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Microwave and millimetre-wave dielectric response of $\text{Rb}_{1-x}(\text{ND}_4)\text{D}_2\text{PO}_4$ dipolar glass

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Abstract

The microwave and millimetre-wave dielectric response of $\text{Rb}_{0.5}(\text{ND}_4)_{0.5}\text{D}_2\text{PO}_4$ dipolar glass has been studied around the frustration temperature $T_f \approx 120$ K. It was found that above the frustration temperature T_f the soft relaxational deuteron mode is responsible for the whole dielectric dynamics below the phonon range. Its frequency decreases from that of submillimetre waves to that of microwaves following the classical law $\nu_R = A(T - T_f)$, with $A = 0.75$ GHz K⁻¹, but in the vicinity of T_f the soft mode gradually shifts towards the glass-like dispersion predominantly related to the diffusion of Takagi defects according to the Vogel–Fulcher law. From the experimental results, the distribution of the relaxation times and of the local polarization at various temperatures is calculated. It is shown that the local polarization distribution function obtained from the dielectric response $\epsilon^*(\nu, T)$ coincides well with that obtained from the NMR results.

1. Introduction

Mixed crystals of $\text{Rb}_{1-x}(\text{NH}_4)\text{H}_2\text{PO}_4$ (RADP) and $\text{Rb}_{1-x}(\text{ND}_4)\text{D}_2\text{PO}_4$ (DRADP) form dipolar glasses for $0.3 \leq x \leq 0.7$; they belong to one of the most thoroughly investigated glass systems (Courtens 1987, Höchli *et al* 1990). The dielectric response of RADP and DRADP was investigated over a broad frequency range—from low frequencies up to microwaves (Courtens 1984, 1986, Brückner *et al* 1988, He *et al* 1990, He 1991), and in the submillimetre and far-infrared (FIR) regions (Petzelt *et al* 1991, 1993, Kamba *et al* 1992). The investigations at temperatures $T \geq 120$ K in the submillimetre-wave region revealed simple relaxation soft-mode behaviour corresponding to a crystal with averaged structure. At temperatures $T < 120$ K, further softening occurred accompanied by a strong decrease in the relaxation strength, and the soft mode transforms into a broad dielectric dispersion whose relaxation frequency ν_r obeys the Vogel–Fulcher law

$$\nu_r = \nu_\infty \exp[-E_0/k(T - T_{VF})] \quad (1)$$

with the following parameters: $T_{VF} = 10$ K, $E_0/k = 95$ K and $\nu_\infty = 1.8 \times 10^{12}$ Hz for RADP and $T_{VF} = 34$ K, $E_0/k = 410$ K and $\nu_\infty = 1.17 \times 10^{12}$ Hz for DRADP.

The dielectric studies supplemented NMR data on deuteron dynamics, which made it possible to determine the Edwards–Anderson order parameter (Blinc *et al* 1989) and the local dynamic behaviour of deuterons (Blinc *et al* 1986a, 1986b) and to distinguish between paraelectric, ferroelectric and antiferroelectric and glass-type order (Kind *et al* 1990).

Dielectric, diffuse neutron and x-ray scattering (Grimm 1989, Cowley *et al* 1986) as well as NMR (Korner 1992) studies revealed the characteristic temperature range around 120 K. Within the framework of existing theories (Pirc *et al* 1987, 1991) it was supposed (Petzelt *et al* 1993) that this temperature corresponds to the region where random interactions begin to dominate over random fields. This temperature was called the frustration temperature $T_f \approx 120$ K. It is probably connected with the freezing of ammonia deuterons (Blinc *et al* 1986a, 1986b), which may create nuclei for quasi-static cluster formation.

Above T_f , the softening of the deuteron mode, which is essentially due to slowing down of the single-particle hopping, completely explains the dielectric response below phonon frequencies. Below T_f , the deuteron dynamics is related to ordered clusters in which the deuterons are frozen and separated by active regions where the deuterons still jump. Structurally, the ordered clusters may consist of regions, where ice rules are satisfied (Matsushita and Fuchizaki 1987), separated by regions with high concentrations of Takagi defects (HPO_4^{2-} and H_2PO_4 groups) where the deuterons are still jumping and causing the local diffusion of these defects. This motion is considered to be responsible for the broad dielectric dispersion in RADP below T_f (Schmidt 1988a, 1988b). In the vicinity of T_f one could expect a more complex dielectric dispersion where both types of dynamics contribute—a higher-frequency dispersion from the hopping inside the clusters and a lower-frequency one predominantly from the diffusion of Takagi defects between the clusters. It was expected (Petzelt *et al* 1993) that these two mechanisms would overlap in the (not investigated) 1–100 GHz frequency range.

The purpose of this paper is to study dielectric response of DRADP-50 dipolar glass in microwave and millimetre-wave ranges around the frustration temperature T_f , and thus to obtain a complete picture of the dielectric dynamics.

2. Experimental details

Single crystals of DRADP-50 grown from a heavy-water solution (Arend *et al* 1986) have been cut and polished to obtain thin cylindrical samples along the *c*-axis for dielectric measurements. The degree of deuteration of the virgin crystals was estimated to be 99%. However, from the permittivity dependence on the deuterium concentration value (He 1991) we estimated that the old and polished samples contained less deuterium due to exchange of deuterium with hydrogen from the water vapour in the air.

Dielectric measurements in the centimetre- and millimetre-wave ranges were performed using a computer-controlled waveguide spectrometer (Grigas 1996). For microwave and especially millimetre-wave ranges, the results of dielectric measurements strongly depend on the electric field homogeneity within a sample. The thinner a sample, the more homogeneous the electric field in the sample. All the measurements were performed with the same crystal. Only the radius of the sample was changed: $r = 0.65$ mm for the frequencies 8–12 GHz and $r = 0.27$ mm for the frequencies 26–55 GHz. Nevertheless, the complex permittivity $\varepsilon_c^* = \varepsilon_c' - i\varepsilon_c''$ was calculated using equations which take into account the inhomogeneous electric field in cylindrical samples. All the measurements were performed in weak electric fields ($E \leq 100$ mV cm⁻¹) with the cooling rate of 0.1 K min⁻¹.

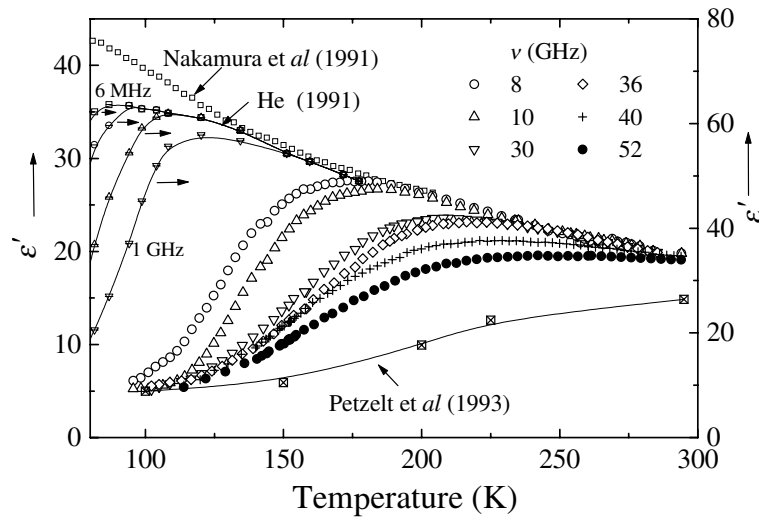


Figure 1. The temperature dependence of the real part of the permittivity of DRADP-50 at various frequencies. Results on the low-frequency values (Nakamura *et al* 1991) and permittivities at RF frequencies (He 1991) and at 150 GHz (Petzelt *et al* 1993) are also included. The solid curves are only guides to the eye.

3. Results

The temperature dependences of the real (ϵ'_c) and imaginary (ϵ''_c) parts of the dielectric permittivity at different microwave and millimetre-wave frequencies are shown in figures 1 and 2. The low-frequency values of ϵ'_c (Nakamura *et al* 1991) for RADP and the results at and below 1 GHz (He 1991) and at 150 GHz (Petzelt *et al* 1993) for DRADP are also included. Although the low-frequency permittivities of RADP and DRADP are different, the microwave values are similar. The values of the permittivity for DRADP given by He (1991) for below 1 GHz are higher than our microwave values. From the permittivity dependence on the deuterium concentration value (He 1991), we estimated that our polished samples contained 50–60% of deuterium due to its exchange with hydrogen from water. The frequency dependences of the real and imaginary parts of the permittivity at different temperatures are given in figure 3. The value of the nearly temperature-independent real permittivity at 1 GHz (He 1991) for 50%-deuterated crystal, as well as submillimetre data available only for 150 and 200 K (Petzelt *et al* 1993), are also included. Therefore, this figure represents the dielectric spectrum of DRADP below phonon frequencies in the temperature range 120–200 K. Two points are worth mentioning:

- (i) The dielectric dispersion covers a very wide frequency range, starting from the low frequencies at low temperatures to millimetre waves at higher temperatures, and the peak of ϵ''_c moves towards room temperature with increasing frequency.
- (ii) It was found that for microwaves and millimetre waves the main dielectric dispersion occurs in the temperature range 120–250 K. The polydispersive behaviour (distribution of the relaxational times) at all temperatures follows from the above results.

The diffuse dielectric spectra can be fitted closely by the empirical Cole–Cole equation:

$$\epsilon^*(\omega) = \epsilon_\infty + \frac{\Delta\epsilon}{1 + (i\omega\tau)^{1-\alpha}}, \quad (2)$$

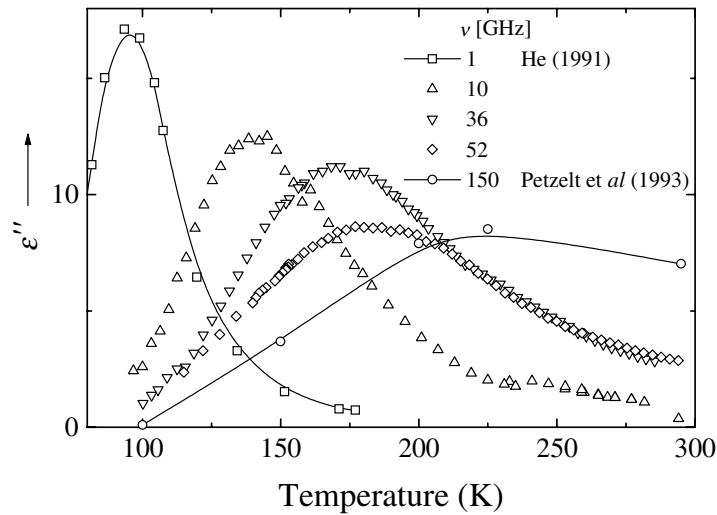


Figure 2. The temperature dependence of the imaginary part of the permittivity at various frequencies. The solid curves are only guides to the eye.

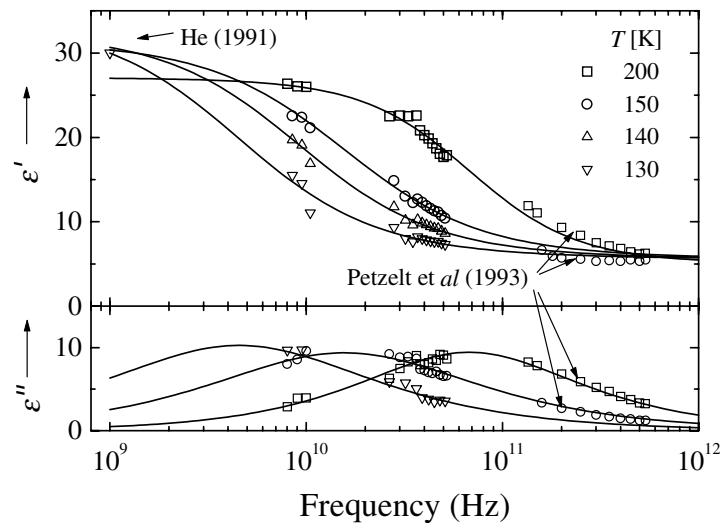


Figure 3. The frequency dependences of the real and imaginary parts of the permittivity at various temperatures. The solid curves are fitted results obtained with the parameters shown in figure 4.

where $\Delta\varepsilon = \varepsilon(0) - \varepsilon_\infty$ is the contribution of the relaxation process to the static permittivity $\varepsilon(0)$ (dielectric strength), ε_∞ is the contribution of the phonon modes and electronic polarization, $\omega = 2\pi\nu$ is the angular frequency and τ is the mean relaxation time. The parameter $0 \leq \alpha \leq 1$ characterizes the distribution of the relaxation times.

We have fitted the parameters of equation (2) to our experimental results $\varepsilon^*(\nu, T)$ and the low-frequency and submillimetre results at different temperatures to equation (2), and determined $\Delta\varepsilon$, τ , α and ε_∞ . The fits were performed only in the limited temperature interval around T_f where the fits are reliable. The temperature dependences of the fitted

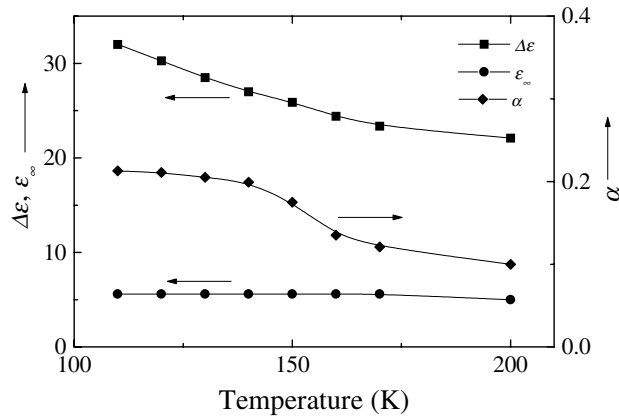


Figure 4. The temperature dependence of the Cole–Cole equation parameters.

parameters $\Delta\epsilon$, α and ϵ_∞ are shown in figure 4. The value $\epsilon_\infty = 5.5$ is almost temperature independent and is in agreement with the contribution of phonon modes derived from IR spectra and electronic polarization (Petzelt *et al* 1993) for DRADP, as well as the value obtained from the Curie–Weiss plot for RADP (Nakamura *et al* 1991). The dielectric strength, $\Delta\epsilon$, and the distribution parameter, α , increase with decreasing temperature without substantial anomalies at $T_f \approx 120$ K. For microwaves and millimetre waves, the mechanism also does not change abruptly at T_f from monodispersive ($\alpha = 0$) to polydispersive, as was suggested by Nakamura *et al* (1991). Even at high temperatures some distribution of the relaxation times ($\alpha > 0$) remains present. However, the value of α below 130 K is slightly smaller, because in our case it was calculated from the experimental results $\epsilon^*(\nu, T)$ outside the centre of dispersion.

The temperature dependences of the mean relaxation time, τ , and the relaxation mode frequency, $\nu_r = 1/2\pi\tau$, are shown in figure 5. Results on a lower-frequency glass-like dispersion and a soft mode from submillimetre-wave studies are also included. All the results are fairly consistent. It should be noted that Petzelt *et al* (1993) have fitted the dielectric dispersion with a single-Debye-relaxation equation. As we can see from the results presented, α decreases with increasing temperature, and at higher temperatures it should go to zero and the dielectric dispersion change to the single Debye relaxation. The rapid increase of the mean relaxation time with decreasing temperature (by about five orders of magnitude) indicates a substantial slowing down of the relaxation processes. From this figure the most important result follows: the relaxation frequency of the soft deuteron mode softens on decreasing the temperature to $T_f = 124$ K according to the classical law

$$\nu_R = A(T - T_f), \quad (3)$$

where $A = 0.75 \text{ GHz K}^{-1}$.

This indicates that in the vicinity of T_f the higher-frequency dielectric dispersion caused by the deuteron hopping inside the clusters gradually changes to a lower-frequency one caused by the diffusion of Takagi defects in cluster walls among the ordered clusters, as has been suggested by Petzelt *et al* (1993). The curves in figure 3 are Cole–Cole fits with the parameters shown in figures 4 and 5. The distribution parameter α remains nonzero above the temperature T_f , as can be seen from the permittivity dispersion width.

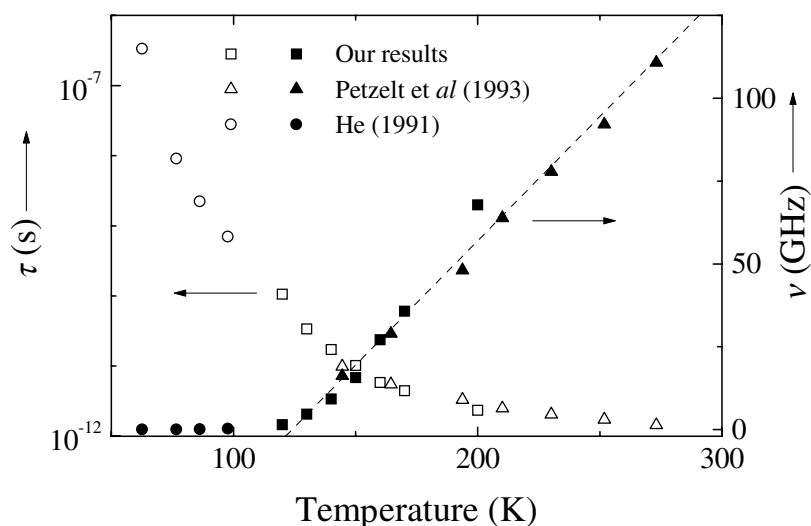


Figure 5. Temperature dependences of the mean (Cole–Cole) relaxation time τ and the relaxation frequency ν_R . The dashed line represents equation (3).

4. Distribution of relaxation times and local polarization

For the dipolar glasses it is usually assumed that the motion of the protons in the double-well O–H··O potentials is randomly frozen out at low temperatures, implying a static quenched disorder (Kutnjak *et al* 1994). Due to the ‘built-in’ disorder, always present in the off-stoichiometric solid solutions, there are a variety of environments for the O–H··O bonds, leading to the distribution of the microscopic parameters of the bonds and, consequently, the distribution of dynamic properties such as the dipolar relaxation times.

We consider a proton or deuteron moving in an asymmetric double-well potential. The movement consists of fast oscillations in one of the minima with occasional thermally activated jumps between the minima. Here we neglect quantum tunnelling, which is negligible for deuterons, although it might be significant for protons at low temperatures. The oscillation frequency is ν_0 . The jump probability is governed by the Boltzmann probability of overcoming the potential barrier between the minima. An ensemble of similar O–H··O bonds has a relaxational dielectric response at lower frequencies. It was shown that the relaxation time of such a system is (Dolinšek *et al* 1996)

$$\tau = \tau_0 \frac{\exp(E_b/k(T - T_0))}{2 \cosh(A/2kT)}, \quad (4)$$

where $\tau_0 = 1/2\pi\nu_\infty$, T_0 is the Vogel–Fulcher temperature. We are assuming that the potential barrier height E_b does not change with temperature, and we are introducing the term T_0 which should effectively account for the increase of the barrier on approaching the temperature T_0 .

We further consider that the O–H··O bonds are not similar, but instead have the asymmetry A and the potential barrier E_b randomly distributed according to the Gaussian law around their mean values A_0 and E_{b0} :

$$w(E_b) = \frac{1}{\sqrt{2\pi}\sigma_E} \exp\left(-\frac{(E_b - E_{b0})^2}{2\sigma_E^2}\right), \quad (5)$$

$$w(A) = \frac{1}{\sqrt{2\pi}\sigma_A} \exp\left(-\frac{(A - A_0)^2}{2\sigma_A^2}\right), \quad (6)$$

where σ_E , and σ_A are the standard deviations of E_b and A respectively. It should be noted that the local polarization p (time-averaged dipole moment) of the $\text{O}-\text{H}\cdots\text{O}$ bond is a function of the asymmetry parameter A :

$$p = \tanh(A/2kT), \quad (7)$$

and thus it is related to the relaxation time (Dolinšek *et al* 1996).

Since we have distributions of A and E_b , there will be distributions of τ and p : $w(\tau)$ and $w(p)$. Also, from the $w(p)$ distribution it is possible to obtain the Edwards–Anderson order parameter:

$$q_{EA} = \int_{-1}^1 p^2 w(p) dp, \quad (8)$$

and the macroscopic polarization:

$$P = \int_{-1}^1 p w(p) dp. \quad (9)$$

Assuming Gaussian distribution of E_b and A , it is possible to obtain the temperature dependence of the relaxation time distribution $w(\tau)$.

The distribution of relaxation times is also implied by the Cole–Cole equation (2) with $\alpha > 0$. It is symmetrically shaped and can be expressed as

$$w(\tau) = \frac{\sin(\alpha\pi)}{\cosh[(1-\alpha)\ln(2\pi\tau_{CC}/\tau)] - \cos(\alpha\pi)}, \quad (10)$$

where τ_{CC} is now the Cole–Cole relaxation time and α is the distribution parameter (see equation (2)). From the experimental results, the values of α have been obtained for different temperatures, and the distribution of the relaxation times has been calculated using equation (10) and is presented in figure 7 as points. The fits were performed simultaneously for six different temperatures using the same set of parameters. The best fit for the distribution of the relaxation times obtained from the Cole–Cole formula with equations (4)–(6) gave the following values: $\tau_0 = 3.5 \times 10^{-14}$ s, $T_0 = 32$ K, $E_b/k = 749$ K, $\sigma_E/k = 83.3$ K, $\sigma_A = 50$ K and $A_0 = 0$. At all temperatures, the soft relaxational mode is diffuse, whereas for the monodisperse mode one would expect the delta functions in figures 6 and 7.

From these results it is possible to calculate the local polarization distribution and the Edwards–Anderson order parameter. From the results obtained from dielectric spectroscopy the local polarization distribution has been calculated (equation (7)). These results (figure 7) are compared with the results obtained from the NMR line shape (Blinc *et al* 1989). From the RBRF model (Pirc *et al* 1991, Blinc *et al* 1989), $\sigma_A = 2(J^2(q_{EA} + \tilde{\Delta}))^{1/2}$, where J is the freezing temperature ($J/k = T_0$), and $\tilde{\Delta}$ is the standard deviation of the random field. From our calculations we have found that q_{EA} in the temperature range 120–170 K changes from 0.2–0.4. The freezing temperature is $J/k = T_0 = 32$ K. As one can see from the figure 7, there is very good agreement with the results obtained by Blinc *et al* (1989). However, the reason for the difference in the T_0 -value could be that NMR is a local probe which integrates the dynamics over all wavevectors, whereas dielectric data probe essentially the zero-wavevector response only.

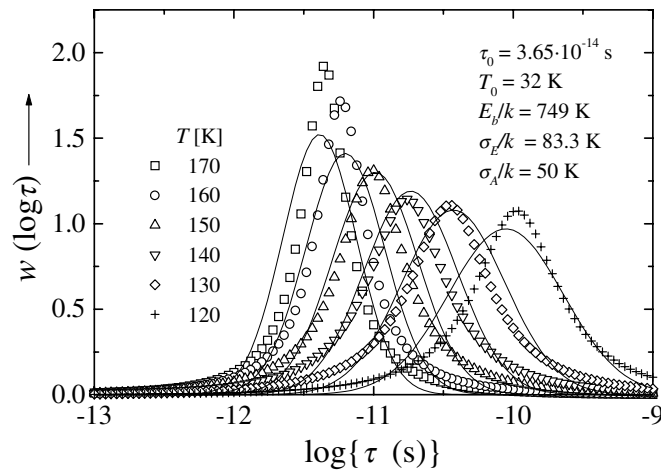


Figure 6. The temperature dependence of the distribution of the relaxation times at various temperatures. Points show the values from equation (10); curves are the best fits with the equations (4)–(6).

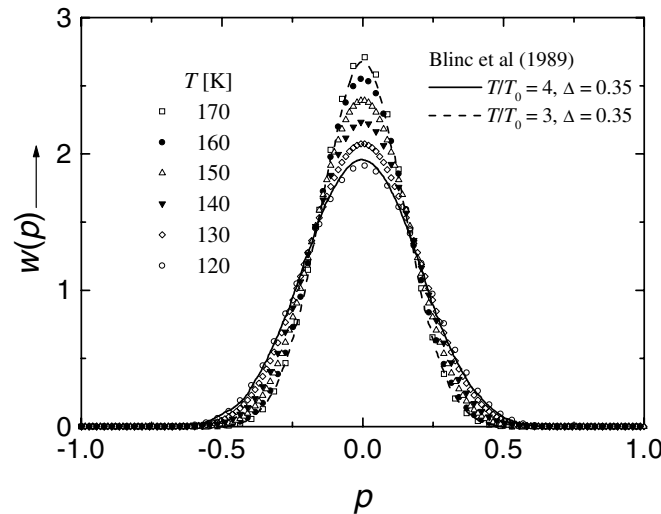


Figure 7. The local polarization distribution at various temperatures. Points show the values calculated from equations (6) and (7); curves are obtained from NMR line shapes given by Blinc *et al* (1989).

5. Conclusions

Microwave and millimetre-wave dielectric studies of DRADP dipolar glass crystal have filled up the frequency gap between low frequencies and submillimetre waves. A picture of the dielectric dynamics is obtained for a dipolar glass crystal over the wide temperature range above the freezing temperature.

Above the frustration temperature $T_f = 120$ K, the soft relaxational deuteron mode is responsible for the dielectric dynamics. Its frequency decreases from that of submillimetre waves to that of microwaves following the classical law $\nu_R = A(T - T_f)$, where

$A = 0.75 \text{ GHz K}^{-1}$. In the vicinity of T_f , the soft mode gradually transforms to the glass-like dispersion predominantly related to the diffusion of Takagi defects.

The soft deuteron mode is polydispersive at all temperatures. On approaching T_f its polydispersivity increases, but only one dielectric dispersion region remains present for all temperatures. This supports the picture of very smeared and broad cluster walls, comparable to the cluster size itself, down to low temperatures and an important role of random fields.

It is shown that the local polarization distribution calculated from the dielectric spectroscopy is in a very good agreement with the results obtained from the NMR line shape.

Acknowledgments

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