Strophoidal Argand Diagram and the Distribution of Relaxation Times in $K_{1-x}Li_xTaO_3$

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We have studied the relaxation of off-center Li^+ ions in $KTaO_3$ by dielectric measurements on 1% and 1.5% crystals, from 20 Hz to 2 MHz and from 4 to 200 K. The shape of the ε'' vs ε' Argand diagrams demonstrates the existence of a distribution of relaxation times. In analogy with spin glasses, a new expression is proposed for the analysis of these diagrams, a strophoidal function, which leads to a distribution function $D(\theta)$ decreasing for large θ as $\theta^{-(1+\alpha)}$ with $0 < \alpha < 1$. The most probable relaxation time θ_{mp} of the distribution follows an Arrhenius law with a barrier height close to 950 K.

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When Li^+ ions are substituted for larger K^+ ions in $KTaO_3$ crystals they occupy off-center positions, therefore inducing an electric dipole moment as well as a nonspherical elastic quadrupole moment. Owing to the randomness of substitution, the interaction between dipoles is also random. This includes the usual dipolar interaction and the indirect coupling due to the soft ferroelectric mode in this highly polarizable crystal. The combination of these two types of interaction is expected to lead to unusual dipole dynamics and, upon cooling, to a phase transition, the nature of which is still not well understood [1,2]. In this Letter, we propose a new description of the dipole dynamics which is believed to play a crucial role in the transition.

In order to investigate the relaxation of the Li dipoles, we have performed a systematic study of the complex dielectric constant $\varepsilon=\varepsilon'-i\varepsilon''$ and the resulting Argand diagrams (AD), also called Cole-Cole diagrams, ε'' vs ε'. The shape of these diagrams clearly reveals the unusual character of the relaxation which we intend, in contrast to previous studies [3–8], to explain more precisely. To this end, we propose a new dielectric susceptibility function, the form of which was inspired by an analogy with the magnetic susceptibility of spin glasses. In both cases, the susceptibility is the response to an external field of an assembly of identically relaxing dipoles (magnetic or electric) when the interactions between dipoles are random. The eigenmodes of the system may be determined by diagonalization of the interaction matrix. The corresponding transformation leads to a distribution of relaxation times for the eigenmodes which, in turn, determines the form of the dynamic susceptibility [9,10].

The dielectric measurements have been carried out on two crystals of $K_{1-x}Li_xTaO_3$ (KLT) with concentrations $x=1\%$ and 1.5% as a function of the temperature (4 K $< T <$ 200 K) and over a broad range of frequency (20 Hz $< f <$ 2 MHz) with Hewlett-Packard 4192A impedance analyzer. All the experiments were performed without any applied static electric field. The 1.5% crystal has already been studied using Raman scattering [11] and acoustic propagation [12] (sample I of Ref. [12]). To keep a consistent labeling scheme in all our publications we refer to the 1% crystal as sample IV.

The variations of ε' and ε'' are shown in Fig. 1 as functions of temperature T at the frequency 1.6 kHz for the 1.5% sample. The peak in the ε'' curve near 50 K and the associated step in the ε' curve are clear manifestations of a relaxation process. They are both displaced towards higher temperatures when the frequency is increased.

Figure 2 represents the AD ε'' vs ε' for the two samples. The most important characteristic shared by these diagrams is their asymmetry, in the sense that they have an infinite slope for high frequencies (left-hand side) and a finite slope for low frequencies (right-hand side).

The simplest possible AD is a semicircle which depicts the case of a Debye relaxation that involves a single discrete relaxation time. Obviously our data can only be interpreted with the use of a distribution of relaxation times. Such a situation is often encountered in liquids and solid materials and numerous distributions have been used by different authors in order to fit their experimental results. However, in view of the shape and the AD, our data cannot be interpreted in terms of known relaxation

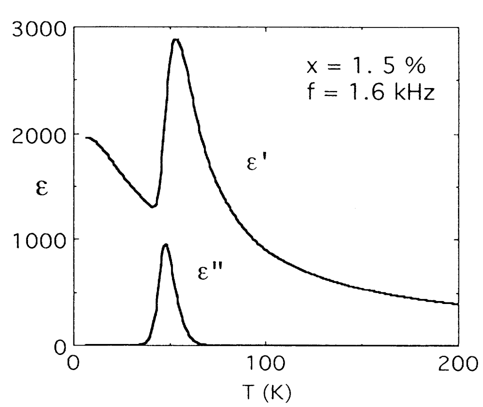

FIG. 1. Real part ε' and imaginary part ε'' of the dielectric constant ε as a function of temperature, measured at 1.6 kHz for the KLT sample I (1.5% Li).

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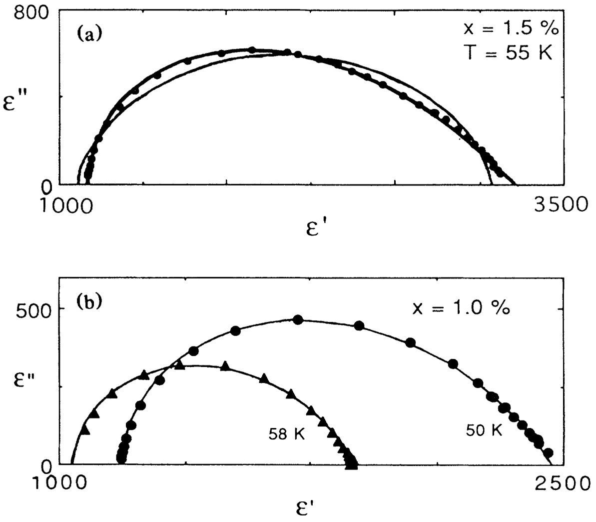

FIG. 2. (a) Argand diagram ε'' vs ε' for sample I (1.5% Li), deduced from measurements at $T=55$ K (circles), with the log-normal fit (thin curve) and the strophoidal fit (thick curve). (b) The same as in (a) for sample IV (1% Li), with measurements performed at $T=50$ K (circles) and at $T=58$ K (triangles); the solid curves represent the strophoidal fits.

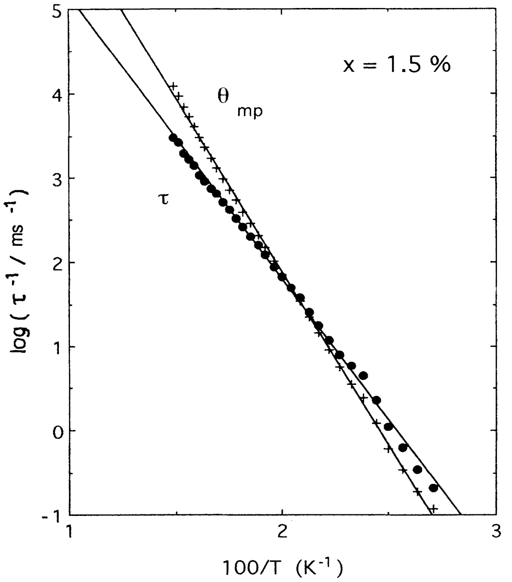

FIG. 3. Arrhenius plots of $\log_{10}(1/\tau)$ and $\log_{10}(1/\theta_{\rm mp})$ (τ and $\theta_{\rm mp}$ in ms) as a function of $100/T$ (T in K) for the KLT sample I. The straight lines correspond to barrier heights equal to 730 K for τ and 970 K for $\theta_{\rm mp}$.

functions. Those proposed by von Wiechert [13] and Wagner [14] (log-normal), Cole and Cole [15], and Fuoss and Kirkwood [16] give symmetric curves, unsuitable in this case. Those introduced by Davidson and Cole [17], Havriliak and Negami [18], Kohlrausch [19], and Williams and Watts [20] must also be discarded since they lead to curves with a finite slope on the left-hand side. Nevertheless, it is possible to invert these curves (exchange of left and right sides) while keeping the low frequencies on the right and the high frequencies on the left. This purely mathematical operation has been applied to the Davidson-Cole relaxation function [21–23], leading to an AD shape similar to ours. Instead, we prefer to use another and new relaxation function which has a physical justification.

In previous dielectric studies on KLT crystals, in spite of the asymmetric shape of the AD, the relaxation of the Li dipoles has generally been analyzed using a log-normal distribution of the relaxation times. The width of the distribution was then found to increase with decreasing temperature while the characteristic time of the distribution (defined through the logarithmic average) followed an Arrhenius law with a barrier height close to 1000 or 1100 K [3,4]. Therefore we have also attempted to fit our data with a log-normal distribution. As expected, the agreement is rather poor [thin curve in Fig. 2(a)], but we also obtain a barrier height of about 1000 K for the jumps of Li^+ ions.

In order to account better for the shape of the AD, we assume the following form (the physical justification of this choice is given later in the Letter) for the contribution of the Li dipoles to the complex dielectric constant at the angular frequency $\omega=2\pi f$:

$$\varepsilon(\omega)=A\left[1+i\omega\tau-(i\omega\tau)^{\alpha}\left(\frac{1}{1-\alpha}+i\omega\tau\right)^{1-\alpha}\right]. \quad (1)$$

In this form which defines the strophoidal relaxation function [24], α is a dimensionless exponent which may depend on the temperature. The right-hand side angle can be shown to equal $\alpha\pi/2$ (therefore $0<\alpha<1$), while the left-hand side angle always equals $\pi/2$. The coefficient $A=\varepsilon(0)$ is the static contribution and τ is a characteristic time, both of which may also be temperature dependent. The free parameters A, τ, and α are computed using the Marquardt method of least squares. There is an excellent agreement over a broad temperature range (not shown) between Eq. (1) and the variations of ε' and ε'' as functions of frequency. This fit is illustrated by the strophoidal curves in the AD [full curves in Figs. 2(a) and 2(b)].

We find that A decreases with temperature in a manner typical of a static susceptibility in a thermally activated dipole system. The time τ follows an Arrhenius law, with a barrier height equal to 640 and 730 K for the samples IV and I of concentration 1% and 1.5%, respectively. This is shown in Fig. 3 for sample I. These values are smaller than previous data. When the temperature is increased, the exponent α varies from a small value to a value close to 1. The variations of α with temperature is given in Fig. 4 for the two samples.

The normalized distribution $D(\theta)$ defined as

$$\varepsilon(\omega) = A\int_0^\infty d\theta \frac{D(\theta)}{1+i\omega\theta} \tag{2}$$

depends on α and τ and is given by

$$D(\theta) = \begin{cases} 0 \text{ for } \theta \le (1-\alpha)\tau, \\ \dfrac{\sin(\alpha\pi)}{\pi\theta}\left(\dfrac{\tau}{\theta}\right)^{\alpha}\left(\dfrac{1}{1-\alpha}-\dfrac{\tau}{\theta}\right)^{1-\alpha} \text{ for } \theta \ge (1-\alpha)\tau . \end{cases} \tag{3}$$

For large values of θ this function behaves as $\theta^{-(1+\alpha)}$. Since $0<\alpha<1$, all of the moments diverge except the norm. Hence, it must be characterized by its asymptotic behavior and its most probable value $\theta_{\text{mp}} = 2\tau(1-\alpha)/(1+\alpha)$. The time θ_{mp} also follows an Arrhenius law but the barrier height is somewhat larger than for τ: 915 and 970 K for samples IV and I, respectively. The case of sample I (1.5%) is illustrated in Fig. 3. The decrease of α implies that the distribution function spreads out more and more towards the long relaxation times when the temperature decreases.

The Fourier transform $\varepsilon(t)$ of the susceptibility $\varepsilon(\omega)$, Eq. (1), is easily calculated; it is expressed in terms of the hypergeometric function ${}_1F_1$. Since $\varepsilon(t)$ is available, it could readily be checked against the transient response measurements.

It should be mentioned that the function $D(\theta)$ given by Eq. (3) does not tend towards a Dirac distribution $\delta(\theta-\tau)$, and therefore a simple Debye relaxation is not recovered, when the temperature tends towards infinity. This is due to our choice of Eq. (1) for $\varepsilon(\omega)$ which is a simplified form. Nevertheless, in the temperature range where we can properly test the function, i.e., where we have nearly complete AD, the simplified form gives an excellent agreement. We do have expressions also valid for high temperatures, but their complexity pushes them beyond the scope of this Letter.

In proposing the form of $\varepsilon(\omega)$, Eq. (1), we have been guided by a formal analogy with that which has been done in [25] for a spin glass for the magnetic susceptibility $\chi(\omega)$ at the critical temperature T_c. This is obtained when applying the Glauber theory [26] to the dynamics of an assembly of spins. Two fundamental hypotheses have to be made: (i) The spins are coupled through Ising interactions; (ii) the interactions are independent centered Gaussian random variables, all with the same probability distribution. Consequently, in the thermodynamic limit, and after some mathematics on infinite random matrices, the distribution of the interaction eigenvalues is found to be the Wigner law [27]. Then the susceptibility is easily deduced and for $T=T_c$, it reads

$$\chi(\omega) = A[1+i\omega\tau - \sqrt{i\omega\tau(2+i\omega\tau)}] . \tag{4}$$

This equation is a particular case of Eq. (1) obtained with $\alpha=\frac{1}{2}$, a value which comes from the square root in the Wigner law. The corresponding AD is a strophoid. In our calculations we keep the first hypothesis as is sometimes done [28], but we give up the second one.

As in the Glauber theory, we regard τ as a microscopic relaxation time (i.e., of an individual Li^+ ion) which should behave smoothly with temperature, consistent with our observations. Moreover, since we find that α is different from $\frac{1}{2}$ and is temperature dependent, the interactions between the relaxing entities are far from centered Gaussian random variables. This feature may be interpreted as the occurrence of effective, temperature-dependent interactions [2] between Li dipoles.

In conclusion, we have interpreted the peculiar shape of the AD of the dielectric constant of $K_{1-x}Li_xTaO_3$ crystals in terms of a new susceptibility function. This function is associated with a long-tailed distribution of relaxation times which decays as $\theta^{-(1+\alpha)}$ at large θ. The time τ which characterizes the distribution and its most probable value θ_{mp} follow Arrhenius laws with activation energies close to 700 and 950 K, respectively, that increase slightly with the concentration x. However, our most striking result concerns the strong influence of the interactions on the distribution $D(\theta)$ even for Li concentrations as low as 1%.

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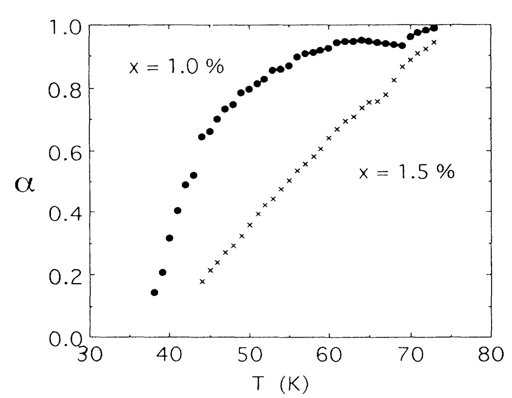

FIG. 4. Temperature dependence of the exponent α for the KLT samples I (1.5% Li) and IV (1% Li).

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[24] A strophoid is a cubic curve of equation $X(X^2+Y^2)-2(X^2+Y^2)+X=0$. It is obtained by inversion of an equilateral hyperbola where the center of inversion is one of the two vertices of the hyperbola. The part which is relevant for the AD is the half loop in the domain $0<X<1$, $0<Y<\frac{1}{2}$. The angle between the axis and the tangent at the crossing point is equal to $\pi/4$. Our susceptibility function gives an exact strophoid when $\alpha=\frac{1}{2}$. For α not equal to $\frac{1}{2}$ we nevertheless use the term strophoidal curve.

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