

Dipolar relaxation and limit of ergodicity in $\text{K}_{1-x}\text{Li}_x\text{TaO}_3$

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Evidence is presented for irreversible polarization of $\text{KTaO}_3\text{:Li}$ upon field cycling. In a certain region of field-temperature space, the polarization is also shown to depend on cooling speed. An experimental criterion for nonergodicity is devised to separate the field-temperature space of $\text{KTaO}_3\text{:Li}$ into two regions. The separating line can be fitted to the formula $E \sim [T_g(0) - T_g(E)]^\gamma$, $1.5 \leq \gamma \leq 2.3$. This form was derived from a model postulating a random interaction of infinite range between spins, and independently from a relaxation-time approach involving superparamagnetic moments. While these models are mutually exclusive, we find reasonable coincidence of the data with either of them. From the parameters derived for the respective fits, we conclude, however, that neither of these two models consistently describes all the data presented in $\text{KTaO}_3\text{:Li}$.

I. INTRODUCTION

Mixed crystals of the type $\text{KTaO}_3\text{:Z}$, $Z = \text{Li, Na, and Nb}$, belong to the class of materials which are paraelectric at high temperature, and have polar character at sufficiently low temperatures.¹⁻³ Polarization of the low-temperature phase has some symmetry-related directions, and the question of reversibility of the polarization between these directions arises. In all of these cases, and also in conventional ferroelectrics, a polarization created in some way will last for at least thousands of seconds after the field has been set to zero. However, symmetry predicts that all polarizations P occur with equal probability if $E = 0$, and any simple polarization experiment with subsequent short circuit shows irreversible phenomena and proves that not all phase space is available to the sample within experimental times. One is tempted to attribute this phenomenon to breakdown of ergodicity. Before doing so, however, we shall recall two examples of earlier studies on these materials which elucidate the problematics.

In the low-concentration limit, Li-associated dipoles in KTaO_3 relax⁴ with a predominant Debye relaxation time τ whose temperature dependence is given by an Arrhenius function $\tau = 10^{-13} \times \exp(1000/T)$. Obviously, at $T < 20$ K, $\text{KTaO}_3\text{:Li}$, once polarized, stays in this state for days. By just increasing the waiting time (to τ below the Arrhenius frequency in a classical model or to the inverse tunnel frequency in a quantum-mechanical context), the polarization observed is reduced to zero. $\text{KTaO}_3\text{:Li}$ in the limit of low Li concentration is thus a poor testing ground for ergodicity.

The opposite example is $\text{KTaO}_3\text{:Nb}$ where there is collective polar motion with a lowest eigenfrequency given by $\omega \sim (T - T_c)^{1/2}$, extrapolating to zero at finite temperature.⁵ Below this temperature, the polarization is strictly static and there is no doubt that ergodicity breaks down.⁶

We are concerned here with $\text{KTaO}_3\text{:Li}$ with Li concen-

trations such that collective effects occur,⁴ i.e., $x_{\text{Li}} \geq 1$ at. %. In this concentration range, slowing down of the polar motion in $\text{KTaO}_3\text{:Li}$ also exists, but depends more strongly¹ on temperature than an Arrhenius function. A consequence thereof is a transition⁷ within a very narrow temperature interval from paraelectricity to a polar configuration with apparently static polarization. It is tempting to attribute breakdown of ergodicity to this rapid freezing process but the problem arises of where to set the limiting temperature for ergodicity. In none of the observations performed in the critical region can we extrapolate by letting some relaxation time go to infinity, for the simple fact that the relaxation phenomenon is nonexponential with time and a whole distribution of times has to be taken into consideration.⁸ We are not aware of any clear-cut criterion for the limit of ergodicity under these conditions, and have thus taken the liberty of defining ergodicity in what we consider the least arbitrary and yet practical way: Rather than postulating that the polarization reaches equilibrium to within some tolerance after some prescribed time, we postulate that the polarization can follow its equilibrium value in a temperature-sweep experiment. The motivation for doing so will become apparent when the experimental methods and results have been described in the section immediately following, where we shall present polarization data in relation to sample history.

II. EXPERIMENTAL RESULTS

Here, we wish to present data on the electric polarization P of $\text{KTaO}_3\text{:Li}$. The samples containing 1.6 at. % Li and 2.6 at. % Li are identical to the ones used for susceptibility measurements and described earlier.¹ The test of reversibility requires sweeping the sample along different paths in E - T space. Since some methods for measuring P rely on sweeping along a prescribed path, we first outline some problems associated with polarization measure-

ments.

Four methods are commonly used to determine static polarizations: A measurement of the charge during polarization reversal,³ the pyroelectric effect,³ birefringence,³ and the piezoelectric effect.⁹ Of these, the first is inapplicable wherever the polarization is irreversible.

The second, based on the *pyroelectric* effect, requires heating the sample in zero field while recording the current i in an electrometer. The polarization is then $P = \int i dt / \sigma$, where σ is the surface of the electroded sample. We have tried to extend this method to field-heated (FH) samples, but additional currents owing to redistribution of space charge and injection precluded the interpretation of the current integrals in terms of P . We note in particular that in FH pure KTaO_3 , the current integrals are nonzero, whereas $P = 0$.

The *birefringence* effect rests on the anisotropic propagation of light in a polar medium. While it may be successfully applied in saturated, i.e., homogeneously polarized samples, its use in samples cooled in zero field is disputed.^{1,5,7}

The *piezoelectric* effect implies linear coupling between the strain and the polarization and allows the excitation of sound waves by ac electric fields.⁹ From the characteristics of the excited sound wave, the piezoelectric coefficient and thus the polarization can be determined. This method is independent of sweep techniques and, as long as space-charge fields are small compared to external fields, also independent of the electronic properties of the sample. The condition that space-charge fields are small limits the range of useful external fields to about 200 kV/m.

The shortcomings of the first three methods for our particular application suggest the use of the piezoelectric method to determine P in FH samples. A more detailed description is found in the literature.⁹

We now present evidence for *irreversible* polarization at $E = 0$, $T = 30.5$ K: We note that trivially, on zero-field cooling (ZFC) (from A to C , Fig. 1), $P = 0$. On cooling

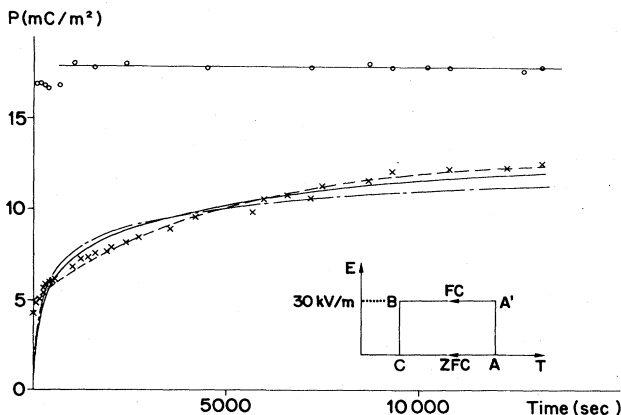


FIG. 1. Polarization vs time after sample treatment: $x = 0.016$, $E = 30$ kV/m, $T = 30.5$ K. Open circles, field cooling; crosses, zero-field cooling, sample subject to field at $t = 0$. Fits to algebraic decay (dashed and points), to stretched exponential (full curve) and to exponential-to-metastable state (dashed curve) (standard deviation errors 0.08, 0.07, 0.05, respectively).

slowly in the presence of a field $E = 30$ kV/m, we obtain $P = 17$ mC/m² for $T = 30.5$ K. Short-circuiting the sample at $T = 30.5$ K, i.e., going from B to C , does not alter the polarization: Denoting t as the time after cooldown, we find that $P(t)$ is represented by a straight horizontal line in Fig. 1. Evidently, the path on which point C was reached is all important. Does this also hold for point B ? Reaching B from A' reproduces the field-cooled (FC) polarization of 17 mC/m². If B is reached from C , i.e., if the sample is cooled at zero field and then subject to a field, a polarization will result which is much smaller than the FC polarization. Its time dependence is also shown in Fig. 1. It cannot be represented by any known function, be it exponential or algebraic. A criterion of ergodicity in terms of some fitting parameter of $P(t)$ therefore does not exist. We note that the application of a field enhances the chance for ergodic behavior, but the value of the field is difficult to tell. On the basis of these data taken after a time-consuming relaxation experiment, we cannot decide whether or not to attribute ergodicity to point B . Clearly, relaxation to equilibrium polarization at C (i.e., to $P = 0$) is infinitely slow, thus at C , the system is nonergodic. To exploit the concept of ergodicity,¹⁰ we note that the part of the relaxation near equilibrium alone provides sufficient information. Any large deviations from equilibrium such as that observed at point B in Fig. 1 take up much experimental time without telling whether the system responds to perturbations at B . This insight suggests the use of a differential method to test for ergodicity, namely, to sweep the temperature at constant $\partial T / \partial t$ and to determine the conditions under which the polarization can follow its time-dependent equilibrium value.

We first determine the range of the sweep speeds, $\partial T / \partial t$, which are reasonable to use for experimental purposes. We require that the polarization stay below its saturation value (all dipoles aligned) at all speeds and fields of interest. For this purpose, we have measured the FC polarization at 30 K following a sweep of constant $\partial T / \partial t$. The result, P_{FC} versus $\log_{10}(\partial T / \partial t)$ as obtained from the pyroelectric method, is plotted in Fig. 2 for several fields, marked as the parameter in kV/m in the figure. We note that P is roughly linear in $\log_{10} T$. Clearly, there is a saturation polarization of 28 mC/m², and this is attained

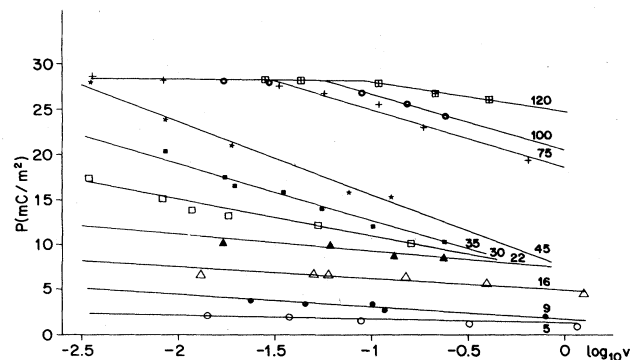


FIG. 2. Polarization after field cooling from 40 down to 30 K, at speed v (in K/sec). Parameter: electric field in kV/m, $x = 0.016$.

faster for larger fields. From studies on pure KTaO_3 , electric fields are known to induce space charge; they should thus be kept low, for example, below 100 kV/m. This limits the range of useful speeds to below 0.1 K/sec. Very low speeds, below 1 mK/sec, are impractical to use. Acceptable speeds are thus between 3 and 100 mK/sec. Practical reasons, namely, the time needed to measure the piezoelectric coefficient from the ultrasonic-resonance characteristics, determine the optimum speed to be near 3 mK/sec. The corresponding results for 2.6 at. % Li are shown in Fig. 3. Fixing the speed for field heating and field cooling at 3 mK, we measured the polarization by the ultrasonic method. The 1.6 at. % sample was first cooled at zero field, and then heated with the field on (30 kV/m for the data in Fig. 4). Clearly, P goes through a maximum at 35.2 K. Upon cooling again, P follows the old curve until $T_g = 35.2$ K but then it continues rising up to 17 mC/m². Upon reheating in the field (FH), P again follows the same curve except for a slight hysteresis. Inspection of the data in Fig. 4 suggests that departure of the FC from the ZFC curve indicates breakdown of ergodicity occurring at 35.2 K for $E = 30$ kV/m. We took analogous data for different fields, and plotted the ergodicity limits in Fig. 5. Clearly, T_g decreases with increasing E , and this confirms the findings that for fixed temperature a sample may be nonergodic at zero field and ergodic at finite field (Fig. 1). In the 2.6 at. % sample, the ultrasonic-resonance line is much broader than in the 1.6 at. % sample, and this restricted us to taking data above ~ 50 kV/m. Still higher concentrations entail large ultrasonic losses preventing a polarization measurement by the ultrasonic method.¹¹

III. ANALYSIS OF THE DATA

In this section, we consider the time-dependent polarization after rapid quenching, and test several models which have been advanced for the magnetic analog. We then interpret the sweep experiments, and finally test the de Almeida-Thouless¹² prediction for ergodicity and the Wenger-Mydosh¹³ proposal for irreversible behavior.

Some authors¹⁴ have fitted decaying magnetizations in

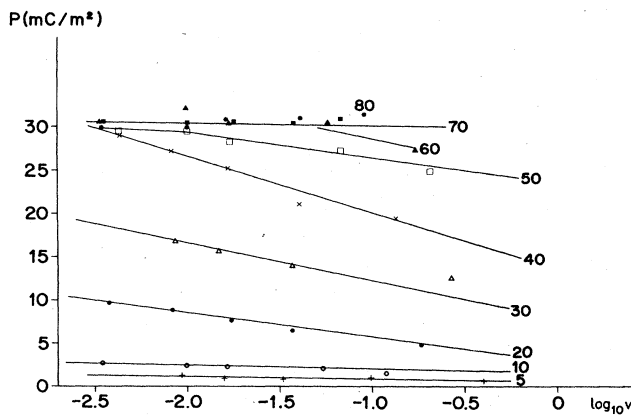


FIG. 3. Polarization after field cooling from 55 down to 40 K at speed v (in K/sec). Parameter: electric field in kV/m, $x = 0.026$.

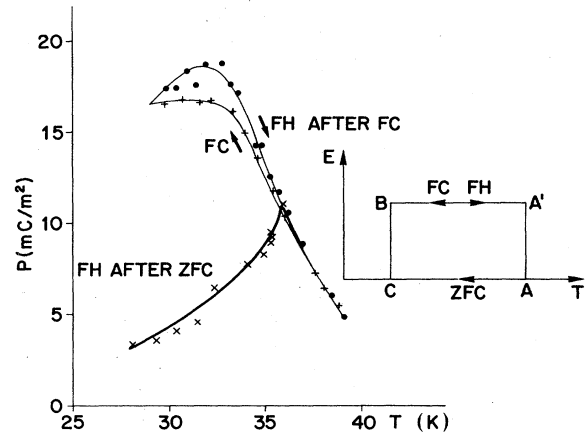


FIG. 4. Polarization vs temperature in a T -sweep experiment. Note that the zero time derivative $\partial P/\partial t = 0$ coincides with the departure of the FC from the ZFC curve. $x = 0.016$, $v = 3$ mK/sec, $E = 30$ kV/m. Inset: temperature cycle.

spin glasses to $M_0(1 - \alpha \log_{10} t)$, an expression which is certainly incorrect for $t \rightarrow \infty$. An algebraic decay of the form

$$M = \frac{M_0}{t^{1-n}} \quad (1)$$

has been predicted on the basis of the mean-field model of spin glasses.¹⁵ We have translated this expression to electrical notation, and assume that for the data taken in an electric field, the equilibrium polarization can be considered an adjustable parameter, thus

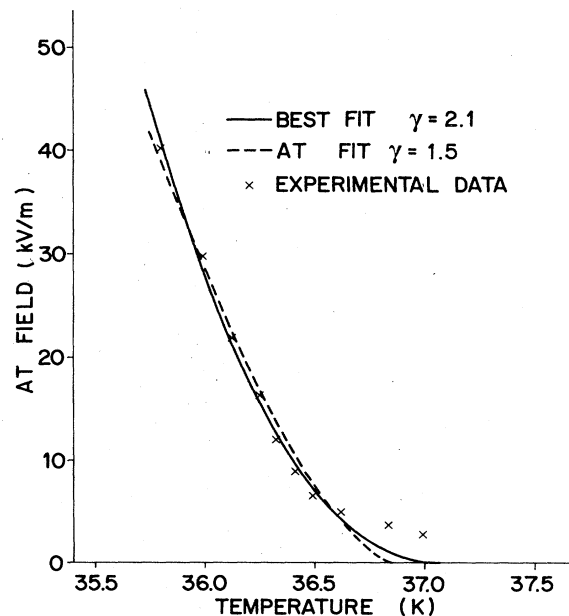


FIG. 5. Limit of ergodicity (crosses, experimental data). The fit to the de Almeida-Thouless line is labeled " $\gamma = \frac{3}{2}$." A modification which leaves γ adjustable is labeled "best fit $\gamma = 2.1$," $x = 0.016$. Cooling speed 3 mK/sec.

$$P(t) - P_{\text{eq}} = \frac{P_0}{t^{1-n}} \quad (2)$$

A best fit yields $P_{\text{eq}} = 25.6 \text{ mC/m}^2$, $P_0 = 33.5 \text{ mC/m}^2$, $n = 0.91$, and an average error of 0.124 mC/m^2 .

An alternative approach consists of considering the dipole configuration as containing many local energy minima. A random distribution of quasidegenerate minima leads to a relaxation function of the form¹⁶

$$P - P_{\text{eq}} = P_{\text{eq}} \exp \left[-\frac{Ct^{1-n}}{1-n} \right] \quad (3)$$

A best fit to the data yields $C = 0.019$, $n = 0.68$, with a standard deviation of 0.075 . Here, P_{eq} has been taken as the FC equilibrium polarization. An independent approach yields a similar equation except for an as-yet-controversial interpretation^{17,18} of parameter C .

We have further attempted to fit the polarization to

$$P = P_m + P_0 \exp \left[-\frac{t}{\tau_0} \right] \quad (4)$$

with the result $P_m = 12.4 \text{ mC/m}^2$, $P_0 = -7.8 \text{ mC/m}^2$, and $\tau_0 = 4700 \text{ sec}$. The standard error is 0.05 . This approach is tantamount to grouping the major relaxation times around τ_0 . To account for the metastable polarization $P_m \neq P_{\text{eq}}$, other, much slower, relaxation times have to be postulated.

All of these fits use three parameters (except for the stretched exponential with two) and neither of these fits is fully convincing. In particular, we note that the fit to the algebraic decay and that to the stretched exponential suffer from an unphysical value of the parameters P_0 and n , respectively. The fit to the decay into a metastable state has the lowest error and suggests that relaxation may be approximated by a lumped time τ which of course depends on experimental conditions. These approaches describe relaxation far from equilibrium.

We now assume that near equilibrium, the polarization decays as

$$\frac{\partial P}{\partial t} = \frac{P_{\text{eq}}(t) - P(t)}{\tau(T, E)} \quad (5)$$

where P_{eq} depends explicitly on time. If $\partial P/\partial t = 0$, then two possibilities will arise: Either $\tau(T, E) = \infty$, a condition reached at low temperature, or $P = P_{\text{eq}}$. Both occurrences are observed in Fig. 4. Upon field cooling, a plateau of the polarization is observed as in the analogous magnetic case. This corresponds to the supercooled metastable state of a glass. On field heating a ZFC sample, effective equilibrium occurs where $\partial P/\partial t = 0$ and at the same time the curves P_{ZFC} and P_{FC} coincide. Below this temperature, these curves are separate and indicate that the polarization measured depends on history. Accordingly, the point of inflection on the polarization versus time curve defines the onset of ergodicity. These inflection points are plotted in Fig. 5 and fitted to^{12,13}

$$E = A \{ [T_g(0) - T_g(E)] / T_g(0) \}^\gamma \quad (6)$$

where A , $T_g(0)$, and γ are adjustable parameters. A best three-parameter fit yields $A = 5.9 \times 10^7 \text{ V/m}$, $T_g(0) = 37$

K, and $\gamma = 2.1$. The de Almeida–Thouless expression requires $\gamma = 1.5$ and the corresponding two-parameter fit (Fig. 5) yields $T_g(0) = 36.8 \text{ K}$, $A = 8.9 \times 10^6 \text{ V/m}$, and an error about twice that of the three-parameter fit. de Almeida and Thouless identify A with $A = 2k_B/[3T_g(0)]^{1/2}$ from which the polar moment per impurity $p = 1.6 \times 10^{-28} \text{ Cm}$ can be deduced. For $x = 0.016$, this moment is in perfect agreement with the moment deduced from the saturation polarization. For $x = 0.026$, this corresponding moment is 25 times larger (Fig. 6). In view of this astonishing difference between $P(0.016)$ and $P(0.026)$, we consider an alternative explanation of limited reversibility recently given in terms of relaxation: Using a constant relaxation time for the exponential decay of a moment, one finds that $E \sim T^\gamma$ crosses over from $\gamma = \frac{1}{2}$ to $\gamma = \frac{3}{2}$ at a field $PE \sim kT_g$, where in this treatment P was the superparamagnetic moment.¹³

The translation of this finding into “electric language” is straightforward: P is the superparaelectric moment, i.e., the displaced Li atom plus the induced polarization cloud associated with it. This moment determines the theoretical crossover field $E = kT_g/P \sim 50 \text{ kV/m}$. Clearly for $x_{\text{Li}} = 1.6 \text{ at. \%}$ the data contradict the hypothesis of crossover, while for $x_{\text{Li}} = 2.6 \text{ at. \%}$ they are quite compatible with it, although, owing to low sensitivity at small fields the crossover could not actually be observed. We find that $\gamma = \frac{3}{2}$ fits the data in both cases, which is compatible with the de Almeida–Thouless¹² (AT) result for 1.6 at. \% Li , and compatible with the relaxation results for 2.6 at. \% Li . Inspection of the relaxation behavior (Fig. 1) shows us that neither of the two hypotheses is fully compatible with experiment: The data clearly show nonexponential decay which can be separated into an initial near-exponential decay into a metastable state, followed by an undetermined very slow decay. Such behavior is observed at all temperatures around T_g . Theories leading to a phase transition, such as the SK model at the basis of the AT prediction,¹² imply critical slowing down, i.e., $\tau^{-1} \sim (T - T_g)^\delta$, $\delta \sim 1$, whereas the independent-moment approach leading to superparaelectric relaxation implies Arrhenius-type relaxation. Neither is observed, and we thus hesitate to attribute our relaxation data to the result of either approach.

Recently, models of hierarchical dynamics have produced a class of relaxation functions which might cover the observed behavior of Li dipoles.^{16–18} They predict a long tail in the polarization versus time curve and attribute it to the fact that some clusters must wait to relax until a number of neighboring clusters simultaneously happens to be in a rare, favorable position. It is this long tail which gives rise to effective nonergodicity.

The problem of nonergodicity has raised particular interest in the field of spin glasses. Relaxation dynamics¹⁹ and Monte-Carlo computations²⁰ of time-dependent order parameters have shown that nonergodicity sets in below T_g . Measurements of the static magnetization have confirmed Eq. (6), but with the prefactor off by an order of magnitude.^{21–23} This prefactor also depended on an observation time but without any sign of convergence towards the theoretical prefactor.²⁴ An evaluation of the distribution of relaxation times from susceptibility data

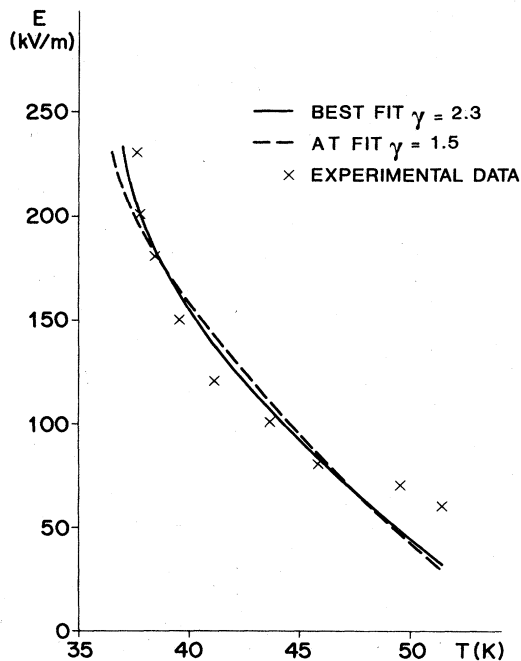


FIG. 6. Limit of ergodicity (crosses, experimental data). The fit to the de Almeida–Thouless line is labeled " $\gamma = \frac{3}{2}$." A modification which leaves γ adjustable is labeled "best fit $\gamma = 2.3$," $x = 0.026$. Cooling speed 3 mK/sec.

suggested that the time needed to perform static measurements becomes prohibitive.²⁵

IV. SUMMARY

The polarization of $\text{KTaO}_3\text{:Li}$, measured 10 K below T_g , depends on the field E applied during cooldown at a

speed v . Very crudely, we can present it as $P = aE(\log_{10}v + 2)$ for fields below 40 kV/m and speeds from 3 to 300 mK/sec. For larger fields, P approaches P_s quickly. The corresponding values are $a = 0.13$ for 1.6 at.%, $a = 0.14$ for 2.6 at.%, $P_s = 28$ mC/m², and 30 mC/m², respectively. We offer no explanation for this behavior. A relatively good fit for the relaxation of P to equilibrium will be obtained if the existence of metastable states is assumed. A fit to exponential relaxation to the true equilibrium state is unsatisfactory. Fractional exponents improve this fit but still leave it unsatisfactory.

The polarization follows the temperature-dependent equilibrium in a sweep experiment down to a field-dependent temperature; below this temperature there are irreversibility effects. The E - T curve for irreversibility can be fitted satisfactorily to either the parametrized de Almeida–Thouless¹² or the Wenger–Mydosh¹³ results. The parameters depend explicitly, although only slightly, on cooling speed, whereas in conventional analyses they depend on observation time. The values of the parameters defy plausible explanations, however,

We conclude that the respective models at the basis of these approaches do not adequately describe $\text{KTaO}_3\text{:Li}$. The SK model assumes an infinite-range interaction between dipoles. Consequences thereof are the existence of a phase transition and independence of the interaction of Li concentration. Both consequences are contrary to the experimental results.

The Wenger–Mydosh proposal assumes tacitly that the superparamagnets (in our language the "dressed" moments of the Li) are independent of one another. Relaxation should then be exponential. This is also contrary to the experiment. Since no closed-form description of these phenomena exists, we are in the process of performing model calculations on this system.

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