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Dielectric measurements of the proton-glass state in $Rb_{0.65}(NH_4)_{0.35}H_2AsO_4$

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Dielectric measurements of the $Rb_{1-x}(NH_4)_xH_2AsO_4$ ($x=0.35$) mixed crystals in the a and c tetragonal directions in the temperature range from 3 to 300 K are reported. Below T_g a dielectric dispersion of $\epsilon'(T)$ and $\epsilon''(T)$ in the applied frequency range from 1 Hz to 30 kHz was observed. A small anisotropy of the proton-glass transition temperature T_g was detected, but we did not find the large anisotropy reported by J. Kim, N. Kim, and K. Lee [J. Phys. C **21**, L663 (1988)].

The proton-glass state in the mixed crystals $Rb_{1-x}(NH_4)_xH_2PO_4$ (RADP-100x) was discovered by Courtens in 1982.[1] Since that time many experimental and theoretical results were found, but only a few[2–8] for $Rb_{1-x}(NH_4)_xH_2AsO_4$ (RADA-100x). Microwave dielectric measurements[6] in RADA show an asymmetric phase diagram. The proton-glass state for this system exists in the concentration range $0.1<x<0.5$. Recently, Kim, Kim, and Lee[8] reported dielectric data for mixed $Rb_{1-x}(NH_4)_xH_2AsO_4$ where $x=0.35$ (RADA-35).

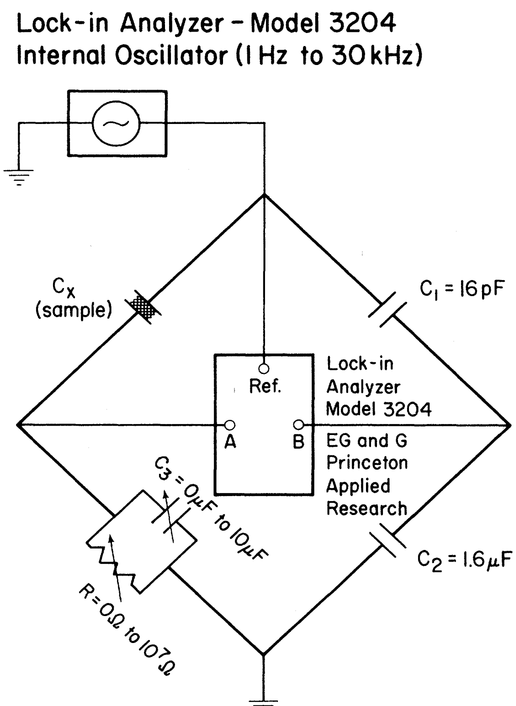

FIG. 1. Bridge circuit for measuring complex dielectric permittivity in the frequency range from 1 Hz to 30 kHz.

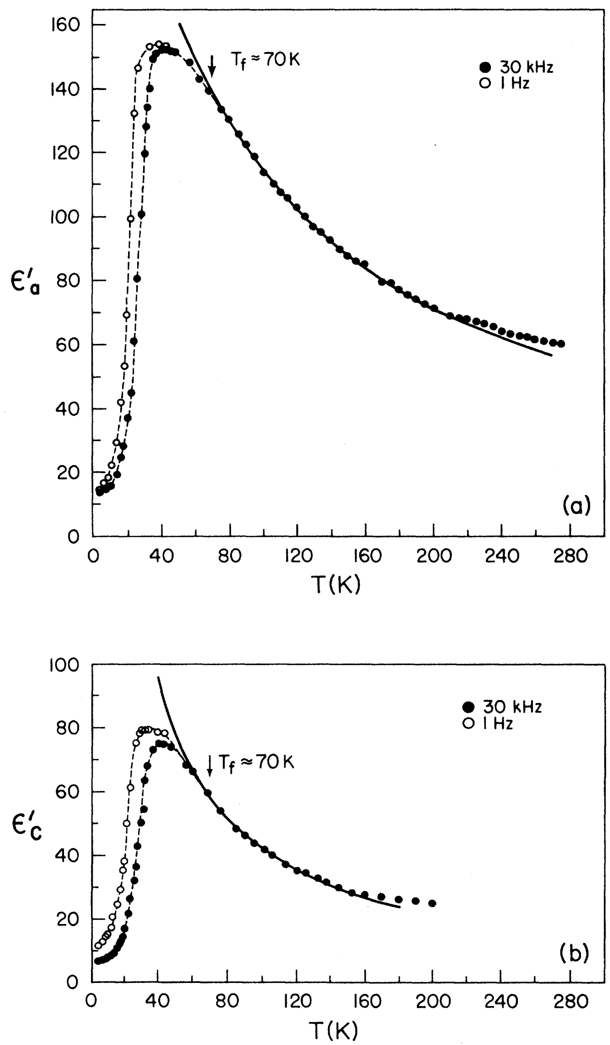

FIG. 2. Temperature dependence of the dielectric permittivity in RADA-35: (a) ϵ'_a; (b) ϵ'_c. Solid lines show Curie-Weiss fits.

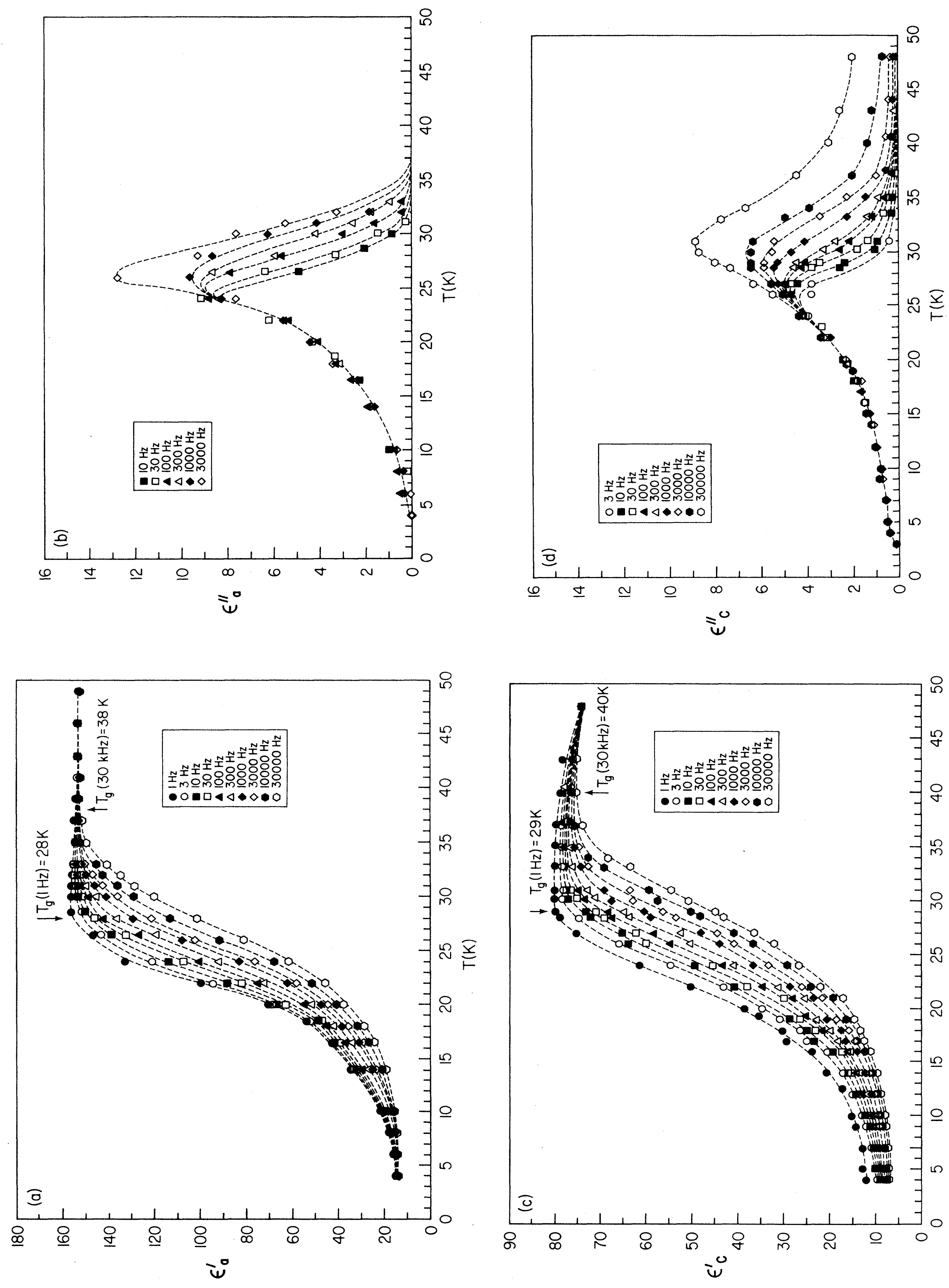

FIG. 3. Dielectric dispersion in the proton-glass regime in RADA-35: (a) $\epsilon'_a(T)$; (b) $\epsilon''_a(T)$; (c) $\epsilon'_c(T)$; (d) $\epsilon''_c(T)$. The dashed lines are guides for the eye.

These results are suprising, because in measurements made down to 20 K they did not observe onset of proton-glass behavior in the a direction, while in the c direction this onset was seen at 42 K. To solve this puzzle we measured dielectric properties in this crystal (RADA-35) in the temperature and frequency range from 3 to 300 K and 1 Hz to 30 kHz, respectively.

The mixed crystals RADA-35 were obtained by slow evaporation of an aqueous solution of RbH_2AsO_4 (RDA) and $NH_4H_2AsO_4$ (ADA) mixed in the proper molar ratios. Small platelets of $2.5\times7.7\times0.9$ mm^3 and $3\times2.4\times0.7$ mm^3 perpendicular to the a and c tetragonal directions, respectively, were cut from a single RADA-35 crystal. After polishing, conducting silver paint electrodes were applied. The complex dielectric constant was measured using the bridge circuit shown in Fig. 1, working from 1 Hz to 30 kHz. The sample holder was inserted into an Oxford Instrument model ESR-900 continuous-flow cryostat. Experiments were performed between 3 and 300 K. The sample's temperature was measured by a calibrated Chromel-Alumel type-K thermocouple.

Figure 2 shows the temperature dependence of the dielectric permittivities $\epsilon_a'(T)$ and $\epsilon_c'(T)$ in the heating part of the temperature cycle. We detected the onset of proton-glass behavior in both the a and c directions. As can be seen from Fig. 2, the Curie-Weiss law is well obeyed down to the onset of freezing temperature, introduced by Courtens[1] and defined as an inflection point of ϵ' where the Edwards-Anderson order parameter q_{EA} starts to increase upon cooling.[9] This temperature T_f is equal to 70 K for both ϵ_a' and ϵ_c'. From the expression[10] for dc permittivity,

$$\epsilon_{idc}=C_i(1-q)/[T-T_{0i}(1-q)] \, ,$$

in which q is the bias order parameter[11] and T_{0i} is the Curie-Weiss temperature, we expected these T_f values to be close together because the same q is applicable for both $i=a$ and $i=c$ (a and c axis permittivities). The reciprocal of ϵ_c' locates the Curie-Weiss temperature T_0 at -7 K. For the a direction, the Curie-Weiss temperature is lower and equal to -69 K. The Curie-Weiss constant C is equal to 4512 and 19 320 K and the c and a directions, respectively. Dielectric dispersion below the glass transition temperature T_g is shown in Fig. 3. The temperature T_g at which ϵ' starts to decrease is a function of frequency. For the c direction, T_g changes from 40 K at 30 kHz to 29 K at 1 Hz. In the a direction T_g is a little lower and changes from 38 K at 30 kHz to 28 K at 1 Hz. Also, the imaginary part of the dielectric permittivity (Fig. 3) shows dispersion between its peak and T_g. The peak of ϵ'' appears about 9° below T_g for all frequencies.

Our experimental dielectric data on RADA-35 show the onset of proton-glass behavior in both the a and c directions, in contradiction to the results of Kim, Kim, and Lee.[8] Near T_g, $\epsilon_c'(T)$ and $\epsilon_a'(T)$ show a flat cusp characteristic for a proton glass. The $\epsilon_a'(T)$ response is more flat than that of $\epsilon_c'(T)$. This behavior is similar to dielectric data in the RADP system.[12-15] The temperatures T_g in our RADA-35 system are about 10 K higher than those for RADP-35,[12] but are close to the Takashige values for RADP-70.[13] It is interesting that T_g for the a and c tetragonal directions are not the same, but differ by about 2°. Some anisotropy is seen in the temperature T_{max}, corresponding to maximum peak of $\epsilon_i''(T)$, also. Matsushita and Matsubara in 1986 (Ref. 16) predicted this anisotropy in the $Rb_{1-x}(NH_4)_xH_2PO_4$ system for $x<0.5$ (ferroelectric side of glassy phase). The phase diagram for RADA obtained from microwave dielectric measurements by one of us (Z.T.) (Ref. 6) shows that proton-glass behavior in RADA exists in the concentration range $0.1<x<0.5$. The midpoint of this asymmetric phase diagram is $x\approx0.3$, while $x\approx0.5$ is the midpoint of the RADP phase diagram. Our samples are close to the middle of the phase diagram (between the ferroelectric and antiferroelectric side), but the dielectric data show small anisotropy of T_g and T_{max}. It will be interesting to examine this phenomenon over the whole concentration range. Samples for these experiments are being prepared.

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