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Dynamic behavior of deuteron glass $Rb_{0.7}(ND_4)_{0.3}D_2AsO_4$

Keum Hwan Noh and Sook-Il Kwun
Department of Physics, Seoul National University, Seoul 151-742, Korea

Jong-Gul Yoon
Department of Physics, University of Suwon, Kyung-gi-do 445-743, Korea

Wolfgang Kleemann
Laboratorium für Angewandte Physik, Gerhard-Mercator-Universität Duisburg, D-47048 Duisburg, Germany

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Temporal relaxation of the field-induced remanent polarization has been investigated on the deuteron glass $Rb_{0.7}(ND_4)_{0.3}D_2AsO_4$ in the temperature range $10<T<30$ K. The data are approximately described by Curie–von Schweidler and Kohlrausch-Williams-Watts decay laws at high ($T>25$ K) and low temperatures ($T<20$ K), respectively. A nearly perfect description is, however, provided by the dynamically correlated domain model, which is based upon Chamberlin's concept of dynamical heterogeneity. On decreasing the temperature, the thermally activated dynamic behavior crosses over into nonactivated dynamics.
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Proton glass (PG) formation occurs in hydrogen bonded ferroelectric (FE) and antiferroelectric (AFE) mixed crystal systems at intermediate concentrations.[1] The location of protons in the hydrogen bonds is described by Ising-type pseudospins, which are subjected to competing FE and AFE interactions. In contrast with magnetic spin glasses (SG), randomly substituted cations create additional random-field interaction.[2] Deuterated proton glass [deuteron glass (DG)] systems show similar freezing behavior with an isotope effect of a relatively high freezing temperature. $Rb_{1-x}(ND_4)_xD_2AsO_4$ (DRADA) is one of the prototype DG systems, the parent compounds of which are RbD_2AsO_4 (DRDA) with a FE transition temperature of $T_C=173$ K and $ND_4D_2AsO_4$ (DADA) with an AFE transition temperature of $T_N=304$ K. Frustrated FE and AFE interactions induce a DG state in DRADA for concentrations of $0.2<x<0.5$ at low temperatures.

Although there have been many dielectric susceptibility measurements for the dynamic behaviors of DG systems, the relaxation of the remanent polarization has never been studied. In SG, the remanent magnetization decay has been described by either the Kohlrausch-Williams-Watts (KWW) stretched exponential[3] $\phi(t)=\phi_0\exp[-(t/\tau)^{\beta}]$, the Curie–von Schweidler (CvS) power law[4] $\phi(t)=\phi_0(t/\tau)^{-\alpha}$, or by combinations of both.[5] These empirical nonexponential descriptions involve the characteristic relaxation times τ and the exponents $0<\beta<1$ or $0<\alpha<2$, respectively. A preliminary study[6] of DRADA showed that the remanent polarization (P_R) relaxation follows approximately a KWW law at low T, whereas a CvS-like relaxation occurs at high T. Significant deviations occur, however, at intermediate temperatures so that the data can be fitted neither to a KWW nor to a CvS law.

Recently,[7] a dynamically correlated domain (DCD) model has been proposed, which turns out to cover both types of relaxation. It is based on the assumption that a macroscopic sample consists of a very large number of independently relaxing regions (DCDs), each of which relaxes exponentially with a locally uniform single relaxation time. The superposition of the relaxation processes of all DCDs results in the observed polydispersivity of the sample. Whether or not the relaxation is thermally activated, a CvS-type power law or a

KWW-type stretched exponential law can describe the system. Furthermore it is expected that systems exhibiting CvS-like behavior generally have a subsequent regime of KWW-like behavior after completing the primary barrier crossing.[7] A wide range of slowly relaxing materials such as random magnets,[8] glass forming liquids,[9] and nanodomain relaxors[10–12] have been successfully described within the framework of the DCD model irrespective of their microscopic relaxation nature. Recently the crossover between CvS-like behavior and KWW-like behavior has been reported on the relaxation of $K_{1-x}Li_xTaO_3$ (KTL), $Sr_{1-x}Ca_xTiO_3$ (SCT), and $PbMg_{1/3}Nb_{2/3}O_3$ (PMN) with the variation of temperature.[10–12]

The purpose of this work is to clarify the dynamic function describing the slow relaxation of the DG system and to make a connection with the general relaxation mechanisms by adapting the DCD model to the DRADA system with $x=0.3$. It is also intended to investigate the crossover dynamic behavior expected by Chamberlin.[7]

Mixed crystals of DRADA with $x=0.3$ were grown by slow evaporation from a deuterated mixed solution. A specimen with silver electrodes on the surfaces normal to the a axis was prepared with a dimension of $5\times5\times0.5$ mm^3. The complex dielectric constants ϵ' and ϵ'' were measured by two different methods. At the frequencies between 10^4 and 10^7 Hz, a conventional LCR meter (HP4275A) was used. At the low frequencies between 1 and 10^3 Hz, a Sawyer-Tower bridge with a standard capacitor (100 nF) was employed and the signal was detected by SRS830 digital lockin amplifier. Polarization data were obtained with a Keithley 617 electrometer. After zero-field cooling (ZFC), zero-field cooled polarization (P_{ZFC}) was observed on field heating (FH) with a bias field of 2 kV/cm at a heating rate of 3 K/min . Field cooled polarization (P_{FC}) and the remanence P_R were obtained in the course of field cooling (FC) and subsequent zero-field heating (ZFH) procedures, respectively.

For the measurements of the isothermal relaxation of polarization, the sample was cooled down from 50 K to the measuring temperature (T_m) under the electric bias field. Typically 150–200 sec was needed to reach the thermal stabilization at T_m. A waiting time of 300 sec was counted from the instant when the temperature crossed $T_f\approx40$K, where the FC and ZFC polarization curves split apart (refer to Fig. 3), to the instant of removing the bias field at T_m. Upon removing the field, the temporal relaxation of P_R was measured. After the measurement, the sample was heated to 50 K in order to remove the remaining remanence and to establish the baseline.

The complex dielectric constants as a function of temperature and frequency are shown in Figs. 1 and 2, respectively. As the temperature decreases, the distribution of relaxation time becomes broader and the frequency of maximum $\epsilon''(\omega)$, ω_p, shifts to lower frequencies showing a freezing behavior of the frustrated deuteron glass. Below 30 K, it is difficult to investigate the slow relaxation from the susceptibility measurements because ω_p becomes lower than 1 Hz. However, it is inferred that the relaxation time distribution at low temperatures extends over 10^4 sec from the extrapolation of the temperature dependence of $\epsilon''(\omega)$.

Figure 3 shows the polarization after various electrical histories: ZFC and subsequent FH, FC, and final ZFH in the temperature range $10<T<50$ K. Whereas P_{FC} decreases slightly upon decreasing T, P_{ZFC} decays to zero since the dipole moments freeze into the random field direction. P_R is observed up to 40 K, which is one of the characteristics of the frozen glass state.[13]

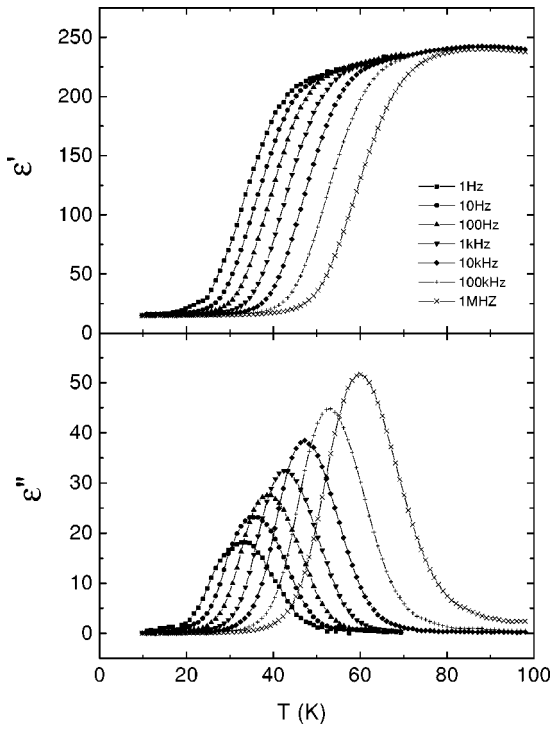

FIG. 1. Temperature dependence of the complex dielectric constants ϵ' and ϵ'' of DRADA with $x=0.3$ along the a axis.

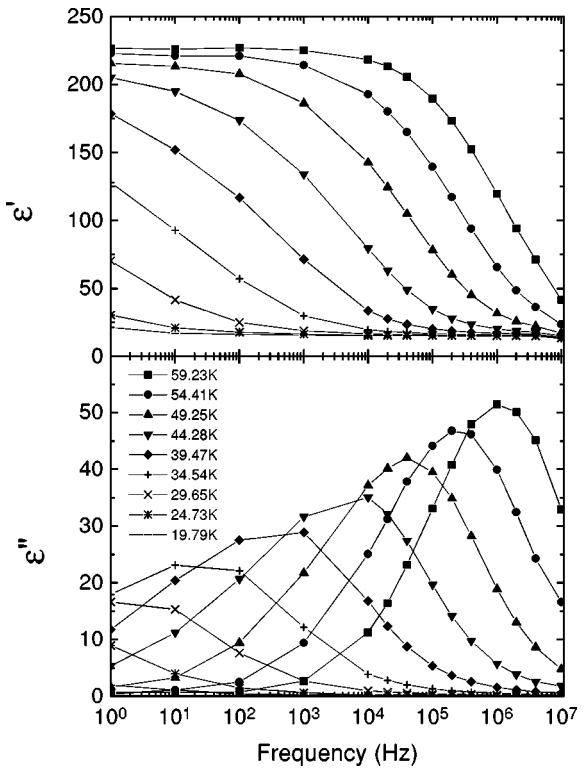

FIG. 2. Frequency dependence of the complex dielectric constants ϵ' and ϵ'' of DRADA with $x=0.3$ along the a axis.

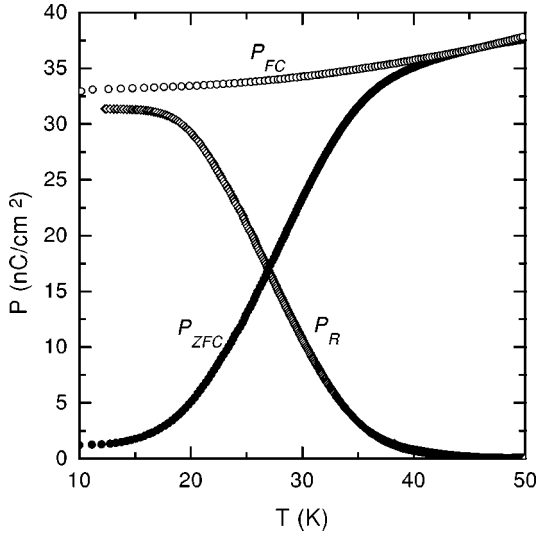

FIG. 3. Temperature dependence of the field cooled (P_{FC}), zero-field cooled (P_{ZFC}), and remanent polarization (P_R) of DRADA with $x=0.3$ along the a axis. The applied electric field was 2 kV/cm and the heating/cooling rate was 3 K/min.

Figure 4 shows the temporal relaxation of P_R measured in the temperature range $10<T<30$ K in DRADA with $x=0.3$. The experimental time domain lies within the relaxation time distribution inferred from $\epsilon''(\omega)$ data. Upon removing the field, slow relaxation following a rapid drop occurs. At lower temperatures, a much slower relaxation is observed. The best fittings of the data with the DCD function

$$P(t)=P_0\int_0^\infty dx[xn(x)]\exp\{-tw_\infty\exp[-C/x]\} \qquad (1)$$

are represented by the solid lines, where w_∞ is the relaxation rate of very large DCDs and C the correlation coefficient. The initial amplitude $P(0)$ is proportional to the amplitude prefactor P_0. The sign of the correlation coefficient determines the universality class. The CvS-like relaxation ($C>0$) requires thermal barrier activation and the KWW-like behavior ($C<0$) describes the relaxation between states with adjacent energy levels in multileveled DCDs. The fitting results with the DCD function are much more successful than the usual fits with single function KWW or CvS.[6] Moreover, in contrast with the KWW or CvS law, the DCD model gives excellent results in the whole temperature range.

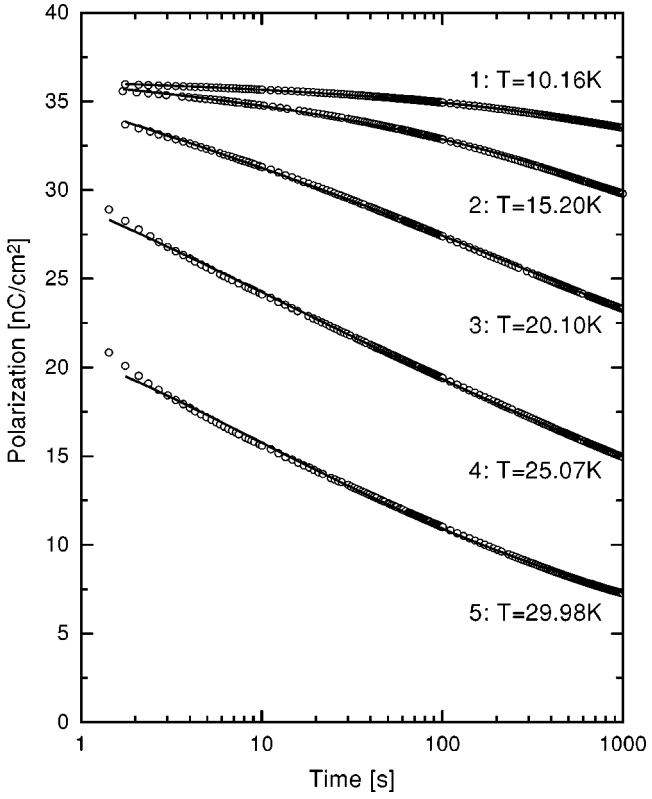

FIG. 4. Temporal relaxation of the remanent polarization (P_R) of DRADA with $x=0.3$ measured at temperatures $10<T<30$ K after switching an electric field $E=2$ kV/cm off at $t=0$. The solid lines are the best fitting results by the DCD model with Gaussian distribution and the parameters listed in Table I.

In the fitting procedures, two kinds of size distribution functions $n(x)$ were tested: the Gaussian distribution $n(x)=\exp[-(x-<x>)^2]$, which describes near equilibrium fluctuations, and Poisson statistics $n(x)=x^{1/9}\exp[-x^{2/3}]$, which is appropriate for random systems with percolative properties in three dimensions. The latter form was found to be successful in the random magnetic system Au:Fe.[8] On the other hand, glass forming liquids seem to obey a Gaussian size distribution.[9] The best-fitting parameters and the statistical errors (χ^2) at various temperatures are summarized in Table I for the two size distribution functions. The Gaussian distribution gives a more satisfactory result than the percolation distribution. The Gaussian distribution seems to be reasonable for the solid solution DRADA which is subject to a normal statistical distribution of RDA and ADA.

The most distinctive result is that the sign of the correlation coefficient C changes between 20.10 and 25.07 K. The relaxation at $T\leqslant 20.10$ K belongs to KWW-like universality ($C<0$), whereas the relaxation at $T>20.10$ K obeys CvS-like universality ($C>0$). These results imply the existence of crossover relaxation behavior in the DRADA system with $x=0.3$. In this crossover temperature region, all the fitting parameters show abrupt changes. The large absolute values of the correlation coefficients ($C=61.0$ at 25.07 K and -41.2 at 20.10 K) indicate extreme polydispersivity and sluggishness. The relaxation rate (w_∞) also exhibits an abrupt change; $\ln(w_\infty/\mathrm{Hz})=19.5$ changes to -36.7. This result shows that the polydispersivity can result in slow relaxation behavior, although the relaxation rate of large DCDs is either much slower or much faster than the average observed relaxation. The initial amplitude $P(0)$ can be obtained by using the fitting parameter. Numerical values of $P(0)$ are presented in Table I rather than the values of the fitting parameter P_0. Values of $P(0)$ are comparable with the field cooled polarization (P_{FC}) at all temperatures except at 20.10 K. The unreasonably large value of $P(0)=62.8$ nC/cm^2 at 20.10 K hints at some failure of the KWW relaxation ($C<0$) in the limit $t\rightarrow 0$ in the crossover region. Obviously the initial stage of the relaxation at 20.10 K is affected by thermally activated relaxation ($C>0$). Very probably this is also the reason for the extreme values of C encountered in this temperature region. They are unphysical compromises determined by the fitting procedure, which involves only one set of parameters despite the occurrence of temporal crossover.

TABLE I. The best fitting parameters of the polarization relaxation data in Fig. 4 by the DCD model using two alternative distribution functions.

	Gaussian					Percolation			
T/K	$\ln(w_\infty/\mathrm{Hz})$	C	$\langle x\rangle$	$P(0)(\mathrm{nC/cm^2})$	$10^3\chi^2$	$\ln(w_\infty/\mathrm{Hz})$	C	$P(0)(\mathrm{nC/cm^2})$	$10^3\chi^2$
10.16	−20.1	−13.0	1.60	36.6	0.24	−14.3	−8.5	37.2	0.34
15.20	−19.0	−9.7	0.74	39.1	2.1	−17.3	−28.2	42.4	9.1
20.10	−36.7	−41.2	0.70	62.8	2.3	−24.1	−117.8	72.4	2.5
25.07	19.5	61.0	2.17	35.2	6.2	1.4	42.9	29.6	25
29.98	9.8	29.6	1.78	23.6	11	0.14	25.9	20.7	53

The above results show that the relaxation of DRADA with $x=0.3$ agrees well with the DCD model. Since DCD model is a mesoscopic view of the universal relaxation, it does not provide insight into the slow relaxation process of the DG from the microscopic point of view. Within the framework of the DCD model it is suggested that the primary response of the sample in the time scale $1<t<1000$ sec may occur from the response of domainlike clusters, the size distribution of which obeys Gaussian statistics, instead of individual dipoles. The physical origin of such DCDs in DG might be due to the quenched random-fields, which are of paramount importance in proton glasses.[2] On the one hand, they enhance polydispersivity.[14] On the other hand, they imply mesoscopic correlations which are at the origin of local cluster formation as verified, e.g., in the dipole glass KTL.[10]

The crossover temperature range from CvS- to KWW-type behavior, $20<T<25$ K, lies far below the conventional freezing temperature as defined by the limit of ergodicity $T_f\approx 40$ K, where the FC and ZFC polarization curves split apart (Fig. 3). This is in contrast with the behavior of relaxor ferroelectrics such as SCT (Ref. 11) and PMN (Ref. 12), where the crossover occurs at the (smeared) phase transition from mobile to pinned nanodomain states. According to Chamberlin[15] the crossover signifies the change of the free energy landscape of the system from an early-stage multivalley scenario to a late-stage nearly flat situation. Obviously in a DG the flattening of the free energy landscape reaches the late-stage situation far below T_f.

About the dynamics of PG and DG, recently several explicit response functions have been suggested. Pirc *et al.*[16] have reported that the dynamic response of deuteron glass $Rb_{1-x}(ND_4)_xD_2PO_4$ (DRADP) can be described by symmetry adapted random bond random field (SARBRF) model which predicts the CvS-like scaling form in susceptibility loss spectrum: $\chi''(\omega)=A\omega^\sigma$. On the other hand, Sinitski and Schmidt[17] have calculated the polarization relaxation by a computer simulation, which shows a KWW-like response or a logarithmic Gaussian form $P=P_i\exp[-\ln^2(1+t/\tau)]$ at low T. It should be stressed, however, that according to our data the relaxation function of DG is not limited by a single empirical function such as KWW or CvS. It clearly varies with temperature and, hence, needs the more general universal DCD function, Eq. (1), covering both types of relaxation.

In conclusion, the temporal relaxation of P_R in deuteron glass DRADA with $x=0.3$ is well described by the recently proposed dynamically correlated domain (DCD) model at all temperatures. It shows crossover from the KWW-like behavior ($C<0$) at $T\leqslant 20.10$ K to CvS-like decay ($C>0$) at $T>20.10$ K. These results are similar to the relaxation behavior of relaxors such as SCT, KTL, and PMN and consistent with the expectations of Chamberlin's DCD model. Further research will be necessary in order to clarify the very existence of independently relaxing domainlike regions in DG systems such as DRADA.

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