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The polarisation decay function and freezing scenario in dipole glasses

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Abstract. Discharge currents and susceptibility functions are given for KTaO_3 doped with Li. These functions are parametrised in terms of a Kohlrausch–Williams–Watts decay function involving a stretched exponential in the time domain. The parameters, namely the size of the relaxation step, the relaxation rate and the stretch index are given as a function of temperature. The step size shows the usual cusp at T_i whereas neither the relaxation time nor the stretch index are critical functions of $T - T_i$, where T_i denotes the transition temperature to the dipolar phase. Below T_i , arithmetic decay is observed.

1. Introduction

Some of the earliest observations in solid state physics were of the release of mechanical stress [1] and the discharge of electrical polarisation as found by Kohlrausch [2]. In both cases it was found that the discharge, while being monotonic, occurred at a time-dependent rate which was not proportional to the polarisation present at that time. Attempts to describe the ensuing non-exponential decay by heuristic functions were numerous [3]: the most prestigious decay function is perhaps the one by Williams and Watts [4, 5], who stretched the time variable from t to t^β , with $0 < \beta \leq 1$, in order to put the polarisation decay into exponential (κ ww) form:

$$\Phi(t) = \Phi_0 \exp(-(\alpha t)^\beta) \quad (1)$$

where Φ_0 is the total polarisation induced by a field applied at all times $t < 0$, α a relaxation rate, and β an adjustable parameter. This decay function has the merit of describing well numerous experiments on decay currents which are proportional to $\partial\Phi/\partial t$.

As a result of the polarisation decay, the dielectric susceptibility $\varepsilon^* = \varepsilon_1 + i\varepsilon_2$ depends on frequency $f = \omega/2\pi$. It is related to the decay function by the Fourier transform

$$\varepsilon^*(\omega) - \varepsilon_\infty = (2\pi\varepsilon_0 E)^{-1} \int \exp(i\omega t) (\partial\Phi/\partial t) dt \quad (2)$$

where $\varepsilon_0 = 8.85 \times 10^{-12} \text{ C V}^{-1} \text{ m}^{-1}$ and E is the field applied at negative t . Only recently

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have there been attempts to model kww behaviour [5–8] and to express its parameters in terms of relaxation processes.

A conceptually simpler approach is to let relaxation take place through a distribution of energy barriers. Wagner [9] has given the result of this model without identifying it explicitly as a Debye relaxation [10] over barriers. In this (WD) model

$$\varepsilon^*(\omega) - \varepsilon_\infty = \Delta\varepsilon \int d\tau \tau^{-1} (1 + i\omega\tau)^{-1} \sigma^{-1} \pi^{-1/2} \exp\{-[\ln(\tau\alpha_0)\sigma]^2\}. \quad (3)$$

The parameters $\Delta\varepsilon$, α_0 and σ depend on temperature and have the meaning of the relaxation step, the most probable relaxation rate (not identical to α in equation (1)) and the logarithmic width of its distribution, respectively. There are numerous approaches [11–15] to fit $\varepsilon^*(\omega)$ to numerical expressions, some quite general [16], but most of them without regard to the temperature-dependent physical relaxation process. To distinguish between the mutually exclusive kww and WD relaxation processes, the susceptibility has to be known in a wide frequency and temperature range. Of particular interest are systems with high susceptibility and thus large decay currents which allow measurements to be extended in the mHz range. Such a system [17, 18] is $\text{KTaO}_3:\text{Li}$, where the perovskite lattice has a high susceptibility. The Li atoms, carrying a dipole moment due to their off-centre positions, are the relaxing species. At sufficient concentration they are known to freeze into a disordered polar state [19].

We wish to establish how this freezing takes place. To this end we present data for $i(t)$ and $\varepsilon(\omega)$, and express the results in terms of the time-honoured kww and WD functions. We shall confront the results with model predictions based on these functions and attempt to express the background of these models in physical terms.

2. Experimental results

Single crystals [20] of KTaO_3 doped with Li have been subjected to an electric field, usually for 3600 s. The release of charge was then measured under short-circuit conditions, typically once every 2 s for about 1000 s. Since the current typically decays by about two orders of magnitude in the time interval of observation, we give our results in terms of plots on log–log scale. Figure 1 shows plots of $\log i$ versus $\log t$ for $\text{K}_{0.966}\text{Li}_{0.034}\text{TaO}_3$ at several temperatures. In the same figure we have drawn the curve resulting from the best fit to the Williams–Watts formula for the decay current, $\partial\Phi/\partial t$. We note that the $\log i$ versus $\log t$ curves are non-linear above about 60 K; they are virtually linear below that temperature. Also given in this figure is a plot of pure KTaO_3 taken at 50 K. The low amplitude of the current in this sample indicates that the lattice contribution is negligible: the major contribution to the current originates from the impurity system.

The decay function $i(t)$ is related to the dielectric susceptibility $\varepsilon(\omega)$ by a Fourier transform. Measurements by AC techniques in the corresponding frequency range, i.e. down to 10^{-3} Hz, however, require impedance matching to the sample impedance which, for a capacitance of 100 pF with $\tan\theta = 10^{-3}$, $|Z| \sim 10^{15} \Omega$ at 10^{-3} Hz, is a non-trivial problem [21]. We have thus resorted to measuring $\varepsilon(\omega)$ at higher frequencies over a sufficiently wide range of temperatures, allowing the connection between $\varepsilon(\omega)$ and $i(t)$ to be made.

The data for $\varepsilon(\omega)$ are shown in figure 2. Following Moynihan *et al* [22], we plot the real and imaginary part of ε , i.e., ε_1 and ε_2 versus $\log f$, $f = \omega/2\pi$, and estimate the size

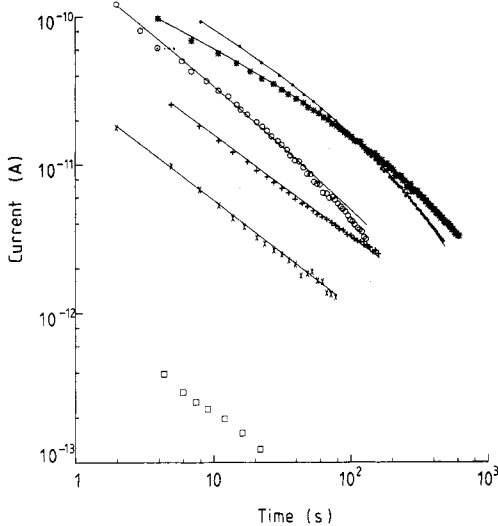


Figure 1. The polarisation decay current and fit to $\partial\Phi/\partial t$. Sample: $\text{K}_{0.966}\text{Li}_{0.034}\text{TaO}_3$; ●: 65.9 K; *: 63.9 K; ○: 60.0 K; +: 55.5 K; ×: 48.0 K. For pure KTaO_3 , □: 48 K.

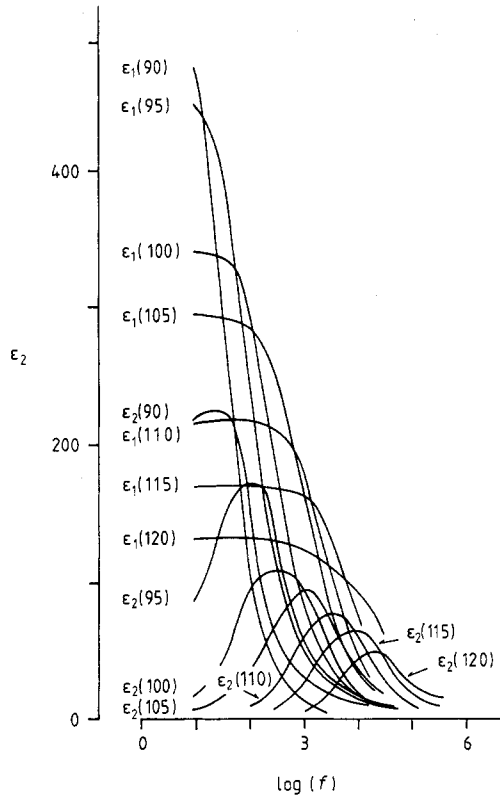


Figure 2. Dielectric susceptibility $\varepsilon^* = \varepsilon_1 + i\varepsilon_2$ versus $\log(\text{frequency})$. The parameter in parentheses is temperature. The sample is, as in figure 1, KTL 34 .

of the dispersion step, its centre frequency and the width of the ε_2 versus $\ln \omega$ curves. These estimates allow us to refine the parameters of the kww and the WD functions.

In figure 3 we give a detailed plot of $\varepsilon_2(\omega)$ at 95 K and 105 K together with best fits to kww and WD. We note that the Gaussian distribution of $\ln(\tau\alpha_0)$ generates a dielectric function with the property [9]

$$\varepsilon_2(\ln(\omega/\alpha_0)) = \varepsilon_2(-\ln(\omega/\alpha_0)). \quad (4)$$

In contrast, the kww dielectric function $\varepsilon_2(\ln(\omega/\alpha_0))$ is asymmetric [5]; it extends further into the high-frequency range. Deviations of $\varepsilon_2(\ln(\omega/\alpha_0))$ from symmetry may thus hint at kww behaviour. An inspection of the data in figure 3(a) and of the variances, suggests that the behaviour of $\varepsilon_2(\omega)$ is intermediate between that of kww and WD. As T decreases, asymmetry increases and fits of ε_2 versus kww and WD tend to confirm this finding (figure 3(b)). The accessible frequency range for $\varepsilon_2(\omega)$ is, however, insufficient to establish kww behaviour with certainty. This is afforded by an evaluation of the $i(t)$ data. For this purpose we have evaluated the Fourier transform of the Wagner [9] integral

$$i = \frac{\partial}{\partial t} \int \exp(-\alpha t) \exp[-(\ln(\alpha/\alpha_0))^2 \Delta^{-2}] d\alpha/\alpha \quad (5)$$

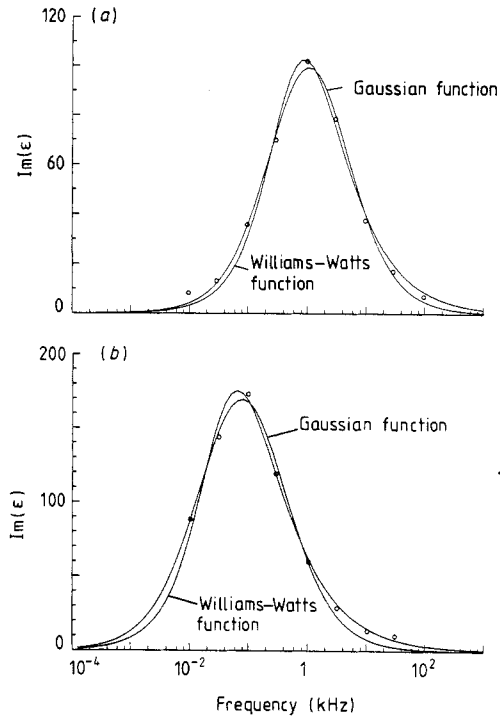


Figure 3. A fit of the susceptibility to wd (equation (3)) and kww (equation (1)) function. (a) $T = 105$ K, (b) $T = 95$ K.

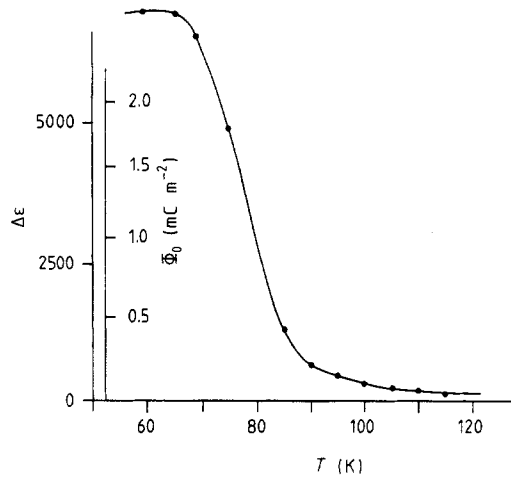


Figure 4. The kww parameter Φ_0 , and dielectric step $\Delta\epsilon$ versus T ; $E = 36$ kV m $^{-1}$.

whose leading [23] term is

$$i \approx t^{-2-1/\Delta^2} \quad (6)$$

for $\Delta \neq 0$.

Clearly, the negative exponent $2 + 1/\Delta^2$ is too large to fit the low-temperature data. On the other hand, the kww function predicts $i \sim t^{\beta-1}$ with $0 < \beta < 1$, which is compatible with the data for $t \ll \tau_0$ and allows a determination of β (but not of α and Φ_0) in the range where $\log i \sim \log t$, i.e. below 60 K. Since the low-temperature data clearly exclude wd behaviour while the numerical discrepancy between the kww and wd fits is rather small at high temperatures, we express all our results in terms of the kww function.

Figure 4 shows the parameter Φ_0 which is the total polarisation induced by the application of a field E . It is readily converted into the dielectric relaxation step $\Delta\epsilon = \Phi_0/E\epsilon_0$, where $\epsilon_0 = 8.85$ pC V $^{-1}$ m $^{-1}$ (scale also shown). Φ_0 increases rapidly as T decreases and below 65 K, which corresponds to the stability limit of remanent polarisation [19], it assumes a constant value of ≈ 2 mC m $^{-2}$. This is only a small fraction of the saturation polarisation [19] of 60 mC m $^{-2}$. Keeping Φ_0 small (by applying small DC fields) ensures linearity and the applicability of the Fourier transform. It has the disadvantage of generating only small decay currents. The kww relaxation parameter is given in figure 5 in an Arrhenius representation, $\ln \alpha$ versus T^{-1} . A quite reasonable fit

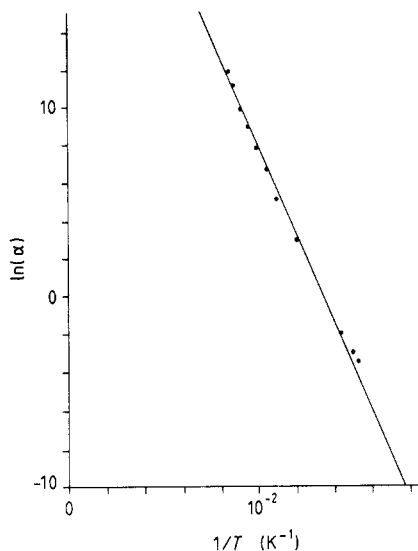


Figure 5. The kww parameter α in Arrhenius representation. Note that the straight-line fitting $\ln \alpha$ to T^{-1} excludes effective freezing at substantially non-zero T .

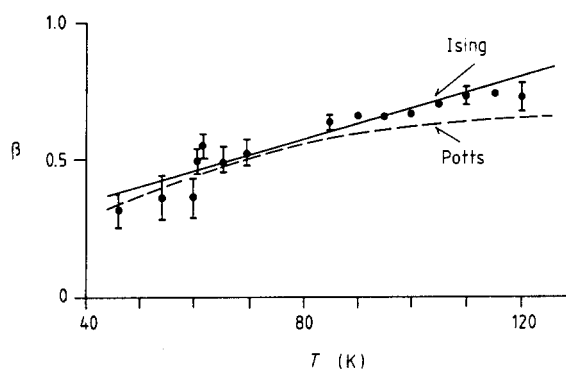


Figure 6. The kww parameter β , the stretched-exponential index, versus temperature. A fit to a linear function with $\beta = 0.1 + 5 \times 10^{-3} T$, and a comparison with Carmesin and Binder's [32] theoretical predictions are shown; note that below 80 K, β was measured by the depolarisation method whereas above 80 K, β was measured with the (more precise) bridge technique. A discrete change of β at T_f is highly unlikely.

to a straight line is possible with a slope of 2000 K and an intercept of $\alpha \sim 10^{13} \text{ s}^{-1}$. The numerical values of α and α_0 as well as of Φ and $\Delta \varepsilon E_{DC}$ are quite close for $T = 95 \text{ K}$ and 105 K .

In figure 6 we plot the Kohlrausch parameter β versus temperature. We note a drop from 0.7 at 120 K to values around 0.3 at 48 K. This corresponds to a broadening of the $g(\tau)$ distribution with an increase from e^4 to e^8 which is 1.5 to 3 decades on each side of τ_{\max} . We find thus that the kww function accounts for the low-temperature behaviour of $\text{KTaO}_3:\text{Li}$ and that a crossover to wd behaviour occurs near T_f . These findings are distinct from the findings [24] for KBrOH , where wd behaviour is present at all

temperatures and where the width of the Gaussian distribution at the base of the WD function decreases strongly with temperature, whereas the temperature dependence of $\Delta\varepsilon$ is weak.

3. Interpretation

In view of the plateau in the relaxation step $\Delta\varepsilon$ below T_f and the change of the relaxation rates by several orders of magnitude near T_f , we focus our attention on relaxation models devised for spin and dipole glasses. They include the self-consistent random-field model of a dipole glass by Fischer and Klein [25], decay hierarchies in glasses [5, 6], randomisation [7] of free energy, Glauber dynamics of spin glasses [26] and numerical simulation [8] of the Ising spin glass [27] by the Monte Carlo method.

Fischer and Klein [25] have evaluated random fields in dipole glasses arising from random dipolar interaction. A self-consistent mean-field treatment led to a spread of fields, $\text{var}(E)$, which increased critically below T_f , and to divergent susceptibilities. We realise that the presence of a local field affects the barrier between dipolar orientations; thus random fields lead to random distributions of barriers whose spread we have deduced from our data. While we agree with Fischer and Klein that the variance increases below T_f , we also find sizable non-zero variance above T_f , where their model has $\text{var}(E) = 0$. On the other hand, we confirm their prediction for the behaviour of the susceptibility. Dynamical effects were studied by Sompolinsky and Zippelius [26], the most conspicuous result being the prediction that, above some minimum ω_0 , $\varepsilon_2 \approx \omega^\nu$ where $\nu = \frac{1}{2}$ at T_f . While in $\text{KTaO}_2\text{:Na}$ a wide range of such behaviour [27] was present for ε_2 , we find here that below some critical time, $\Phi \approx t^{-x}$ which is compatible with $\varepsilon_2 \approx \omega^{x-1}$ below T_f where $x \approx 0.3$.

As an alternative, it has been proposed that a dipolar system may relax through a cascade of states and that it may be constrained by some condition on occupancy of the target state [5]. A particular choice of density of states and of a constraint hierarchy lead to a Kohlrausch decay. An attempt to evaluate the Kohlrausch parameters in terms of constraint parameters led us to contradictory findings: from the value of $\beta(T)$ we are led to believe that the constraint parameter (number of spins in the preselected state in the target level) changes from 1.2 at $T - T_f = 50$ K to 1.5 at T_f . Evaluating the same parameter from the relaxation rate leads to a change of a factor of 15 in the same temperature range. We also note that the relaxation rate given in terms of the Vogel–Fulcher law $\tau \sim \exp(-E/(T - T_f))$ is in contradiction to our data and also to data taken on spin and dipole glasses unless we choose to fit τ to a law of the kind $\tau \approx \exp(-E/(T - T_{VF}))$ where the Vogel–Fulcher temperature T_{VF} is a variable. Here, T_{VF} is negligibly small and, as in spin glasses [28], certainly very different from T_f . While relaxation in hierarchical and ultrametric spaces leaves the question of a cusp of $\Delta\varepsilon$ at T_f open, theories on spin glasses give affirmative answers to this question [28].

The dynamics of spin glasses have been analysed in detail by computer simulation [8]. The result for the autocorrelation function which is proportional to the derivative of the decay function was parametrised as

$$d\Phi/dt = \Phi_0 \alpha^\beta \exp(-(\alpha t)^\beta) t^{-x} \quad (7)$$

which deviates from the Kohlrausch function by the exponent x being different from $\beta - 1$. The parameters α and β behave much as in our experiment, but x is so small that t^{-x} could be replaced by $1 - x \ln t$.

The results displayed [8] for $d\Phi/dt$ resemble $i(t)$ in our figure 1: above T_f , $\ln i$ versus $\ln t$ is bent downward, below T_f it is a straight line. The transition to power-law behaviour occurs where α equals the maximum time of measurement, namely near T_f in Ogielski's simulation (after 10^9 Monte Carlo steps) and near T_f in the experiment (after about 1000 s) as well. Except for slight deviations in the short-term behaviour, t^* instead of $t^{\beta-1}$, which might be due to different initial conditions, Ogielski's simulation agrees extremely well with our data, which are therefore largely compatible with the Ising model of a nearest-neighbour random ± 1 interaction, called the Ising spin glass.

The attribution of $\text{KTaO}_3\text{:Li}$ to the class of Ising spin glasses raises (at least) two questions; that of dimensionality and that of dynamical scaling. We offer plausible arguments for both. (i) The restriction of dipolar motion to 180° flips, i.e. to one dimension, was proposed on the grounds of dielectric, ultrasonic and NMR relaxation data [29] (the latter two being absent for our relaxation branch). It was argued that the dipole deformed the lattice such that an adjacent deformation by 90° cost too much energy. (ii) Scaling implies [28] that $\ln(\tau\alpha_0) \approx \xi^z$, where ξ is the correlation length, or cluster size, of the polar object and $z \approx 2$. Since $\varepsilon \sim \xi^{2/3}$ nearly diverges at T_f , $\ln(\tau\alpha_0)$ should also diverge, but instead we find $\tau\alpha_0 \sim \exp(-E/kT)$. Unlike in spin glasses, α_0 is also strongly dependent upon T , so τ remains undetermined. Both effects originate from the strong anisotropic dipole–lattice interaction which in our opinion distinguishes dipole glasses from spin glasses. What they have in common, as far as the present investigation is concerned, is a crossover from relaxation over distributed barriers [9] to hierarchical [5, 6] kww relaxation and a susceptibility rising to a plateau.

It has been suggested [30] that barrier distributions were caused by random strains. The data for KBr:CN are very suggestive: the distribution width of such strains does not alter upon cooling, these strains merely become larger and determine the barrier for dipolar reorientation as well. Many other findings in cyanide glasses have indeed been attributed to random strains [31].

We suggest thus that crossover from random-strain to hierarchical (kww) relaxation behaviour is associated with the freezing transition of a *random-bond* glass. The transition does not occur where motion reaches a complete standstill (which is the hypothetical Vogel–Fulcher temperature) but where a hierarchy of states is established. This is at the transition from independent-dipole (Wagner–Debye) relaxation to kww hierarchical relaxation.

4. Conclusions

Susceptibility and related polarisation-decay data in dipole glasses allow the nature of the freezing process to be evaluated. Upon cooling, the susceptibility increases in a Curie–Weiss-like fashion and evidence of growing disorder is gained from its frequency dependence. This disorder is best described by a Gaussian distribution of barriers which hinder free rotation of Li dipoles. At some temperature T_f , the susceptibility stops increasing and below T_f the Gaussian distribution no longer fits the data. In this temperature range, excellent fits are obtained to the Kohlrausch–Williams–Watts function which is regarded as evidence for sequential relaxation through cascades of states. These states reveal the nature of glass originating from random bonds rather than from random fields.

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