching of the sample.

These findings shed light on the controversy that arose regarding the nature of the ground state in highly concentrated  $\text{KTaO}_3: \text{Li}$  [3, 4]. It is clearly established here that the dynamics of the Li displacements are the same whether probed by ultrasound or electric fields. At high temperature, the dipole moment and the quadrupole moment thus behave in the same way. Accordingly, at concentrations up to at least 5%, dipolar interactions and the crystal field determine the dynamics of the freezing process. Below  $T_f$ , ultrasound propagation reveals a domain-like structure. It appears that quadrupoles order, in contrast to dipoles. The quadrupolar order extends to near-macroscopic distances and appears to increase with concentration [7]. This explains the marked differences between low- $x$  and high- $x$  behaviour seen in many experiments [5–8].

Obviously, a sample appears ordered if the coherence length of the probing field is smaller than the domain size and appears otherwise disordered. Coherence lengths in x-ray and light scattering experiments are in the submicrometre range. Therefore, the crossovers from apparently ordered to apparently disordered configurations at some critical concentration refer to an observation at a particular, although important, length

scale. Such experiments give, however, no evidence for a crossover from frustrated to ferroelectric interaction between dipoles. On the contrary, we find that the dynamics of the dipoles are independent of  $x$  and suggest that the dominant interaction is between Li dipoles and is frustrated at all concentrations investigated.

#### 4. Conclusion

The quadrupole moment associated with the Li displacement has the same dynamical properties as the dipole moment, provided  $T > T_f$ , and at Li concentrations up to and including 5%. As the dipole moments freeze out to form a disordered, glassy state at  $T_f = 70$  K, the quadrupole moments correlate over distances comparable with the ultrasonic wavelength,  $1 \mu\text{m}$ . The dynamics of the quadrupoles deviate from those of the dipole only near  $T_f$ . Such deviations are revealed by near-static, but not by ultrasonic experiments.

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