Dissipative Quantum Tunneling and Absence of Quadrupolar Freezing in Glassy $K_{0.989}Li_{0.011}TaO_3$

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Stretched exponential relaxation of stress-induced quadrupolar order is found in $K_{0.989}Li_{0.011}TaO_3$ at temperatures $T < 30$ K. In contrast to expectations for glasses, however, the stretching exponent increases upon cooling and reaches unity as $T \rightarrow 0$. In parallel with the observed loss of polydispersivity the relaxation time crosses over from Arrhenius to dissipative-quantum-tunneling behavior, $\tau(T) = \tau(0)\exp(-aT^4)$ at $T < 20$ K. The absence of quadrupolar freezing seems to be due to the onset of tunneling and to coupling with the frozen-in dipolar degrees of freedom.

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Very probably, three-dimensional three-state Potts glasses and their physical realizations, orientational glasses with cubic anisotropy, have a glass transition at a nonzero freezing temperature T_f.[1] However, it is not at all clear if the quadrupolar models used in Monte Carlo simulations[1] can describe real quadrupolar glasses like $K(CN)_xBr_{1-x}$ or $K_xNa_{1-x}CN$.[2] In contrast with the model investigations,[1] intermediate- or even long-range interactions are involved in these systems. Moreover, in addition to the random-bond disorder, interactions with random fields occur.[3] Clearly, this enhances the tendency of freezing into a glassy state at finite temperatures. The cyanide glasses[2] are, hence, unsuited to answer the question,[1] if $T_f \neq 0$ results in a canonical quadrupolar glass.

In this Letter we consider another candidate for quadrupolar freezing, the diluted perovskite $K_{1-x}Li_xTaO_3$ (KTL) with $x \sim 0.01$. It is regarded[4] as a realization of the three-state Potts model because of the three easy $\langle 100 \rangle$ directions of the elastic quadrupoles, which are connected with the off-center Li^+ impurities.[5] To our surprise and in contrast with the cyanide glasses,[2] however, quadrupolar freezing does *not* occur at finite temperatures. In accordance with a previous study of quadrupolar relaxation in KTL,[6] the low-T dynamics is confirmed to be very slow, but still considerably faster than expected from an Arrhenius law. In the limit $T \rightarrow 0$ the quadrupolar relaxation time even saturates at a finite value, $\tau_Q(0) \simeq 10^4$ s, and the dynamics becomes monodispersive. Obviously, the interaction with random fields, which are also present in the KTL system,[7,8] does not promote the freezing process.

We have, hence, the peculiar situation that the glass seems to decouple into an ensemble of identical two-level systems, similarly as observed recently[9] on the random dipolar magnet $LiY_{1-x}Ho_xF_4$, $x = 0.045$. There is strong evidence that quantum tunneling[10] of the off-center Li^+ ions is at the origin of both the low-T saturation of τ_Q and the simultaneous loss of polydispersivity. Very probably, coupling of the quadrupolar relaxation to the very slow dipolar dynamics[7,11] enhances the tendency towards low-T monodispersivity. Clearly, KTL is, again, unsuitable to check predictions made for "simple" orientational glasses.[1] For the first time, however, KTL allows us to check recent predictions of dissipative quantum tunneling in an ionic medium. The influence of linear friction on the Li^+ tunneling rate at zero and finite temperatures will be shown to agree quantitatively with theory.[10]

The experiments were carried out on a single-crystal sample[12] of KTL with $x = 0.011$, dimensions $2 \times 2 \times 2$ mm^3, and $\{100\}$ surfaces. Quadrupolar relaxation was measured via linear birefringence[6] (LB) at $\lambda = 589.3$ nm, induced by [100] stress from a pneumatic stress cell. In order to reduce residual strain-induced LB,[6] the sample was kept at room temperature prior to slow zero-stress-field cooling (ZFC) to below $T = 30$ K. A strain-free region of typical area 20×20 μm showing virtually vanishing LB during waiting times[6] up to 4 h was selected by means of a polarizing microscope, through which the subsequent measurement was carried out.[13]

Figure 1 shows the temporal evolution of the (001)-plane LB under the action of [100] stress, $\sigma = 5$ MPa, measured at various constant temperatures, $13.6 \leq T \leq 29.2$ K (curves 1-4). All curves start with a piezo-optic jump of approximately constant height, $|\Delta n(0)| = (n_0^3/2)|\pi_{11} - \pi_{12}|\sigma \sim 2 \times 10^{-5}$. This value is expected for $\sigma = 5$ MPa when using the piezo-optic constant $\pi_{11} - \pi_{12} = -0.7 \times 10^{-12}$ Pa^{-1}, and the cubic refractive index of $KTaO_3$, $n_0 = 2.26$. The subsequent slow increase is due to the polarization-optic effect, $|\Delta n(t) - \Delta n(0)| = (n_0^3/2)(g_{11} - g_{12})\langle P_x^2(t) \rangle$, where $g_{11} - g_{12} = 0.16$ m^4C^{-2} for $KTaO_3$. An LB change of 10^{-4}, hence, corresponds to a stress-induced polarization $\delta(\langle P_x^2 \rangle^{1/2}) = 0.01$ Cm^{-2}. $\langle P_x^2(t) \rangle$ is the autocorrelation function of the induced polarization and is conjugate to the external stress field.

In order to describe the saturation behavior of $\langle P_x^2(t) \rangle$,

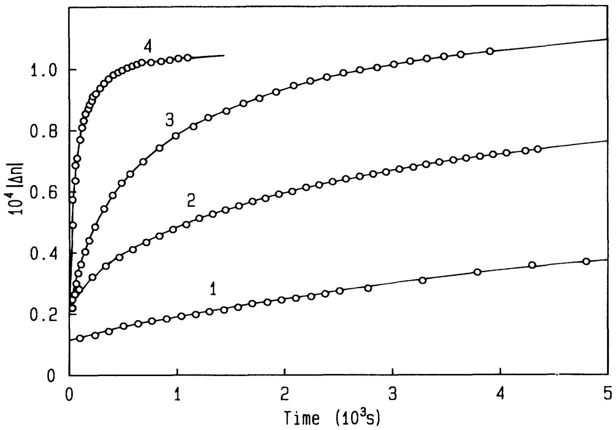

FIG. 1. (001)-plane birefringence induced by [100] stress, $\sigma=5$ MPa, in KTL ($x=0.011$) at $T=13.6$, 21.6, 26.0, and 29.2 K (curves 1-4, respectively). The experimental data points (only partly shown) are best fitted by stretched exponential functions, Eq. (1).

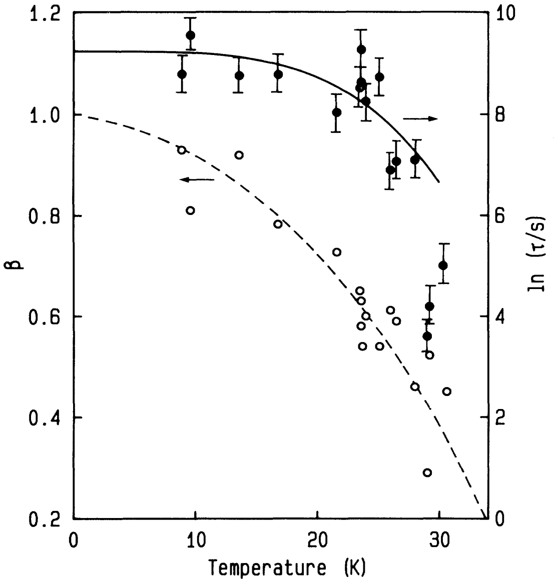

FIG. 2. Stretching exponents β (open circles, interpolated by eye-guiding dashed line) and median relaxation times τ (solid circles with estimated systematic error bars) determined from best fits of relaxation curves as shown in Fig. 1 with Eq. (1). A T^4 power law, best fitted for $T<25$ K, is shown as a solid line.

the usual[14] set of decay functions (exponential, stretched exponential, power law, and logarithmic) was tested by least-squares-fitting routines. Without doubt the stretched exponential,

$$|\Delta n(t)-\Delta n(0)| \\ =[\Delta n(\infty)-\Delta n(0)][1-\exp(-\{t/\tau_Q\}^{\beta})]\,, \qquad (1)$$

fits best with χ^2 values being orders of magnitude inferior to those of the other functions. The data points coincide perfectly with the fitting curves as shown in Fig. 1. The prefactor $\Delta n(\infty)-\Delta n(0)\sim 1.1\times10^{-4}$ in Eq. (1) is approximately independent of T,[15] but the median relaxation time τ_Q and the stretching exponent β are strongly T dependent. In Fig. 2 a large number of ZFC polarization curves, including those shown in Fig. 1, have been analyzed. It is seen that τ_Q increases steeply from about 50 to 3000 s, when decreasing T from 30 to 20 K, but below 20 K gradual saturation is observed, $\tau_Q \rightarrow 14000$ s as $T\rightarrow 0$. Owing to the difficulties in controlling the initial conditions of the stress experiments (see above) τ values repeatedly taken at the same temperature may differ by a factor of 2. This explains the scatter of the data in the logarithmic plot of Fig. 2. Within the estimated error margins, however, they allow for a reasonable best fit to a T^4 power law,

$$\ln(\tau_Q/s)=9.2-3\times10^{-6}[T/(1\text{ K})]^4 \qquad (2)$$

for $T\leq 25$ K (solid line in Fig. 2).

The stretching exponent β also increases with decreasing temperature. Near $T=30$ K values as small as $\beta\sim0.3$ characterize a very large width of the distribution function of relaxation times, $f(\tau)$, extending over about six decades.[11] On the other hand, $\beta=1$ and, hence, monodispersivity, $f(\tau)=\delta(\tau-\tau_Q)$, is achieved asymptotically in the low-T limit as indicated by an eye-guiding dashed line in Fig. 2.

The results shown in Fig. 2 are in complete contradiction with what is usually found in spin glasses. There, as a rule, the average relaxation time τ *increases* rapidly, whereas the stretching exponent β *decreases* with decreasing temperature.[16] This was also confirmed for the Potts glass[17] by Monte Carlo simulations. Moreover, the KTL system fails to reveal waiting-time effects similar to those shown in spin glasses by numerous experiments[18] and explained by the droplet theory.[19] As an example, Fig. 3 shows three relaxation curves taken at $T=24.0$ K after waiting times $t_w=300$, 3600, and 14400 s, respectively. Careful annealing at room temperature took place between each run. All of these curves are, again, excellently described by Eq. (1), with virtually the same parameters, $\beta\sim0.63$ and $\tau_Q\sim5400$ s within $0\leq t\leq5000$ s. Hence, the maximum of the relaxation rate, $S=d\langle P_x^2\rangle/d(\ln t)$, lies at $t_m=\tau_Q\sim5400$ s, irrespective of the waiting time. Contrary to the experience with spin glasses,[18] there is obviously *no* correlation between t_m and t_w, indicating crossover from equilibrium to nonequilibrium relaxation of the glassy system.[19] $t_m=\tau_Q$ merely plays the role of a median time governing the relaxation within a hierarchy of metastable states,[20] which does not necessarily yield a long-range-correlated equilibrium state as $t\rightarrow\infty$. We notice only one trivial waiting-time effect: The relaxation amplitude, $|\Delta n(\infty)-\Delta n(0)|$, decreases from 2×10^{-4} to 1.1×10^{-4} for t_w

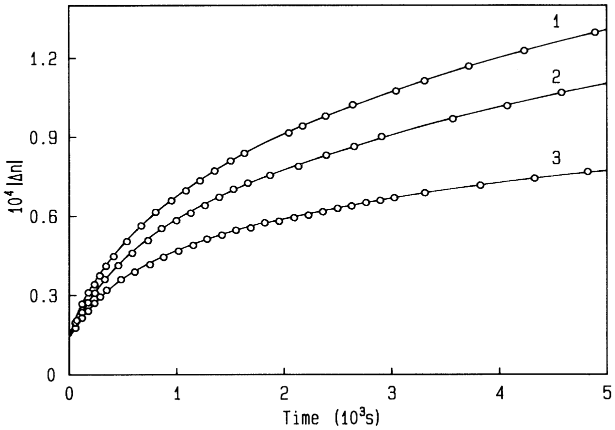

FIG. 3. Stress-induced birefringence (see Fig. 1) at $T=24.0$ K as measured after waiting times $t_w=300$, 3600, and 14400 s (curves 1-3, respectively, presented as in Fig. 1).

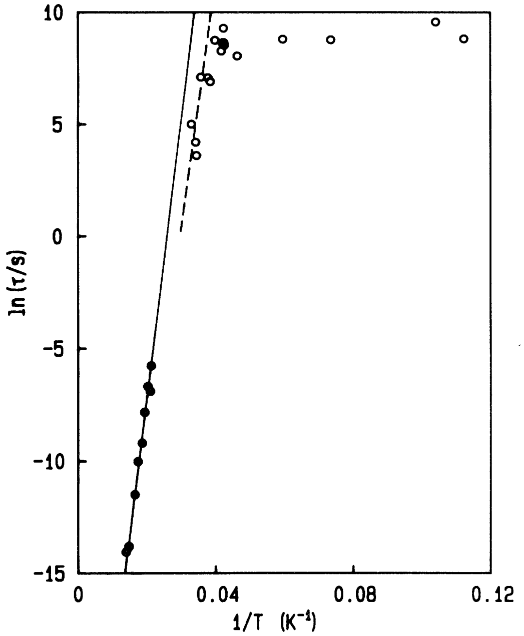

FIG. 4. Arrhenius plots of dipolar and quadrupolar relaxation times (solid and open circles, respectively) of KTL ($x=0.011$). They are best fitted with the parameters $\tau_\infty=1\times10^{-13}$ and 2×10^{-14} s, and $\Delta E/k_B=1140$ and 1000 K within $42\leq T\leq 75$ K and $20\leq T\leq 30$ K (solid and dashed lines, respectively).

increasing from 3×10^2 to 1.4×10^4 s (Fig. 3). This is probably due to pinning of the Li^+ centers to point defects or dislocations.[21] Obviously, the absolute number of freely relaxing elastic Li^+ quadrupoles decreases at increasing t_w, similarly as observed after waiting under stress, $\sigma\neq0$ (not shown).

The observed power law (2) strongly supports a model of phonon-assisted tunneling of the Li^+ ions from metastable into equilibrium off-center positions. A T^4-dependence was predicted[22] for the logarithmic decay rate in case the tunneling centers are coupled to the phonon bath of a solid, whose density of acoustic-phonon states varies as ω^2. The crossover temperature from thermal hopping (Arrhenius-like) to quantum-mechanical tunneling (T^4 power law) is given by[22] $T_0=\kappa_2 h\omega_0/2\pi k_B$, where ω_0 is the frequency of small oscillations about the metastable equilibrium. The transmission factor κ_2 is connected with the damping factor $\eta=M\omega_0(1-\kappa_2^2)/\kappa_2$ of the particle with mass M. Estimating $T_0=20$ K (Fig. 2) and $\omega_0=5\times10^{13}$ s^{-1} (dashed Arrhenius line in Fig. 4, best fitted to τ_Q vs T at $T>25$ K) and inserting the mass of the ${}^7_3Li^+$ ion, we find $\kappa_2=0.26$ and $\eta=4.1\times10^{-13}$ kg/s or $\eta/M\omega_0=3.58$. We are, hence, in the strong-damping limit,[22] where the transmission rate is strongly decreased by backscattering. In this limit the T^4 law of the transition rate $\Gamma=\tau^{-1}$ reads[22]

$$\ln[\Gamma/\Gamma(0)]=(\pi^3\eta\Omega_0^2/15M\omega_0\omega_D^2)(k_BT/h\omega_0)^4,$$

where Ω_0 is a "dispersion frequency" and ω_D the Debye frequency of the crystal. Inserting the result (2) and the above estimates of $\eta/M\omega_0$ and $\omega_0\sim\omega_D$, we obtain $\Omega_0=3.7\times10^{13}$ s^{-1}. This allows us to estimate the amplitude of the zero-point vibrations of the Li^+ ions, since $\langle q\rangle^2=h/M\Omega_0$.[22] We obtain $\langle q^2\rangle_0^{1/2}=0.16$ Å, which appears to be reasonable in view of the barrier width $q_0\sim1$ Å.[5]

The $T=0$ tunneling rate, $\ln\Gamma(0)=-\ln\tau_Q(0)$, is strongly affected by the coupling to the external heat bath.[10] Linear friction suppresses quantum tunneling by a factor $\exp(-A\eta q_0^2/h)$, where A is of order unity.[10] The decay time through a rectangular energy barrier of height ΔE and width q_0 is then given by $\tau_Q(0)=\exp(B)/\omega_0$, where $B=[q_0(8M\Delta E)^{1/2}+A\eta q_0^2]/h$ is the modified Gamow factor and ω_0 the attempt frequency. This relation can be used to cross-check the orders of magnitude of the experimental parameters involved. For example, if we start from the tunneling distance of 90° jumps, $q_0=\sqrt{2}x_0$, where $x_0=1.2$ Å is the [100] displacement of the Li^+ ions,[5] we may calculate the energy barrier ΔE. Inserting $\ln\tau_Q(0)=9.2$, $\omega_0=5\times10^{13}$ s^{-1}, $A=1$ and the above η value, we find $\Delta E/k_B=1550$ K. This agrees satisfactorily with the roughly determined experimental value, $\Delta E/k_B\sim1000$ K (dashed line in Fig. 4), and seems to support our quantum tunneling hypothesis. More precise experiments and a more realistic tunneling potential model are needed for more quantitative research on this new and interesting tunneling system.

Here we have to discuss a possible connection between the tunneling mechanism and the observed tendency towards monodispersivity, $\beta=1$ as $T\rightarrow0$ (Fig. 2). In fact, a system of tunneling centers feels the interaction with the surrounding crystal essentially like friction.[10] At zero temperature its relaxation is solely determined by the potential barriers in the immediate vicinity of the centers and the multivalley free-energy landscape is simply ignored. It starts to play a role only at finite temperatures, when thermal activation contributes to the relaxation processes. Similarly as introduced in the case of the magnetic dipole system $\mathrm{LiY_{0.955}Ho_{0.045}F_4}$ we adopt, hence, a model of local clusters, which are noninteracting at $T=0$.[9] In a natural way we identify those clusters with the tunneling Li^+ centers themselves.

The increase of β starts already near $T=30$ K, where tunneling does not yet seem to play a major role (Fig. 2). KTL thus represents one of the rare cases, where β increases and the apparent activation energy, $\Delta E/k_B = d\ln\tau/d(1/T)$, decreases on cooling. Similar behavior was observed on the ionic conduction of the molten salt $0.4\mathrm{Ca(NO_3)_2}\cdot 0.6\mathrm{KNO_3}$ as T is cooled towards T_g.[23] In KTL the anticorrelation between the trends of β and ΔE is proposed to be due to coupling of the quadrupolar to the electric dipolar system via the indirect quadrupole-quadrupole interaction, $V_Q = \sum_{\alpha\beta} Q_{\alpha\beta} P_\alpha P_\beta$ ($\alpha,\beta = 1,2,3$; $\mathbf{P}$ represents polarization).[4] Experimentally, dipolar relaxation involves primarily 180° flips of the off-center Li^+ ions,[24] but a small fraction of 90° flips, i.e., quadrupolar relaxation steps, is encountered as well. The dipolar system is much slower than the quadrupolar one at all temperatures. This is seen from the Arrhenius plots of both quadrupolar (Fig. 2) and dipolar[25] relaxation times obtained on our $x=0.011$ sample in Fig. 4. Although dipolar freezing has not been evidenced yet,[26] V_Q may essentially be treated as a static random field. This being sufficiently strong will tend to align the Li^+ quadrupoles at random orientations. Thus the direct quadrupolar interaction becomes ineffective. Quadrupolar decoupling and, hence, monodispersive quadrupolar dynamics are the natural consequences. Very clearly, this mechanism promises to be particularly effective in the case where the suspected[26] dipolar freezing occurs at $T_f \neq 0$. Experiments towards these ends are currently underway.

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[1] K. Binder, Ferroelectrics **104**, 3 (1990).

[2] K. Knorr, Phys. Scr. **T19**, 531 (1987); A. Loidl, Annu. Rev. Phys. Chem. **40**, 29 (1989).

[3] K. H. Michel, Phys. Rev. B **35**, 1405 (1987); **35**, 1414 (1987).

[4] M. D. Glinchuk and I. M. Smoljaninov, Fiz. Tverd. Tela (Leningrad) **30**, 1197 (1988) [Sov. Phys. Solid State **30**, 693 (1988)]; Phase Transitions (to be published).

[5] Y. Yacoby and S. Just, Solid State Commun. **15**, 715 (1974); J. J. van der Klink and S. N. Khanna, Phys. Rev. B **29**, 2415 (1984).

[6] W. Kleemann *et al.*, Phys. Rev. B **37**, 5856 (1988).

[7] W. Kleemann *et al.*, Europhys. Lett. **4**, 239 (1987).

[8] The strains with local A_{1g} symmetry of the randomly distributed small Li^+ ions, superimposed at a given Li^+ site, act as static random fields on the Li^+ quadrupole.

[9] D. H. Reich *et al.*, Phys. Rev. Lett. **59**, 1969 (1987).

[10] A. O. Caldeira and A. J. Leggett, Phys. Rev. Lett. **46**, 211 (1981); H. Grabert *et al.*, *ibid.* **52**, 2193 (1984).

[11] U. T. Höchli, Phys. Rev. Lett. **48**, 1494 (1982); J. J. van der Klink and F. Borsa, Phys. Rev. B **30**, 52 (1984); U. T. Höchli *et al.*, J. Phys. Condens. Matter **1**, 2241 (1989); **2**, 4259 (1990).

[12] D. Rytz and H. Scheel, J. Cryst. Growth **59**, 468 (1982).

[13] F. J. Schäfer and W. Kleemann, J. Appl. Phys. **57**, 2606 (1985).

[14] D. A. Huse and D. S. Fisher, Phys. Rev. B **35**, 6841 (1987).

[15] Actually, $\Delta n(\infty) - \Delta n(0)$ decreases similarly with T as the LB of slowly cooled strained samples (cf. curve 2 in Fig. 2 of Ref. 6).

[16] P. Granberg *et al.*, Phys. Rev. B **35**, 2075 (1987).

[17] H. O. Carmesin and K. Binder, J. Phys. A **21**, 4053 (1988).

[18] L. Lundgren *et al.*, Phys. Rev. Lett. **51**, 911 (1983).

[19] D. S. Fisher and D. A. Huse, Phys. Rev. B **38**, 373 (1988).

[20] R. G. Palmer *et al.*, Phys. Rev. Lett. **53**, 958 (1984).

[21] H. Uwe *et al.*, Phys. Rev. B **33**, 6436 (1986).

[22] H. Grabert *et al.*, Phys. Rev. Lett. **53**, 1787 (1984); Phys. Rev. B **36**, 1931 (1987).

[23] K. L. Ngai, in *Non-Debye Relaxation in Condensed Matter,* edited by T. V. Ramakrishnan and M. Rajlakshmi (World Scientific, Singapore, 1987).

[24] U. T. Höchli and D. Baeriswyl, J. Phys. C **17**, 311 (1984).

[25] V. Schönknecht (unpublished).

[26] In all investigations of low-x KTL, Arrhenius-like behavior of the dipolar median relaxation time τ_D was reported (Refs. 7 and 11). A careful analysis of τ_D vs T in the vicinity of the suspected freezing temperature [$T_f \sim 37$ K for $x=0.015$ (Ref. 11)] is still lacking.