Aging and memory effects in β-hydroquinone-clathrate

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The out-of-equilibrium low-frequency complex susceptibility of the orientational glass methanol(73%)-β-hydroquinone-clathrate is studied using temperature-stop protocols in aging experiments. Although the material does not have a sharp glass transition, aging effects including rejuvenation and memory are found at low temperatures. They turn out to be much weaker, however, than in conventional magnetic spin glasses.

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I. INTRODUCTION

Disordered and frustrated systems have attracted considerable attention during the past decade. Much effort in the recent years has been devoted to investigations of the slow dynamics in these systems. Structural glasses, magnetic spin glasses, and their electrical pendant, orientational glasses, are the typical examples of out-of-equilibrium systems. The most remarkable and common peculiarity of these materials is physical aging as has been extensively studied in spin glasses[1] and also observed in orientational glasses [for instance, $K_{0.989}Li_{0.011}TaO_3$ (Refs. 2 and 3)] and disordered ferroelectrics [for instance, $KTa_{0.973}Nb_{0.027}O_3$ (Ref. 4)].

Recent experiments on the insulating (Heisenberg-like) spin glass $CdCr_{1.7}In_{0.3}S_4$ showed that spin glasses can even memorize some of the features of the way in which the system has been prepared[5]: Prolonged aging at a constant temperature T_1 during slow cooling, a so-called temperature stop, causes a dip around this temperature in the temperature dependence of the imaginary part of the magnetic susceptibility upon reheating. Even multiple aging temperatures T_i can be memorized in a corresponding multi-temperature-stop experiment.[6] Other materials, like an Ising spin glass $Fe_{0.5}Mn_{0.5}TiO_3$ (Ref. 7), an interacting Fe-C nanoparticle system (Ref. 8), and the disordered ferroelectrics $Pb(Mg_{1/3}Nb_{2/3})O_3$ (Ref. 9) and $KTa_{0.973}Nb_{0.027}O_3$ (Ref. 4) displayed similar but less-pronounced memory features in these temperature-stop experiments.

Whereas many aging features of disordered materials in general and of spin glasses in particular are theoretically quite well understood on a phenomenological and on the mean-field level,[10] the theoretical status for these memory experiments is less clear. Two ingredients appear to be important: (1) A pronounced sensibility of the spin-glass state with respect to temperature changes to explain so-called rejunvenation effects when the temperature is changed during aging (sometimes also called *chaos* in spin glasses[11]) and (2) strongly coupled regions in equilibrated domains whose once-developed correlations are hard to destroy when the temperature is changed and which can serve as nucleation centers when the temperature is raised again to explain the memory effect. Obviously such features are absent in, for instance, pure ferromagnets, which show neither rejuvenation effects when the temperature is changed during domain growth nor memory effects. However, strongly disordered ferromagnets display a very weak form of memory which is commonly attributed to the reconformation of domain walls upon temperature changes.[12] Loosely speaking one might summarize the current status of the theoretical picture as the following: The walls are the glassy objects in random ferromagnets, whereas spin-glass domains behave glassy as a whole, in particular because they are most probably fractal objects[13] and surface (wall) as well as bulk contributions to aging effects are comparable. This variation of the strength with which the materials mentioned above display the chaos and memory effect in aging experiments can be interpreted as an indication of the underlying mechanism for slow relaxation: The weaker theses effects are, the more appropriate might a simple domain growth concept be, like in random ferromagnets or random field systems (see, for instance, the discussion in Sec. II).

From this viewpoint we discuss in this paper the electric dipole ''pseudospin'' glass system methanol ($x=73\%$)-β-hydroquinone-clathrate. It does not have a sharp transition temperature; glassy features become simply more and more pronounced as the temperature is decreased, similar to two-dimensional magnetic spin glasses,[14] which shows strong aging effects at low temperature but do not have a spin-glass transition. We demonstrate that the clathrate we study even displays at low temperatures a rejuvenation and memory effect in one-temperature-stop experiments and also a weaker effect in two-temperature-stop experiments. The paper is organized as follows: In Sec. II we discuss some of the physical properties of the methanol-clathrate that we studied. In Sec. III we present our results on temperature-stop aging experiments, and in Sec. IV we discuss our findings on the background of the current theoretical understanding of aging in disordered and glassy systems.

II. MATERIAL

In the β modification the quinol ($HO\text{-}C_6H_4\text{-}OH$) molecules form a H-bonded rhombohedral $R\bar{3}$ lattice with nearly spherical cavities, one per unit cell.[15] The methanol guest molecule residing in such a cavity is bound to the quinol host lattice by weak dispersion forces, only. Therefore, it can reorient relatively freely. At 65 K the methanol ($x=0.97$)-clathrate shows an antiferroelectric transition.[16] The structure consists basically of ferroelectric chains running along the hexagonal axis which are arranged in sheets

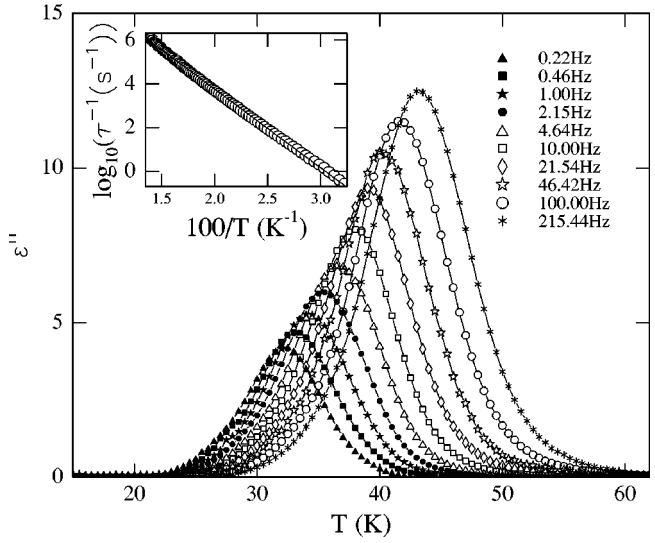

FIG. 1. Temperature dependence of the imaginary part of the dielectric constant ε_c''. The insert shows the inverse average relaxation time τ^{-1} as a function of $1/T$ (determined from the temperature of maximum ε_c'' for frequencies ranging from 0.1 Hz to 1 MHz).

of alternating sign. Samples with a larger percentage x of filled cavities ($x > x_c \approx 0.76$) show conventional ordering via a first-order phase transition, whereas the others ($x < x_c$) freeze into dipole glasses.

Woll *et al.*[16] have studied the dielectric response as a function of temperature, frequency, and methanol concentration. The static dielectric constant along the hexagonal c axis, ε_{cs}, shows a strong deviation from the Curie-Weiss behavior already at 250 K. The temperature dependence of ε_{cs} at higher temperatures is well described by the quasi-one-dimensional (quasi-1D) Ising model with a coupling J_c to nearest neighbors within the chain and a mean-field interchain interaction with coupling constant $J_\perp$. The coupling constants are consistent with the electrostatic dipole-dipole interaction, the elementary dipole moments being practically identical with that of the free methanol molecule. At lower T, $\varepsilon_{cs}(T)$ deviates from the Ising behavior and finally decreases with decreasing T, indicating the onset of 3D antiferroelectric interchain correlations. Such a behavior persists also for samples with lower concentrations of methanol: the static dielectric constant possesses a broad maximum in the region of about 55 K. For samples with a higher concentration, 3D correlations eventually lead to the antiferroelectric phase transition. For samples with lower concentration the antiferroelectric fluctuations presumably prevent total ferroelectric ordering. Accordingly, in the low-temperature region one can expect the coexistence of different types of locally ordered regions, i.e., clusters of polar and antipolar types. The dielectric relaxation therefore depends strongly on the dynamics of polarization clusters in an ac field.

As was shown before,[16] the relaxation processes are characterized by rather broad distribution of relaxation times τ, which is typical for disordered systems. In Fig. 1 the imaginary part of the dielectric constant ε_c'' is shown for frequencies from 0.2 Hz to 200 Hz. In the insert the inverse average relaxation time is plotted against the inverse temperature in a log-linear plot. The data lie on a straight line, which implies an Arrhenius law

$$\tau^{-1} \sim \tau_0^{-1} \exp(-E_A/T) \tag{1}$$

(with the ''pseudospin''-flip rate $\tau_0^{-1} = 9 \times 10^{10}\ \mathrm{s}^{-1}$ and an energy barrier $E_A = 828$ K) rather than the Vogel-Fulcher behavior $\tau^{-1} \sim \tau_0^{-1} \exp[-E_A/(T - T_{vf})]$ as in many structural glasses[17] or critical slowing down $\tau^{-1} \sim (T - T_c)^{z\nu}$ of spin glasses.[18] In spin glasses the critical temperature T_c at which the relaxation time diverges is identical to the spin glass transition temperature at which the nonlinear susceptibility and hence the spin-glass correlation length diverges. In structural glasses the Vogel-Fulcher temperature T_{vf} can serve as a lower bound for the strongly cooling-rate-dependent concept of a glass transition temperature. Figure 1 tells us that our methanol (73%)-clathrate does *not* show a well-defined glass transition in the temperature range 25–100 K, the dynamics simply gets slower with decreasing temperature according to Eq. (1) and this behavior appears to hold for all parts of the relaxational spectrum $g(1/\tau)$.[16] Early investigations on dipolar-glasses-favored Arrhenius laws,[19] but more recently there is growing evidence for a Vogel-Fulcher behavior at least in the low-frequency part of $g(1/\tau)$. In this sense the clathrate differs from other popular examples of dipolar glasses, e.g., $Rb_{1-x}(NH_4)_xH_2PO_4$ (Ref. 20) (member of KDP family), or cubic perovskites, such as $K_{1-x}Li_xTaO_3$ (Ref. 21). Nevertheless, the freezing of the dipole moments of the 73% clathrate is to some part a collective process, as discussed in Ref. 16. Not only the crystal field of the cavity, but also the interaction between the dipoles contribute to the Arrhenius barrier E_A in Eq. (1). As we will demonstrate in this paper, aging, rejuvenation, and memory phenomena are observable in the aforementioned temperature range.

III. TEMPERATURE STEP EXPERIMENTS

Motivated by recent aging and memory experiments on spin glasses[5] we performed such experiments on methanol(73%)-clathrate using the following temperature protocol. First reference curves of $\varepsilon_c''(T)$ are recorded as a function of temperature at rather slow cooling and heating ($|dT/dt| = 0.1\ K/\mathrm{min}$) and a frequency of 2 Hz. The reference curve at heating is always somewhat lower than at cooling, thus clearly indicating on an out-of-equilibrium behavior. However, if cooling is interrupted for a time t_a (in our experiment $t_a \approx 50$ ks) at constant temperature, e.g., $T_a = 31.5$ K, the imaginary part ε'' decreases by the effect of aging (inset of Fig. 2). Upon a subsequent cooling $\varepsilon''(T)$ approaches its reference value ε_{ref}'' at somewhat lower temperature of about $T \approx 25$ K (rejuvenation). During the next re-heating the temperature dependence $\varepsilon''(T)$ shows a little dip at about the aging temperature. Accordingly, the system ''remembers'' its aging temperature T_a (memory effect). This dip disappears in subsequent cooling-heating cycles.

In order to highlight the consequences of isothermal aging it is quite convenient to present the data as difference be-

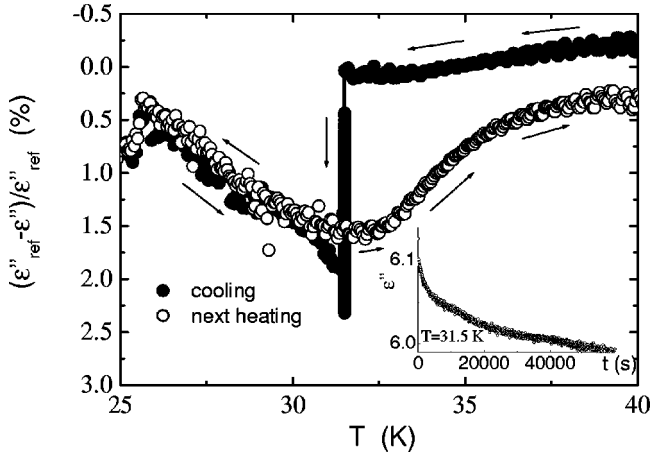

FIG. 2. Difference $[\varepsilon''_{ref}(T)-\varepsilon''(T)]/\varepsilon''_{ref}(T)$. The inset shows the aging of ε'' recorded at $T_a=31.5$ K.

tween the curves recorded during the second and the first (reference) cooling-heating circles, normalized to the reference curve, $[\varepsilon''_{ref}(T)-\varepsilon''(T)]/\varepsilon''_{ref}(T)$ (see Fig. 2). One can clearly see the sequence of the several effects: aging at $T=T_a$ with long-time evolution (see insert in Fig. 2), the rejuvenation upon the subsequent cooling, and the memory effect at further re-heating leading to the broad dip centered close to the aging temperature T_a. Quite similar behavior has been recently reported in disordered ferroelectric $KTa_{0.973}Nb_{0.027}O_3$.[4]

Figure 3 presents so-called double-aging and memory experiment: the cooling process was interrupted twice at the temperatures $T_{a1}=31.5$ K and $T_{a2}=29$ K for a time $t_{a1}=t_{a2}=50$ ks. For both temperatures the imaginary part ε'' decreases by the effect of aging. Upon a subsequent cooling one can see rejuvenation, whereas during reheating $[\varepsilon''_{ref}(T)-\varepsilon''(T)]/\varepsilon''_{ref}(T)$ shows a minimum which is clearly broader than that of the one-stop experiment. Two anomalies which are expected to occur due to the memory effect are not well separated in our case. The temperature

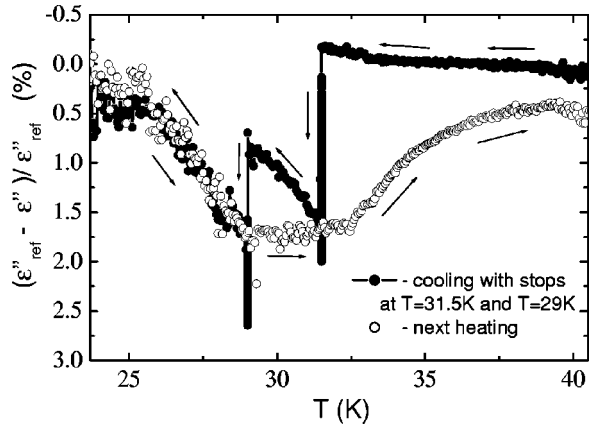

FIG. 3. Double-aging and memory experiment in methanol (73%)-clathrate. The dependence $e=[\varepsilon''_{ref}(T)-\varepsilon''(T)]/\varepsilon''_{ref}(T)$ vs the temperature is shown for cooling and heating runs. The cooling run was twice interrupted at the temperatures $T_{a1}=31.5$ K and $T_{a2}=29$ K for the time of about 50 ks in each case.

interval ($\Delta T=T_{a1}-T_{a2}=2.5$ K) is too small for that, and additionally, the aging and memory at the lower temperature T_{a2} are characterized by much weaker anomalies. Similar observation of the double-aging and memory effects was recently reported in Ref. 4 for $KTa_{0.973}Nb_{0.027}O_3$ crystals. By choosing a larger temperature interval between the aging temperatures (of about 5 K), the authors obtained here two well-separated dips corresponding to the memory effect.

IV. DISCUSSION

Since spin glasses, in contrast to structural glasses, have an order parameter, the Edwards-Anderson order parameter, it appears natural to interpret aging phenomena at low temperatures in terms of a slowly increasing domain length—indications for this have been found numerically in microscopic spin-glass models[22] as well as in recent experiments.[23] A simple domain growth, however, cannot explain the memory effect as evidenced in these multiple-temperature-stop experiments: in spin glasses domains at different temperatures have to be uncorrelated to some extent, in contrast to domains in a ferromagnet, for instance. This feature is often called *chaos* in reminiscence of the notion of a finite overlap length of *equilibrium* states in finite-dimensional spin glasses.[11] In addition to this temperature chaos in spin glasses to explain the memory effect the once-grown domains should also not be completely destroyed when the temperature is lowered but should retain one or several nuclei at least for times comparable to the aging time at lower temperatures—such an idea was put forward recently in Ref. 6.

Comparing the outcome of our experiments, in particular the two-temperature-stop experiments depicted in Fig. 3 with the corresponding experiments on the insulating spin glass $CdCr_{1.7}In_{0.3}S_4$,[5] shows that the aforementioned spin-glass features, including rejuvenation and memory, are still present but much less pronounced. An obvious difference is of course that $CdCr_{1.7}In_{0.3}S_4$ has a clear phase transition at a temperature $T_g=16.7$ K to a spin-glass phase at (and below) which any relaxation time of the system diverges and below which the multiple-temperature-stop experiments have been performed. On the other hand, no indication of a sharp transition can be found in our clathrate, although the relaxation time below 20 K already exceeds the experimental time scales accessible to us. Quite frequently aging properties of spin glasses at very low temperatures that do *not* have a phase transition at finite temperatures—like pseudo-two-dimensional materials or thin films[14]—resemble those of real spin glasses (i.e., those with a clear phase transition) in the frozen phase. It is usually assumed that one needs to have a spin-glass phase for chaos and memory effects to occur. According to what we know, the clathrate does not enter into a glassy state in the thermodynamic sense. Nevertheless, one expects glassy dynamics at low T: the dipoles can be modeled as classical spins. The interaction is long ranged and quasiantiferromagnetic within the triangular basal plane. The dipoles are arranged on a diluted lattice. This leads to a strong frustration of the interactions and hence to a large

number of metastable states. An extremely slow dynamics at low T is unavoidable. The interesting observation is that we find memory effects in spite of the absence of a spin-glass phase. Perhaps the clathrate resembles more the disordered dielectric $K_{1-x}Li_xTaO_3$: Here aging effects can be interpreted as a simple domain growth of varying speed and the system appears to be more closely related to a random field system rather than a spin glass. Certainly it would be worthwhile to scrutinize the details of the microscopic mechanism underlying the aging effects we presented in a more detailed form.

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