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Scaling dielectric data on $Rb_{1-x}(NH_4)_xH_2PO_4$ structural glasses and their deuterated isomorphs

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Temperature- (T) and frequency- (ν) dependent dielectric losses on $Rb_{1-x}(NH_4)_xH_2PO_4$ single crystals (RADP), and their deuterated isomorphs (D-RADP), can be collapsed to single curves with a scaling variable $E(T,\nu)$. This applies for T sufficiently high that equilibrium is established within the sample-thermalization time. If $E(T,\nu)$ follows the Vogel-Fulcher law, the scaling will depend only on the freezing temperature T_0 and on the attempt frequency ν_0. For RADP, values in excellent agreement with a study covering a very broad frequency range are thus obtained, while significantly different values apply to D-RADP.

Mixed crystals of $Rb_{1-x}(NH_4)_xH_2PO_4$ (RADP) at room temperature have the acid-proton disorder characteristic of the KH_2PO_4 (KDP) family. For intermediate concentrations x, on lowering the temperature T the disorder freezes into a glass,[1,2] which is in many ways a structural analog of spin glasses. For $x=0.35$, the electric susceptibility $\chi(\omega,T)$ has been measured with various techniques covering over 16 orders of magnitude in frequency ω.[3] It is well described by an integral of a Debye relaxator over a distribution $g(\tau,T)$ of relaxation times τ which is broad in $\ln\tau$, just as for spin glasses,[4]

$$\chi(\omega,T)=\chi_0(T)\int_0^\infty \frac{g(\tau,T)}{1-i\omega\tau}d(\ln\tau) \quad , \tag{1}$$

with the normalization $\int_0^\infty g(\tau,T)d(\ln\tau)=1$. In a recent Letter,[5] I showed that the dielectric loss data could be collapsed to a single curve, using instead of τ a related energy variable $E(T,\nu)$. The latter was defined by

$$\nu=\nu_0\exp[-E/(T-T_0)] \quad , \tag{2}$$

a transformation suggested by the Vogel-Fulcher law.[6] Here $\nu=1/2\pi\tau$, and ν_0 is an attempt frequency measurable by Raman scattering.[3,7] This law was found to apply to RADP over a remarkable range of relaxation frequencies.[3] Although several proposals have been made to justify it theoretically,[8] its use in the present case has been empirical so far. Using (2), the energy distribution $f(E)$ derived from $g(\tau,T)$ is experimentally found to be independent of T,[5] and it is thus the scaling function.

In performing that scaling in Ref. 5, seven fitting parameters were used and it was implicitly assumed that data collapsing could be performed over the full range of T. It is, however, likely that, even if $f(E)$ remained constant in T down to T_0, the resulting relaxation-time distribution would not reach its equilibrium value $g(\tau,T)$ as soon as the longest time in g become of the order of the sample-equilibrium time or "laboratory time" τ_l. That field-cooled (and thus also zero-field-cooled) states are not necessarily the equilibrium states is indeed known for spin glasses.[9] This long-time metastability occurs at a temperature T_l below which equilibrium scaling is not expected to apply. In this Communication, it is shown that if the scaling is limited to temperatures above T_l, it can be performed with only two adjustable parameters, T_0 and ν_0, giving values in agreement with those derived from the investigations extending over about 17 orders of magnitude in ν.[3] New dielectric results are also presented for the first time for a fully deuterated sample showing that also in that case the same scaling procedure is rather successful, but with a scaling function $f(E)$ and a Vogel-Fulcher T_0 that are significantly modified. Finally, it is emphasized that dielectric data alone, because of the restricted frequency range, are not able to determine the functional form of $E(T,\nu)$, and other forms are given that also collapse the D-RADP data quite well.

Let us first rescale the $\epsilon_c''(\omega,T)$ data of Ref. 5. From Eq. (1), the imaginary part of the dielectric constant is

$$\epsilon''(\omega,T)=\chi_0(T)\int_0^\infty g(\tau,T)\frac{d(\omega\tau)}{1+\omega^2\tau^2} \quad . \tag{3}$$

For $g(\tau,T)$ broad in $\ln\tau$, the important contribution to the integral comes only from the region $\omega\tau\simeq 1$.[4] This is easily seen with the change of variable $x=\ln(\omega\tau)$, which gives a factor $(\mathrm{sech}x)/2$ in the integrand. This is a relatively narrow peak of area $\pi/2$ located at $x=0$. Approximating the sech by a δ function, one obtains

$$\epsilon''(\omega,T)\cong\frac{\pi}{2}\chi_0(T)g\left(\frac{1}{\omega},T\right) \quad . \tag{4}$$

In the following, it will be assumed that the rounding effects of the integration in (3) can be neglected and that (4) is exact. From $g(\tau,T)d(\ln\tau)=f(E)dE$, and using the Vogel-Fulcher ansatz (2), one obtains $g(\tau,T)=(T-T_0)\times f(E)$. Replacing this relation in (4), the scaling equation becomes

$$\epsilon''(\omega,T)=\frac{\pi}{2}(T-T_0)\chi_0(T)f((T-T_0)\ln(\nu_0/\nu)) \quad , \tag{5}$$

where $\nu=\omega/2\pi$. In this case, the scaling only depends on ν_0, T_0, and the very-low-frequency electric susceptibility $\chi_0(T)$.

For RADP ($x=0.35$), the real part of the dielectric constant $\epsilon_c'(\omega,T)$ reaches a maximum near 30 K (Fig. 1 of Ref. 1). That maximum becomes progressively broader, the lower the frequency [Fig. 1(a) of Ref. 5]. Hence, one expects $\chi_0(T)$ to be practically constant in the narrow temperature region of interest for scaling the $\epsilon_c''(\omega,T)$ data of Fig. 1(b) in Ref. 5. This is supported by the practically constant value obtained for the field-cooled electrooptic coefficient r_{63} between 30 and 15 K.[1] To obtain χ_0, one must

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subtract from the maximum of $\epsilon_c'(\omega,T)$ ($\simeq 146$) a constant corresponding to the background lattice contribution which gives no losses. From the Curie-Weiss fit to the high-temperature data,[1] this constant is approximately 8. The scaling is then made with $\chi_0 = 138$. For $x = 0.35$, one already has excellent values for $T \cong 8.74$ K and $\ln\nu_0 \cong 28.9$, where ν_0 is in Hz.[3] With the range of E in $f(E)$ extending up to ~ 300 K, using (2) one calculates $T_l \simeq 16$ K for $\tau_l = 1$ h. Hence, only the high-temperature part of the data is scaled, down to the points at $T = 15.6$ K. This is done with a nonlinear least-squares routine with variables $\ln\nu_0$ and T_0. Using (5), $f(E)$ is calculated from data at one particular frequency where it is well determined, here 1064 Hz. With $f(E)$, one obtains the deviations between the values measured at other frequencies and those calculated using (5). The mean-square deviations are minimized, for a total of 95 points (17 temperatures at five frequency values) in this case. One finds $\ln\nu_0 = 29.5 \pm 1.0$ and $T_0 = 8.58 \pm 1.0$ K in perfect agreement with Ref. 3. The uncertainties correspond to the 90% confidence interval.

The scaled $\epsilon_c''(\omega,T)$ data, with f calculated from (5) and $E = (T - T_0)\ln(\nu_0/\nu)$, where T_0 and ν_0 are the best-fit values, are shown in Fig. 1. One sees that the scaling is generally excellent down to the set of points at 15.6 K, which have too high losses at low frequencies. Departures from scaling occur earlier, the lower the frequency, and increase on further cooling as illustrated for the sets of points at 14.7 and 13.7 K, also shown in Fig. 1, but not included in the fit. This can be understood if below T_l the distribution of relaxations does not reach its equilibrium value imposed by $f(E)$. It will be the case if the development of long relaxation times requires a transient of similar duration. Such behavior can be expected for several spin-glass models, for example, for the one proposed by Hertz.[8] In that case, on lowering the temperature, freezing progresses from localized modes of short relaxation times to more extended modes of longer relaxation times, requiring the "melting" of the former. Thus a metastable "pileup" at intermediate times around τ_l should occur. This explains qualitatively the derivations observed below 15.6 K, and the fact that those are stronger the lower the frequency.

Finally, one should note that provided the χ_0 were properly selected, the $f(E)$ curve (Fig. 1) should automatically be normalized to 1. The area under the curve formed by the experimental points extrapolated by the dashed-dotted line is too large ($\simeq 1.26$). This suggests that there should exist a low-energy cutoff in $f(E)$, centered around 60 K in this case, as illustrated by the dahsed line, which is just an example of what $f(E)$ might look like.

Dielectric measurements were performed on a- and c-cut platelets of D-RADP with $x = 0.62$. The data for an a-cut platelet of 23.16 mm^2 area and 0.575 mm thickness are reported here in detail. Results on c cuts are qualitatively extremely similar. However, on the antiferroelectric side, the dielectric constant ϵ_a is larger than ϵ_c at all temperatures. Furthermore, large sample areas are easier to obtain and disturbing piezoelectric resonances occur at higher frequencies in a cuts than in c cuts, so that a higher precision and a larger frequency range can be achieved with an a cut. The deuterated samples used in this study were grown from D_2O solutions by means of a temperature-difference procedure ensuring constant supersaturation and bath composition.[10] A large crystal from the same batch was used for coherent neutron-scattering investigations,[11] confirming that the deuteration of both ammoniums and acid bonds is better than 99%, as already indicated by an NMR proton titration.[12] Figure 2 illustrates the dispersion in ϵ_a' over the full T range. The nondispersive limit of the data in the range 70 to 110 K is well approximated by $\epsilon_a' = a - bT^3$, a very slowly varying function used to estimate χ_0 as shown in the figure. The scaling is not sensitive to the precise choice of χ_0, which alternatively can be taken as constant below 70 K. The detail of the dispersion region is shown in Fig. 3. Similar curves are obtained below 300 Hz, but with insufficient precision, and above 3 MHz, where they are seriously perturbed by resonances.

In this case, $T_l \simeq 56$ K, so that the data between 56 and 110 K were scaled using the Vogel-Fulcher ansatz (5) with the procedure described above for the protonated sample. Here, $f(E)$ was calculated from the 3-MHz data, the corresponding losses being mostly above T_l. This gives $\ln\nu_0 = 28.5 \pm 0.25$ and $T_0 = 30.3 \pm 0.7$ K, and the $f(E)$ shown in Fig. 4(a). The data collapsing is not perfect near the maximum of f, suggesting that the distribution of barriers might still have some weak T dependence. It should

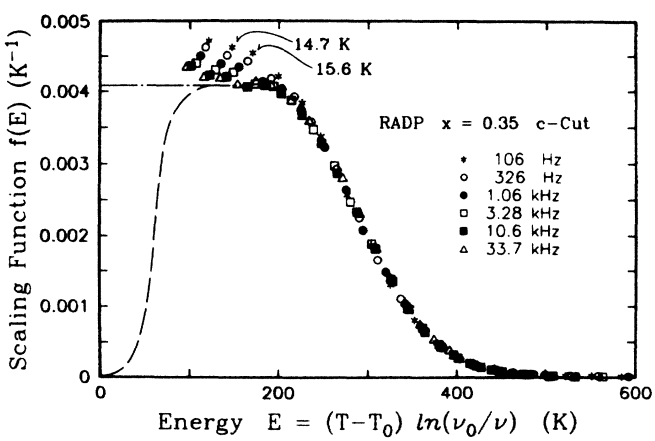

FIG. 1. The scaling function $f(E)$ for a protonated crystal using the Vogel-Fulcher law (2).

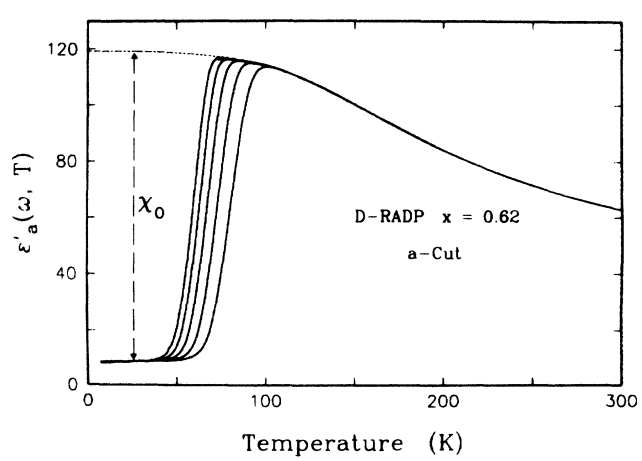

FIG. 2. The real part of ϵ_a for a fully deuterated crystal at frequencies from 300 Hz to 3 MHz increasing in powers of ten from left to right. The dashed line is the extrapolation of the high-temperature data used to estimate $\chi_0(T)$ as shown.

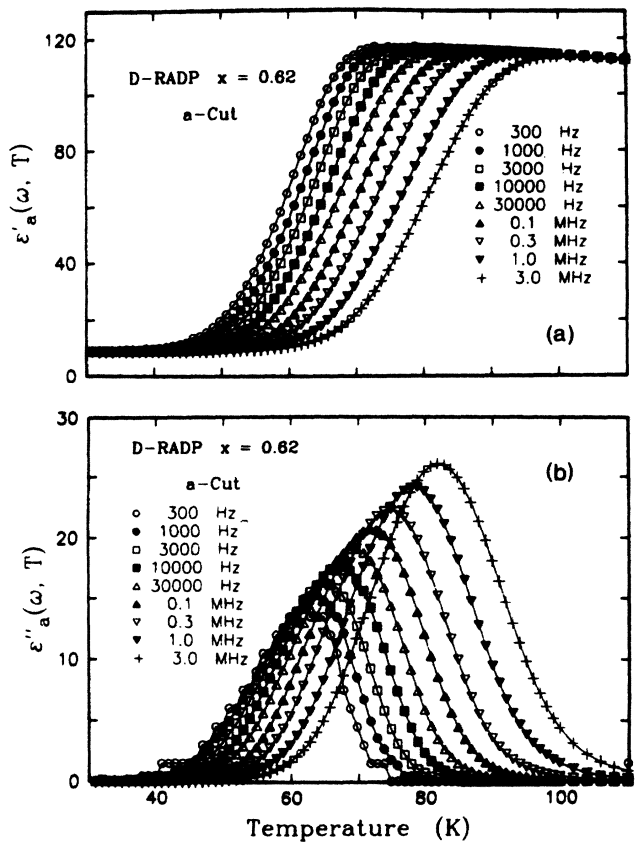

FIG. 3. The real and imaginary parts of the dielectric constant for the fully deuterated sample in the region of strong dispersion.

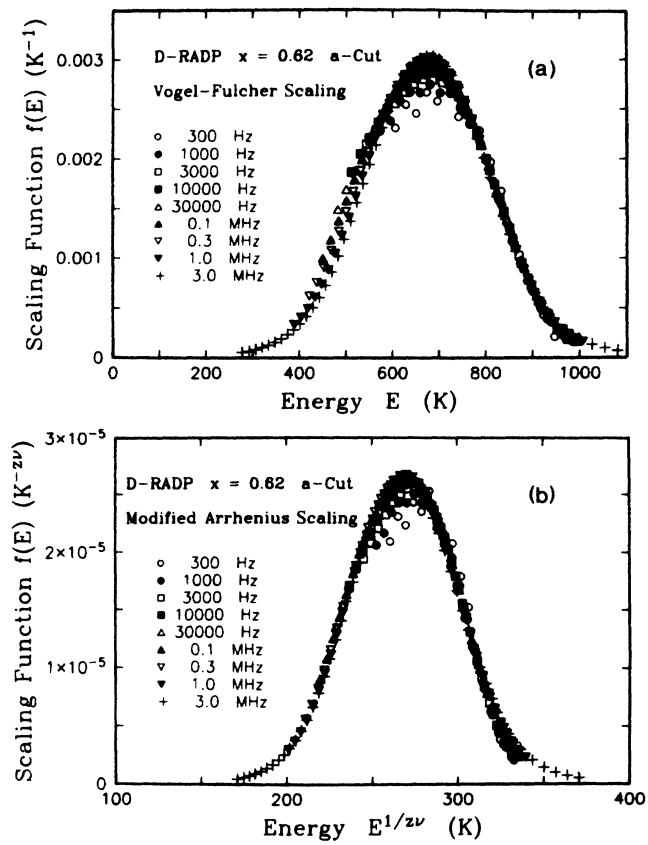

FIG. 4. Scaling functions for a deuterated crystal using (a) the Vogel-Fulcher law (2), and (b) the modified Arrhenius law.

be noted that in D-RADP, as opposed to RADP, the ammonium dynamics might still play some role at the temperatures where the scaling is performed.

With $f(E)$ extending up to ~ 1000 K, one verifies that T_l has indeed the value indicated for $\tau_l = 1$ h. In the present case, $f(E)$ is properly normalized within the uncertainty on χ_0. Comparing Figs. 1 and 4(a), one sees that the distribution of barriers is shifted towards much higher energies in the deuterated case. Similarly, T_0 is much higher. That the dispersion region moves to higher temperatures with deuteration was already observed for a 72% deuterated sample with $x = 0.48$.[13] Whether the same scaling can apply for samples with incomplete deuteration remains an open question.

It should be noted that the main result obtained here is that the ϵ'' data can be scaled in terms of a function $f(E)$. As the Vogel-Fulcher ansatz does not rest on solid theoretical ground, Eqs. (2) and (4) represent just one of many possible functional forms. With dielectric data extending only over four orders of magnitude in frequency, unfortunately it is not possible to establish uniquely the functional form of $E(T,\nu)$ as will be shown presently. One can, for example, use the modified Arrhenius law[14] $\nu = \nu_0 \times \exp(-E/T^{z\nu})$, where $E^{1/z\nu}$ is a temperature. This gives

$$\epsilon''(\omega,T) = \frac{\pi}{2} T^{z\nu} \chi_0 f\left(T^{z\nu} \ln(\nu_0/\nu)\right) . \tag{6}$$

With the same number of data points used previously, the satisfactory scaling of Fig. 4(b) is obtained, with $z\nu = 1.98 \pm 0.04$ and $\ln\nu_0 = 26.0 \pm 0.25$. As already noted for the protonated case,[3] the modified Arrhenius law has the tendency to give low values for ν_0, low-energy barriers, and an exponent $z\nu$ which is only ~ 2 while it should be ~ 4 for the wall-nucleation theory.[14] Note that systematic deviations near the peak of $f(E)$ remain. Alternatively, one can use the law $\nu = \nu_0 \exp[-E/(T-T_0)^{z\nu}]$. With one additional free parameter, the deviations are improved. One obtains $z\nu = 1.45 \pm 0.09$, $\ln\nu_0 = 26.7 \pm 0.3$, and $T_0 = 17.1 \pm 2.6$ K, but the difficulties near the peak of $f(E)$ also remain. This confirms that only an investigation over a very large frequency range can possibly give indications as to the most appropriate functional form of the scaling variable E. This is what was done for RADP,[3] with the result that the Vogel-Fulcher ansatz is the most successful one describing broad T and ν ranges in that case.

In closing, the distinction between our scaling approach and a "parametrization" of the ϵ'' data, as recently performed for K(Br,CN),[15] must be emphasized. The latter assumes Arrhenius dynamics and a given functional form for the distribution of activation energies for which *T-dependent* parameters are found. The former does not imply a particular form [as exemplified by the difference between Figs. 1 and 4(a)], but makes the physical assumption of a universal behavior, provided temperatures and times are properly scaled. *T-independent* constants describing $E(T,\nu)$ are then derived. Inasmuch as the scaling function is almost Gaussian in Fig. 4(a), the parametrization of Ref. 15 can be ap-

plied successfully to the data of Fig. 3. One then finds a T-dependent Gaussian width whose inverse extrapolates linearly to zero near $T_0 \sim 30$ K. The fact that $T_0 \sim 0$ K for *dielectric* measurements on K(Br,CN) might be compatible with *quadrupolar* freezing with $T_0 \neq 0$, as already pointed out.[2] Finally, the form under the exponential in (2) can alternately be interpreted as $(1/T)[ET/(T-T_0)]$, implying Arrhenius activation over a distribution of barriers which all diverge as $T \rightarrow T_0$, very much in keeping with recent views on mean-field spin glasses.[16]

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