Aging in $K_{1-x}Li_xTaO_3$: A Domain Growth Interpretation

F. Alberici-Kious,[1] J. P. Bouchaud,[2] L. F. Cugliandolo,[3] P. Doussineau,[1] and A. Levelut[1]
[1]*Laboratoire des Milieux Désordonnés et Hétérogènes, Université P. et M. Curie, Case 78, 75 252 Paris Cedex 05, France**
[2]*Service de Physique de l'Etat Condensé, CEA-Saclay, 91191 Gif-sur-Yvette CEDEX, France*
[3]*LPTENS, 24, rue Lhomond, F-75231 Paris Cedex 05, France*
and LPTHE, Tour 24, 4, Place Jussieu, F-75231 Paris Cedex 05, France

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The aging behavior of the ac susceptibility of randomly substituted $K_{1-x}Li_xTaO_3$ crystals reveals marked differences with spin glasses in that cooling rate effects are very important. The response to temperature steps (including temperature cycles) was carefully studied. A model based on thermally activated domain growth accounts for all the experimental results, provided one allows for a large distribution of pinning energies, in such a way that "slow" and "fast" domains coexist. Interesting similarities with deeply supercooled liquids are underlined. [S0031-9007(98)07804-1]

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The ac susceptibility of "glassy" materials becomes time dependent at low temperatures: this is the aging phenomenon [1]. Such a behavior has been observed on spin glasses [2], on disordered dielectrics such as ammonium perchlorate [3] or $K_{1-x}Li_xTaO_3$ (KLT) (which is an orientational glass [4–6]), and more recently on a deeply supercooled liquid (glycerol) [7]. All these systems share common properties, but also important differences. The prominent features are the following.

(i) When the system is cooled to a certain temperature T_1 below the glass transition T_0, its frequency dependent response (which in the present paper is the real part of the dielectric constant ϵ') depends on the time Δt since the quench. This dependence can be parametrized as [1]

$$\epsilon'(\omega, t) = \epsilon'_{\mathrm{ST}}(\omega) + f(\Delta t) g(\omega), \qquad (1)$$

where $f(\Delta t)$ is a (slowly) decreasing function describing the aging part and $\epsilon'_{\mathrm{ST}}(\omega)$ is the stationary part of the response. In spin glasses, the functions $f(u)$ and $g(u)$ both behave similarly (as u^{-b} [2,8]), which means that the aging part of the response obeys approximatively a simple $\omega \cdot \Delta t$ scaling (but see [1,2]). On KLT crystals, $g(\omega)$ is nearly independent of frequency, at least for temperatures not too close to T_0, while $f(\Delta t)$ behaves as a power law with a small exponent [5] or a logarithm; see Fig. 1. The situation is intermediate for glycerol, where the variation of $g(u)$ is somewhat weaker than that of $f(u)$ [7].

(ii) The stationary part of the susceptibility is nearly independent of the cooling rate $\mathcal{R}$ in spin glasses [10]. This is in striking contrast with the case of KLT, where $\epsilon'_{\mathrm{ST}}(\omega)$ markedly depends on the cooling rate (see Fig. 1), decreasing roughly as $\log \mathcal{R}$, as the cooling rate is reduced. In other words, the apparent asymptotic value of the dielectric constant depends on the history, and thus certainly cannot be associated with an "equilibrium" response function. Several cooling histories were probed in Ref. [5], with the conclusion that it is essentially the time spent around T_0 which determines the value of $\epsilon'_{\mathrm{ST}}(\omega)$.

(iii) Upon a negative temperature cycling $T_1 \to T_2 = T_1 - \Delta T \to T_1$, the ac response function shows both *rejuvenation* and *memory,* in the sense that new out of equilibrium processes are induced during the low temperature interval, but are erased once the temperature is back at T_1: dynamics resume as if the intermediate regime had not taken place. Memory is nearly perfect in spin glasses when $\Delta T > 1$ K, while in KLT (or glycerol) there appears an interesting "overshoot"—see Fig. 2—before the dynamics corresponding to the initial temperature can resume. The amplitude of this overshoot grows with the time t_2 spent at temperature T_2.

The aim of this paper is to develop a picture based on domain growth impeded by static impurities, which accounts very well for all the experimental data on KLT. The relation with the "droplet picture" for spin glasses will also be discussed. Interestingly, the similarities between KLT and glycerol suggest that some sort of pinned domain growth, with a characteristic length scale, might also be present in supercooled liquids.

When lithium is absent, $KTaO_3$ is known to be an "incipient" ferroelectric at $T = 0$, where quantum fluctuations prevent total ordering. Thus, the ferroelectric correlation length $\xi(T)$ is expected to be large at low temperatures: assuming that $\epsilon \propto \xi^2$, one finds that $\xi(T) \propto 1/\sqrt{T}$. When lithium ions are randomly substituted, they create large local dipoles which are known to freeze individually around $T_0 = 40$ K, due to the energy barrier for dipole reorientation. Below this temperature, the lithium ions can thus be seen as giving rise to a random static electric field, which acts as a pinning field for the ferroelectric domain walls [11]. The growth of the ferroelectric order towards its equilibrium value $\xi(T)$ is thus strongly impeded. The model we have in mind is thus the random field Ising model (RFIM) *above* its ferromagnetic transition, but close to it so that the equilibrium domain size is somewhat larger than the lattice spacing a. A numerical simulation of the three dimensional RFIM with different

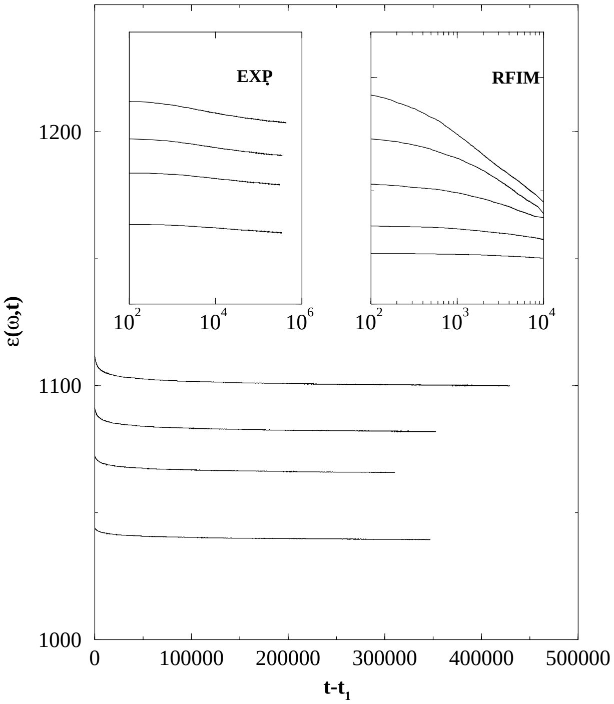

FIG. 1. Plot of $\epsilon'(\omega/2\pi = 100\ \mathrm{kHz}, t)$ for KLT ($x = 0.025$) as a function of the time $\Delta t = t - t_1$ spent at temperature $T_1 = 4.2$ K, for various cooling rates: $\mathcal{R} = 0.045$, 0.024, 0.011, 0.0058 K/s. The slowest cooling rate corresponds to the lowest value of the apparent asymptote $\epsilon'_{\mathrm{ST}}(\omega)$. Insets: EXP, same data, in a log-linear scale; RFIM, numerical simulation of the time evolution of the domain wall density in the 3D random field Ising model, for different numerical cooling rates [9]. Note that the simulation actually corresponds to much smaller times than the experiment; this is why the rate of changes in the former case is much larger than in the experiment.

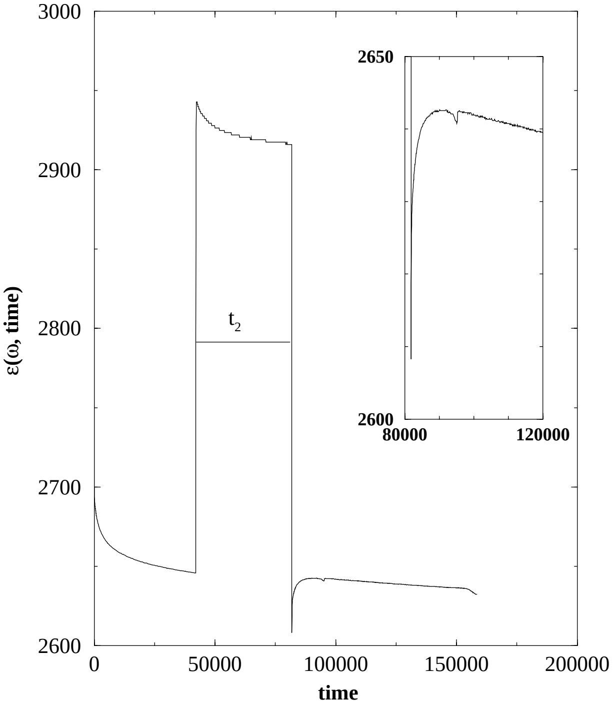

FIG. 2. Effect of a negative temperature cycle on $\epsilon'(\omega/2\pi = 100\ \mathrm{kHz}, t)$ for KLT ($x = 0.011$). The first period is spent at temperature $T_1 = 18.4$ K during 40 000 sec, then the sample is cooled to 4.2 K for a time $t_2 = 40\,000$ sec, and heated back again to T_1. The "overshoot" can be seen at the beginning of the third period, where $\epsilon'(\omega, t)$ has a nonmonotonic behavior. We have shown in the inset an expanded view of the overshoot region.

cooling rates actually reveals qualitatively similar features (Fig. 1—inset) [9].

In the presence of pinning, several arguments [12] suggest that the typical energy barrier which impedes upon the motion of a domain of size R is of the order of $E(R) \sim \Upsilon(\frac{R}{a})^\theta$ where $\theta \simeq \frac{4}{3}$ for nearest neighbor interactions in three dimensions and Υ is an energy scale which depends both on the random fields and on the surface energy of the domain walls. Note that dipolar fields are long range, so that θ might have a somewhat larger value ($\theta \sim 2$). The effect of pinning becomes noticeable when $E(R) \simeq kT$. For large times, the growth law is thus governed by thermal activation $t \simeq \tau_0 \exp[\frac{E(R)}{T}]$, where τ_0 is a microcopic time scale, and the Boltzmann constant k has been set to one. One thus obtains [12]

$$R(t) \simeq \left[\frac{T}{\Upsilon} \log(t + e^{\Upsilon R_0^\theta/T})\right]^{1/\theta} \qquad R_0 = R(t = 0), \tag{2}$$

where from now on we measure t in units of τ_0 and R in units of a. Equation (2) holds until the equilibrium size $\xi(T)$ is reached, beyond which domains no longer grow. Taking the derivative of Eq. (2), one obtains the growth rate $\Gamma(t, T)$, in which the temperature can now be considered as time dependent, for example, as $T(t) = T_0 - \mathcal{R}t$. Noting that at $t = 0$ domains are in equilibrium at T_0 [i.e., $R_0 = \xi(T_0)$], one can integrate back $\Gamma(t, T(t))$ and find the domain size as a function of time at temperature T_1. In order to compare with experimental results, we make the natural assumption that the domain walls contribute to the dielectric susceptibility proportionally to their total surface. Per unit volume, this leads to an excess susceptibility given by

$$\Delta\epsilon'(\omega, t) \propto \langle R(t)^2 \rangle / \langle R(t)^3 \rangle g(\omega), \tag{3}$$

where $g(\omega)$ is the (frequency dependent) wall mobility and $\langle \cdots \rangle$ denotes an average over all the domain sizes present in the sample. Numerically, however, this simple model fails to reproduce the experimental results in the following sense: Υ is either too small, and one observes a decay of ϵ' which can be slow but towards an asymptotic value which is independent of the cooling rate, or too large, in which case ϵ' indeed strongly depends on the cooling rate but does not relax at all at T_1 (at least over the experimental time window). The *simultaneous* observation of the two effects actually requires some fast growing domains coexisting with slower ones, corresponding to different local barrier heights Υ. This is actually expected: since the pinning field is random, Eq. (2) can describe only a typical behavior, with large fluctuations corresponding to particularly efficient (or inefficient) pinning regions. We shall thus assume that Υ has a rather broad distribution. Let us consider the situation at time t_1 when the temperature T_1 is first reached (i.e., $T_0 - \mathcal{R} t_1 = T_1$). There, three types of domains can be distinguished.

(i) "Fast" domains, which have been able to remain in equilibrium during the whole cooling phase, and follow the evolution of the equilibrium length ξ. Their size is thus $\xi(T_1)$, and they evolve no further after t_1. Imposing that $\Gamma(t, T) > d\xi/dt$, one can check that fast domains correspond to $T_p < \ell T_1^{1+\theta/2}/T_0^{\theta/2}$, where $T_p = \Upsilon \xi(T_0)^\theta$ is the "initial" pinning energy and ℓ is approximately given by $\ln[T_1/\mathcal{R}\tau_0]$.

(ii) "Slow" domains, which are in equilibrium in the first stages of the cooling process, but fall out of equilibrium before the temperature reaches T_1. This occurs when the domain growth rate $\Gamma(t, T)$ becomes less than $d\xi/dt$, which occurs at a temperature $(T_p^2 T_0^\theta/\ell^2)^{1/(2+\theta)}$. This corresponds to $\ell T_1^{1+\theta/2}/T_0^{\theta/2} < T_p < \ell T_0$.

(iii) "Frozen" domains, which fall out of equilibrium as soon as $T < T_0$ because of a large local pinning energy $T_p > \ell T_0$. Of course, these domains are not really frozen but evolve only on extremely long time scales.

Collecting the contribution of these different domains to $\langle R(t_1)^2\rangle/\langle R(t_1)^3\rangle$, and assuming that the scale T^* of the distribution of pinning energies T_p is much larger than ℓT_0, we find [13] that the contribution of the walls to the dielectric susceptibility is proportional to $1 - \alpha \ell T_0/T^*$, where α is a certain function of T_1/T_0 [13]. Hence, this model predicts that the excess dielectric susceptibility (measured by ϵ'_{ST}) is linear in $\ln \mathcal{R}$, as indeed reported in [5]. The model also allows us to compute the temporal evolution of ϵ. Physically, after a time $t_1 + \Delta t$, the "fastest" slow domains have managed to reach $\xi(T_1)$, while the others slowly grow. Adding the different contributions, we find that, for large Δt [more precisely for $\ell(T_1/T_0)^{(1-\theta)/2} \ll \ln \Delta t \ll T^*/T_0$], the dielectric constant decreases as $-\beta T_0/T^* \ln \Delta t$, where β is another function of T_1/T_0 (but independent of $\mathcal{R}$). This logarithmic decay is again in good agreement with the experimental data (at least for large enough Δt): see Fig. 1. Of course, for exponentially long times, all domains (even the frozen ones) reach their equilibrium size $\xi(T_1)$; the point is that the logarithm is such a slowly varying function that, even on the rather long time scales investigated here (3×10^5 sec), the dielectric susceptibility appears to asymptote a logarithmically cooling rate dependent value $\epsilon'_{\mathrm{ST}}(\omega)$.

The interpretation of the cycling experiments, shown in Fig. 2, follows very similar lines [14]. The main ingredient is again the existence of the fast and slow domains discussed above. When the temperature is reduced from T_1 to T_2, the equilibrium length ξ suddenly increases. Hence, the fast domains are driven out of equilibrium and must restart growing. Since the temperature has decreased, this is now a slow process, which accounts for the fact that ϵ' decreases much like after the initial quench. (Note that the large positive instantaneous change of ϵ' is due to the bulk contribution which is itself temperature dependent.) The slow domains, which were already slow at T_1, are completely frozen at T_2 and hardly move. Now, when the system is heated back to T_1, two things happen. First, the fast domains now have to shrink back to their equilibrium size. They have grown beyond $\xi(T_1)$ during their stay at lower temperature, and consequently, the domain wall density is smaller than it should be. However, since the size of these domains is large, the barriers they have to jump are now high at T_1 and their shrinking is very slow. A more efficient process then occurs: internal nucleation of smaller domains. These nuclei grow according to Eq. (2) from an initial size of the order of the lattice parameter a, until they reach the equilibrium domain size $\xi(T_1)$. This growth, rapid at the beginning, generates new walls which induce an increase of the dielectric constant. This accounts for the overshoot observed just after the temperature step. Second, the slow domains, which have been nearly unaffected by the temperature decrease, resume their dynamics in perfect continuity with the first period of time. Concerning the overshoot, its amplitude $\mathcal{A}(t_2)$ depends on the time t_2 spent at low temperature, since the number of net nucleation of domains is proportional to the volume occupied by domains which have grown beyond $\xi(T_1)$. We thus expect $\mathcal{A}(t_2)$ to grow slowly with t_2 [since $R(t_2)$ grows only logarithmically] and then to saturate for very long times. This is indeed what one observes experimentally: see Fig. 3. The overshoot contribution can be parametrized as $\mathcal{A}(t_2) \exp -(\Delta t/\tau_1)$, where $\mathcal{A}(t_2)$ *decreases* with T_1, a feature which our model also predicts [13]. τ_1, on the other hand, only weakly depends on t_2 or T_1 (see Fig. 3).

Finally, we would like to discuss the differences between domain growth in a random field-like system, which we argue to be a good model for KLT crystals, and "droplet" growth in spin glasses [15–17], which has been advocated to be the relevant picture (as opposed to models inspired from Parisi's mean field "hierarchical" solution [8,18,19], or exactly soluble dynamical mean field models [1,20]). First of all, domain growth cannot be trivial in spin glasses, otherwise strong cooling rate dependence would be seen, for example, in the apparent asymptote of $\chi'(\omega, t)$, as is observed in KLT (see Fig. 1). This is avoided by arguing that the growing "phase" depends chaotically on temperature [15–17], and thus the growth of the domains at temperature $T + \Delta T$ is useless to bring the system closer to equilibrium at T. The rejuvenation effect seen in KLT was attributed above to a change of the *finite* equilibrium correlation length ξ when the temperature is reduced, which leads to an overshoot effect not observed in spin glasses. Conversely, in the droplet picture, the equilibrium size of the domains is infinite [16]. The interpretation of *rejuvenation* is then related to the fact that domains of the new phase (i.e., the one stable at temperature T_2) do grow at the expense of the old phase

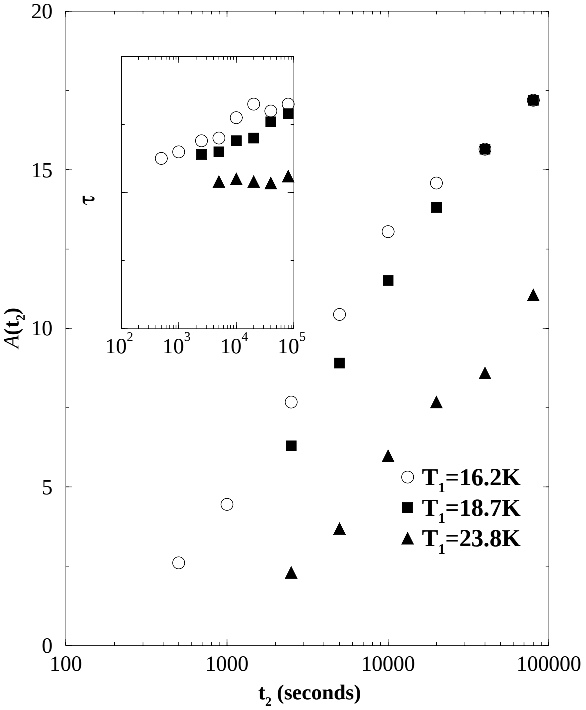

FIG. 3. Amplitude of the overshoot $\mathcal{A}(t_2)$ as a function of the time t_2 spent at $T_2 = 4.2$ K, in log-linear scales, and for different temperatures T_1. Note that $\mathcal{A}$ increases roughly as $\ln t_2$ and decreases when T_1 increases. Inset: Dependence of the relaxation time of the overshoot τ_1 on t_2. The y-axis scale is 0−2000 sec.

(the one stable at temperature T_1). However, this must also be compatible with the observed *perfect memory* upon reheating. How this is possible is still very much a subject of debate (see, e.g., [10,19]), but the conclusion that different phases must somehow coexist (at least for finite times) appears difficult to avoid.

To summarize, we have argued that the observed aging effects and strong history dependence of the dielectric susceptibility in KLT crystals could be understood in terms of slow, inhomogeneous ferroelectric domain growth in the presence of random pinning fields. An important aspect, needed to interpret the overshoot observed after a positive temperature jump, is that the equilibrium correlation length ξ is finite. It would be interesting to compare our results with similar experiments on well characterized random field systems, in particular, in the ordered phase where $\xi = \infty$. No overshoot has been reported in spin glasses for large enough temperature jumps, while the data on glycerol is quite similar to the one discussed here, and raises the interesting possibility that some kind of domain growth, with a finite equilibrium size, might also be relevant in supercooled liquids.

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*Associé au C.N.R.S., U.M.R. 7603.

[1] J.P. Bouchaud, L.F. Cugliandolo, J. Kurchan, and M. Mézard, in *Spin-glasses and Random Fields*, edited by P. Young (World Scientific, Singapore, 1997).
[2] For a review, see E. Vincent, J. Hammann, M. Ocio, J.P. Bouchaud, and L.F. Cugliandolo, in *Sitges Conference on Glassy Systems*, edited by M. Rubí (Springer-Verlag, Berlin, 1997).
[3] J. Gilchrist, Phys. Lett. A **156**, 76 (1989); J. Mol. Liq. **69**, 253 (1996).
[4] U. Hoechli, K. Knorr, and A. Loidl, Adv. Phys. **39**, 405 (1990); B. Vugmeister and M. Glinchuk, Rev. Mod. Phys. **62**, 993 (1990).
[5] F. Alberici, P. Doussineau, and A. Levelut, J. Phys. I (France) **7**, 329 (1997).
[6] F. Alberici, P. Doussineau, and A. Levelut, Europhys. Lett. **39**, 329 (1997).
[7] R.L. Leheny and S. Nagel, Phys. Rev. B **57**, 5154 (1998).
[8] J.P. Bouchaud and D.S. Dean, J. Phys. I (France) **5**, 265 (1995).
[9] The simulation of the 3D RFIM was performed on a lattice with 64^3 sites. In units of the ferromagnetic coupling, the initial temperature is $T_0 = 5$, and the final temperature is $T_1 = 0.57$. The random field is $h = \pm 2$, and the cooling times are 10, 20, 40, 80, 160 Monte Carlo sweeps per spin. Note that we have simulated, for convenience, the RFIM below its ordering temperature, instead of finite tuning the temperature to obtain a large (but finite) correlation length, as is the case for KLT.
[10] K. Jonason, E. Vincent, J. Hammann, J.P. Bouchaud, and P. Nordblad, Phys. Rev. Lett. **81**, 3243 (1998).
[11] A somewhat related picture of domains pinned by random fields has been invoked by S. Galam, J. Phys. I (France) **1**, 1195 (1991), to account for the static properties of KCN-KBr, another orientational glass.
[12] For a recent review, see T. Nattermann, in *Spin-glasses and Random Fields* (Ref. [1]). In the context of random dipolar systems: T. Nattermann, Ferroelectrics **104**, 171 (1990).
[13] F. Alberici-Kious, J.P. Bouchaud, L.F. Cugliandolo, P. Doussineau, and A. Levelut (to be published).
[14] For a recent investigation of temperature changes in the RFIM, see M. Alava and H. Rieger, cond-mat/9804136.
[15] A.J. Bray and M.A. Moore, J. Phys. C **17**, L463 (1984); Phys. Rev. Lett. **58**, 57 (1987).
[16] D.S. Fisher and D.A. Huse, Phys. Rev. B **38**, 373 (1988); D.A. Huse, Phys. Rev. B **43**, 8673 (1991).
[17] G.J. Koper and H.J. Hilhorst, J. Phys. (Paris) **49**, 429 (1988).
[18] V.S. Dotsenko, J. Phys. C **18**, 6023 (1985); V.S. Dotsenko, M.V. Feigel'man, and L.B. Ioffe, *Spin-Glasses and Related Problems*, Soviet Scientific Reviews Vol. 15 (Harwood, Chur, Switzerland, 1990).
[19] F. Lefloch, J. Hammann, M. Ocio, and E. Vincent, Europhys. Lett. **18**, 647 (1992). See also J.O. Andersson, J. Mattsson, and P. Nordblad, Phys. Rev. B **48**, 13 977 (1993).
[20] L.F. Cugliandolo and J. Kurchan, Phys. Rev. Lett. **71**, 173 (1993); J. Phys. A **27**, 5749 (1994).