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Dielectric study of $Rb_{0.75}(ND_4)_{0.25}D_2AsO_4$

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Abstract. The complex dielectric constant of $Rb_{0.75}(ND_4)_{0.25}D_2AsO_4$ along the tetragonal crystallographic c axis has been measured as a function of temperature for frequencies between 100 Hz and 1 MHz. The dielectric relaxation is described using a Fröhlich-type distribution function. The expressions for ε' and ε'' are evaluated on this basis and fitted to the experimental data. The characteristic central frequency f_c obeys an Arrhenius law and the relaxation process is polydispersive. Below the freezing temperature $T_f = 68.9$ K the dielectric intensity $\varepsilon(0) - \varepsilon(\infty)$ is decreasing with decreasing temperature and its temperature dependence can be described by the replica-symmetry-breaking solution of the infinite range Ising spin glass model in the presence of random fields.

1. Introduction

The substitutionally disordered mixed crystals $Rb_{1-x}(NH_4)_xH_2AsO_4$ (RADA) and $Rb_{1-x}(ND)_4)_xD_2AsO_4$ (D-RADA) have recently attracted considerable interest [1–3]. It has been shown that these crystals represent frustrated H-bonded systems with random competing interactions. For small x values the systems show a paraelectric–ferroelectric transition, whereas for x-values close to one a paraelectric–antiferroelectric transition occurs. For intermediate values of x no long range ordering occurs and the system exhibits typical proton or deuteron glass behaviour at low temperatures. Contrary to the case for the isomorphous phosphate system which shows a nearly symmetric phase diagram, the phase diagram for the arsenate system is not symmetric [4]. In the arsenates the antiferroelectric transition temperature is much higher than the ferroelectric one.

Recently dielectric relaxation in RADA with $x = 0.35$ was reported [5]. The first dielectric measurements on deuterated rubidium ammonium arsenate were made by Schmidt *et al* [1].

Here we present dielectric results for $Rb_{0.75}(ND_4)_{0.25}D_2AsO_4$ (D-RADA-25) as a function of temperature for frequencies between 100 Hz and 1 MHz. The results show a broad distribution of relaxation frequencies. The distribution broadens with decreasing temperature (figure 1). Using a Fröhlich-type distribution function [6] we calculate analytically the expressions for $\varepsilon(\omega, T)$ and compare them with experimental data (figure 2). Below the freezing temperature T_f the temperature dependence of the

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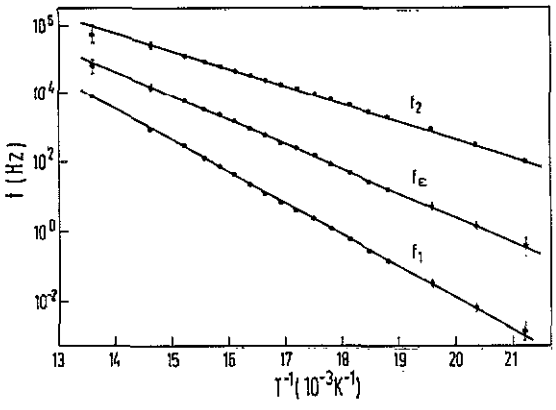

Figure 1. Semilogarithmic plot of the central relaxation frequency f_ε and the edge frequencies f_1 and f_2 as functions of the inverse temperature.

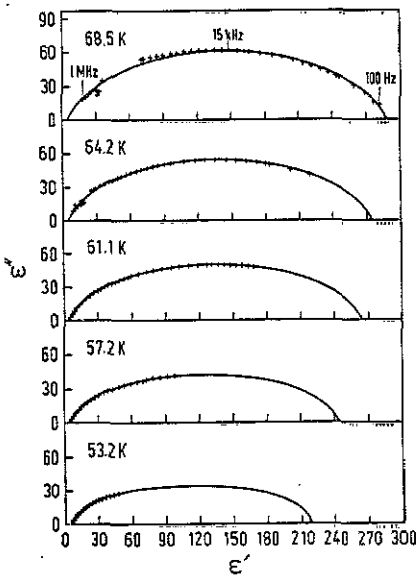

Figure 2. ε'' as a function of ε' for various temperatures in $Rb_{0.75}(ND_4)_{0.25}D_2AsO_4$. The full curves are fits using equations (1) and (2).

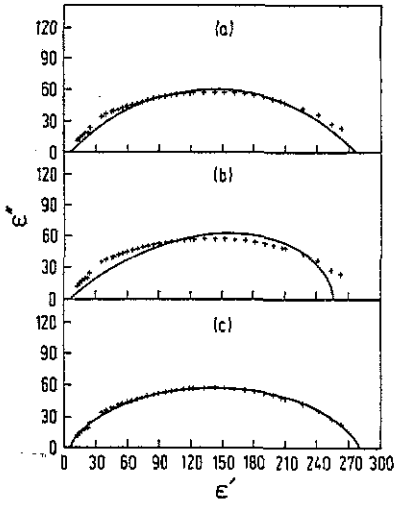

Figure 3. ε'' as a function of ε' at $T = 65.6$ K. The full curves are fits to the Cole–Cole function (*a*), the stretched exponential function (*b*), and to a Fröhlich-type function (*c*).

calculated static dielectric constant can be described by the replica-symmetry-breaking solution of the infinite range Ising spin glass in the presence of random local fields [7].

2. The experiment

Crystals of D-RADA-25 grown from aqueous (D_2O) solutions were cut and polished to yield platelets about 1 mm thick, having (001) surfaces. The ammonium content of the crystals investigated was determined by absorption measurements using Nesslers reagent. The electrodes were made using Degussa silver paint. The frequency dependence of the complex dielectric constant was measured using a HP 4192A LF impedance

analyser and a HP 4284A Precision LCR meter. The temperature of the sample was stabilized at ±0.1 K using a liquid nitrogen bath cryostat and an Oxford Instruments continuous flow cryostat. The complex dielectric constant was measured at 50 frequencies between 100 Hz and 1 MHz. Above 70 K, piezoelectric resonances in the 100 kHz range strongly influence the dielectric constant.

3. Results and discussion

Figure 2 shows ε'' as a function of ε' for different temperatures. As seen from the diagrams, the relaxation process in D-RADA is polydispersive.

Phenomenologically the complex dielectric constant can be represented by a sum of Debye relaxations:

$$\varepsilon^*(\omega, T) - \varepsilon(\infty) = (\varepsilon(0) - \varepsilon(\infty)) \int_{-\infty}^{+\infty} \frac{g(x, x_1, x_2)}{1 + i\omega \exp(-x)} \, dx \tag{1}$$

where for $g(x, x_1, x_2)$ a Fröhlich-type distribution function is chosen [6]:

$$g(x, x_1, x_2) = \begin{cases} A[1 + \tanh(\frac{1}{2}(x - x_1))] & -\infty < x < \frac{1}{2}(x_1 + x_2) \\ A[1 - \tanh(\frac{1}{2}(x - x_2))] & \frac{1}{2}(x_1 + x_2) \leqslant x < \infty \end{cases} \tag{2}$$

with $A = 1/[4 \ln(1 + (f_1/f_2)^{1/2})]$, $x = \ln(f)$, $x_1 = \ln(f_1)$ and $x_2 = \ln(f_2)$. Here f is the frequency of the Debye relaxation, while f_1 and f_2 are the edge frequencies where the distribution function $g(x, x_1, x_2)$ decreases to half its maximum value. Relaxation processes with frequencies greater than f_2 and lower than f_1 are taken into account by this distribution function.

Fitting the resulting equations for ε' and ε'' to the experimental values yields the full curves in figure 2. For the temperatures $T = 68.5$ K and $T = 64.2$ K piezoelectric resonances at frequencies around 200 kHz can be seen that become less pronounced at lower temperatures. Equations (1) and (2) determine the frequency dependence of ε' and ε'' and have four adjustable parameters $\varepsilon(0)$, $\varepsilon(\infty)$, f_1 and f_2. For comparison we display, in figure 3, the fits of the experimental results at $T = 65.7$ K with three different expressions:

(i) the Cole–Cole function;
(ii) the stretched exponential function;
(iii) equations (1) and (2).

It should be noted that in all these cases the number of adjustable parameters is four. In the first two cases the value of $\varepsilon(\infty)$ was held fixed at six during the fitting procedure, as $\varepsilon(\infty)$ would tend to zero or even to negative values otherwise. Since the experimental data indicated that $\varepsilon(\infty)$ was independent of temperature and was of value six, this value was used for $\varepsilon(\infty)$ during all further fitting procedures. The temperature dependence of the edge frequencies f_1 and f_2 as defined in equation (2), and of the characteristic central frequency $f_\varepsilon = (f_1 f_2)^{1/2}$ is presented in figure 1 in a semilogarithmic plot as a function of the inverse temperature. All frequencies obey an Arrhenius law: $f_1 = f_{10} \exp(-U_1/kT)$, $f_2 = f_{20} \exp(-U_2/kT)$ and $f_\varepsilon = f_0 \exp[-(U_2 + U_1)/2kT]$ with $U_1 = 2075$ K, $U_2 = 1190$ K, $f_{10} = 1.4 \times 10^{16}$ Hz, $f_{20} = 1.0 \times 10^{13}$ Hz and $f_0 = 3.7 \times 10^{14}$ Hz. The width of the distribution, $f_2 - f_1$, is exponentially increasing with decreasing temperature. If one

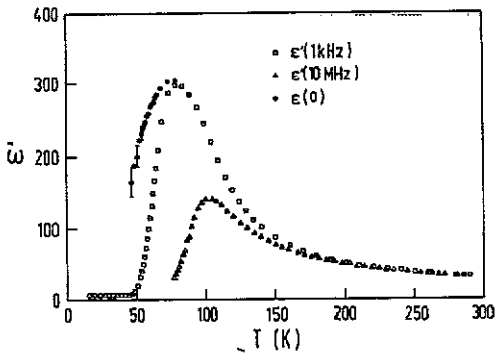

Figure 4. Temperature dependence of ε' (1 kHz, 10 MHz) and of the static dielectric constant $\varepsilon(0)$ derived from equations (1) and (2).

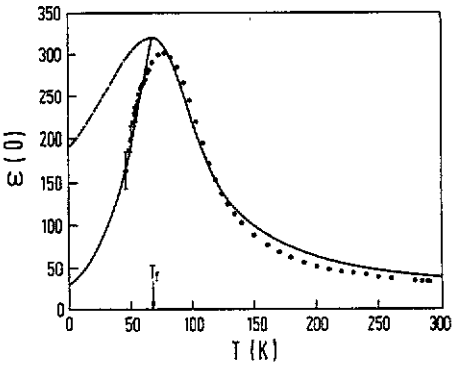

Figure 5. Static dielectric constant $\varepsilon(0)$ fitted to the theoretical expression (4). T_f denotes the freezing temperature. For $T > T_f$ replica-symmetric theory. For $T < T_f$ the replica-symmetry-breaking solution (full curve) gives a better fit than the replica-symmetric one (broken curve).

assumes the same temperature dependence to be valid at higher temperatures it can be shown that the width tends to zero at $T = 122$ K. This does not imply, however, that the relaxation process becomes monodispersive, since the tails of the distribution remain effective.

The temperature dependence of the dielectric constant measured at 10 MHz and 1 kHz is shown in figure 4. Also shown is the corresponding value of the static dielectric constant $\varepsilon(0)$ obtained analytically from equations (1) and (2) in the limit $\omega \to 0$. Above 90 K, $\varepsilon(0)$ is equal to the dielectric constant measured at 1 kHz. Below 70 K the static dielectric constant decreases steeply with temperature and reaches half its maximum value at 47.1 K.

To describe the temperature dependence of the static dielectric constant, the mean field theory of deuteron glasses based on the infinite range Ising spin glass model in the presence of random local fields [7–9] is applied. The corresponding Hamiltonian is given by:

$$H = -\tfrac{1}{2}\sum_{ij} J_{ij}\sigma_i\sigma_j - \sum_i E_i\sigma_i \tag{3}$$

where the pseudospin $\sigma_i = \pm 1$ represents the deuteron degrees of freedom in the two-site O–D $\cdots$ O potential. The random bond interactions J_{ij} and the random local electric fields E_i have independent Gaussian distributions with mean values J_0/N and zero and variances J^2/N and Δ, respectively. In the high temperature phase the replica-symmetric solution holds [7–9] and the static dielectric constant can be written as

$$\varepsilon(0) = \varepsilon(\infty) + CJ\chi/(1 - J_0\chi) \tag{4}$$

where $\chi = \beta(1 - q)$ is the static local spin glass susceptibility with $\beta = 1/kT$ and q represents the deuteron glass order parameter. Note that q is non-zero at all temperatures due to the random fields. The replica-symmetric solution for q is stable for

$T > T_f$ where the freezing temperature T_f is independent of J_0 (we assume $J_0 < J$) and is determined by the relations [8]:

$$T_f^2 = J^2 \int \mathrm{D}z \cosh^{-4}[J(q + \Delta/J^2)^{1/2} z/T_f] \tag{5a}$$

$$q = \int \mathrm{D}z \tanh^2[J(q + \Delta/J^2)^{1/2} z/T_f]. \tag{5b}$$

$\int \mathrm{D}z f(z)$ represents an integral of the form

$$(2\pi)^{-1/2} \int \exp(-z^2/2) f(z)\, \mathrm{d}z.$$

For $T < T_f$ replica symmetry is broken and the spin glass is characterized by an order-parameter function $q(x)$ [10]. Using Parisi's two-step parametrization of the order parameter function ($q(x) = q_0$ for $0 \leqslant x < m$ and $q(x) = q_1$ for $m \leqslant x \leqslant 1$) the free energy becomes [7]:

$$\beta F = -(\beta J/2)^2[(1 - q_1)^2 - m(q_1^2 - q_0^2)] - m^{-1} \int \mathrm{D}z \ln \int \mathrm{D}y\, Z^m(y, z) \tag{6}$$

where $Z(y, z) = 2\cosh[\beta h(y, z)]$ with $h(y, z) = J[(q_1 - q_0)^{1/2} y + (q_0 + \Delta/J^2)^{1/2} z]$. The parameters q_0, q_1 and m can be determined by a maximization of the free energy (6).

In the low temperature phase $T < T_f$ the static dielectric constant can still be described formally by equation (4) provided that the local susceptibility χ is identified as the zero-field-cooled susceptibility $\chi_{zfc} = \beta(1 - q_1)$. Hence the measured dielectric constant $\varepsilon(0)$ has been fitted to expression (4) with $\chi = \beta(1 - q)$ for $T > T_f$ and $\chi = \beta(1 - q_1)$ for $T < T_f$. As shown in figure 5 the temperature dependence of $\varepsilon(0)$ can be well represented by the theoretical expression (4). The values of the parameters thus obtained are: $J = 90.4$ K, $J_0 = 72.7$ K, $\Delta/J^2 = 0.027$, $C = 82.4$ and $T_f = 68.9$ K. It is interesting to note that a linear interpolation for the mean bond interaction, $J_0 \approx J_0^{FE}(1 - x) - J_0^{AFE} x$, between the corresponding values for the pure ferroelectric and antiferroelectric systems J_0^{FE} and J_0^{AFE}, respectively, yields $J_0 \approx 63$ K in reasonable agreement with the above best fit value. As indicated in figure 5 the replica-symmetric solution (broken curve) cannot describe the static dielectric constant in the low temperature phase.

4. Conclusions

The dielectric dispersion in D-RADA is well described by a Fröhlich-type distribution function. The expressions for $\varepsilon'(\omega, T)$ and $\varepsilon''(\omega, T)$ have been derived and compared with the experimental data. The characteristic central frequency f_ε obeys an Arrhenius law. The dielectric dispersion is polydispersive and the width of the distribution is exponentially increasing with decreasing temperature. The static dielectric constant decreases steeply below the freezing temperature $T_f = 68.9$ K. Above T_f the static dielectric constant is well represented by the replica-symmetry solution of the infinite range Ising spin glass model in the presence of random local fields, whereas for $T < T_f$ the Parisi replica-symmetry-breaking solution offers a better description.

Acknowledgments

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