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Ferroelectric–antiferroelectric fluctuations in the dipolar glass $\text{Rb}_{1-x}(\text{NH}_4)_x\text{H}_2\text{PO}_4$: an electron paramagnetic resonance study

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Abstract. Electron paramagnetic resonance studies of $\text{Rb}_{1-x}(\text{NH}_4)_x\text{H}_2\text{PO}_4$ ($x = 0, 0.5, 0.8, 0.9, 0.95$ and 1.0) containing an AsO_4^{4-} probe gave a clear indication of the fluctuations between ferroelectric (FE) and antiferroelectric (AFE) regions in the mixed crystals right from room temperature. This has become possible because the AsO_4^{4-} probe has different ^{75}As hyperfine coupling constants in pure RDP (FE) and ADP (AFE) crystals ($x = 0$ and 1). This fluctuation is manifested as the averaging of the ^{75}As hyperfine coupling constant, with compositional dependence of the form $\langle A \rangle_{\text{mixed crystal}} = (1-x)A_{\text{FE}} + xA_{\text{AFE}}$. The characteristic fluctuation time $T \approx 3 \times 10^{-8}$ s. The existence of this fluctuation in the mixed crystal also shows up in the washing out of ^1H superhyperfine structure from the close protons which is of the order of 30 MHz.

1. Introduction

Mixed crystals of RbH_2PO_4 (RDP) and $\text{NH}_4\text{H}_2\text{PO}_4$ (ADP) have been shown to be archetypal dielectric glasses at low temperatures [1–4] over a wide concentration range. This glass formation occurs because of the competing ferroelectric (FE) and antiferroelectric (AFE) ordering that occurs in pure RDP and ADP, respectively, close to 147 K. This is further facilitated by the nearly equal ionic sizes of Rb^+ and NH_4^+ and the miscibility of these systems over a wide concentration range. The mixed system $\text{Rb}_{1-x}(\text{NH}_4)_x\text{H}_2\text{PO}_4$ (RADP) has been the subject of a number of investigations directed towards understanding the mechanism of glass formation and elucidating the similarity or contrast to magnetic spin glasses. A characteristic feature associated with the mixed system RADP is the tremendous slowing down of $\text{O}-\text{H} \cdots \text{O}$ dynamics on cooling into the glass phase, as shown by ^{87}Rb , ^1H and ^2H NMR studies [5, 6]. This feature was recently investigated by Ceyc *et al* [7] and Kind *et al* [8] for $x = 0.34, 0.43$ and 0.70 in the EPR of Tl^{2+} in RADP on two characteristic time scales corresponding to the splitting of the low-field (440 MHz) and high-field (669 MHz) hyperfine lines of $^{203}\text{Tl}^{2+}$. Dynamic effects were not directly observed in the line splitting at 130 K but were inferred from the different temperature dependences of the linewidths of the low-field and high-field lines. These workers also noted that the Tl^{2+} probe is not selectively sensitive to FE and AFE ordering [8]. The Tl^{2+}

experiment, therefore, does not directly allow the investigation of the dynamic aspects of competing interactions of FE and AFE order, which are expected to play the central role in glass formation.

The EPR of AsO_4^{4-} has been extensively studied in KDP- and ADP-type hydrogen-bonded FES and AFES [9–15] and it has been shown that protonic motion in the $\text{H}-\text{O} \dots \text{H}$ bond is slowed at temperatures much higher than the transition temperatures, resulting in the onset of local polarizations in the bulk paraelectric (PE) phase itself. Further, there is significant difference in the large hyperfine tensors in RDP (FE) and ADP (AFE) (50 MHz in A_{zz}), this difference being brought about by the differences in the corresponding Slater configurations of H_2AsO_4 units. The up and down Slater configurations characterizing the FE phase were reported to be modified in the AFE phase by the internal AFE domains [15] and hence a fluctuation between FE and AFE would result in modulation of ^1H superhyperfine structure (SHFS) at the frequency of fluctuation. Therefore, the AsO_4^{4-} probe is complementary to Tl^{2+} in the sense that it acts as a time keeper around 30–40 MHz and it can be selective to local FE and AFE ordering and fluctuations thereof. We have investigated these aspects using the AsO_4^{4-} probe in mixed RADP crystals and shown that fluctuations between local FE and AFE configurations of the $(\text{H}_2\text{AsO}_4)^{2-}$ probe exist right from room temperature, suggesting that progressive slowing down of this process results in glass formation. The time scale corresponding to 50 MHz or below for this process would thus make this fluctuation appear as static with the Tl^{2+} probe.

2. Experimental details

Single crystals of RDP, ADP and RADP with $x = 0.5, 0.8, 0.9$ and 0.95 were grown from aqueous solution. 1–2 mol% of $\text{NH}_4\text{H}_2\text{AsO}_4$ (ADA) were added to the growth solution for incorporating the probe. The crystals were elongated along the c axis, with well developed (100) and (010) faces. Crystals were γ irradiated at room temperature, and EPR spectra were recorded on a Bruker ESP-300 X-band spectrometer. The temperature dependence of the spectra was studied using a Varian variable-temperature accessory in the temperature range 90–570 K and a CTI cryogenics closed-cycle helium refrigerator in the 25–300 K range.

3. Results and discussion

3.1. EPR spectra at room temperature

The EPR spectra of the AsO_4^{4-} radical ion in γ -irradiated RDP, ADP and RADP with $x = 0.5$ and 0.9 recorded at room temperature with the magnetic field along the c axis are shown in figure 1. The essential features of the spectra are similar in all these samples. The spectra can be grouped into three categories, as reported by Gaillard *et al* [12] and Dalal *et al* [13] for the arsenates of the RDP family. These are

- (i) the quartet ^{75}As hyperfine lines due to the AsO_4^{4-} radical,
- (ii) a set of quartet lines believed to be due to AsO_3^{3-} -type centres and
- (iii) a few lines in the $g = 2$ region.

We shall concentrate mainly on the AsO_4^{4-} spectra (indicated in figure 1 by arrows).

In ADP, the AsO_4^{4-} quartet lines show SHFS due to the acid protons whereas, in RDP and RADP with $x \leq 0.8$, no resolved SHFS was observed. In going from the NH_4 -rich to

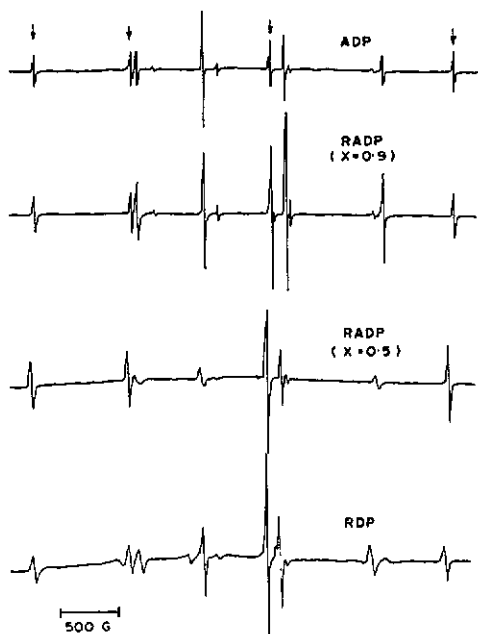


Figure 1. The EPR spectra of γ -irradiated ADP, RADP with $x = 0.9$ and 0.5 and RDP doped with 2 mol% ADA. The spectra are recorded with the magnetic field parallel to c , at room temperature. The lines indicated by arrows are due to the AsO_4^{4-} radical. The linewidth dependence on the nuclear quantum number m_I can be seen for $x = 0.5$.

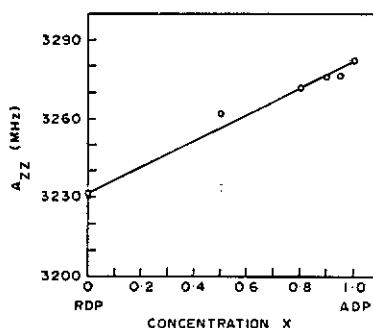


Figure 2. The dependence of the z -component of the hyperfine constant of AsO_4^{4-} on the relative concentration of NH_4^+ and Rb^+ in RADP. This linear dependence clearly illustrates the fluctuation between local FE and AFE configurations (see text).

the Rb-rich side of RADP, the SHFS becomes progressively less resolved. For this reason, the mixed phase was approached from the NH_4^+ -rich side, for investigating the PE-glass \rightarrow FE-AFE transition region.

The angular variation in the AsO_4^{4-} spectra of RDP, ADP and RADP showed axial symmetry about the c axis at room temperature. The spectra can be described by the spin Hamiltonian

$$H = \beta H \cdot gS + S \cdot \mathbf{A}I - g_n \beta_n H \cdot I \quad (1)$$

with $S = \frac{1}{2}$ and $I = \frac{3}{2}$. The successive terms represent the electron Zeeman, hyperfine and nuclear Zeeman interactions, respectively. The last term may be neglected in equation (1). Since the experimental results show that the principal axes of the \mathbf{g} and \mathbf{A} tensors are parallel and that the \mathbf{A} tensor is axially symmetric, the solutions of equation (1) for $H \parallel c$ and $H \perp c$ given in [11] were used for calculating the g - and A -values. The values of g_{\parallel} , g_{\perp} , A_{\parallel} and A_{\perp} calculated using the field values for $H \parallel c$ and $H \perp c$ in RDP, ADP and RADP are shown in table 1. The g -value is very nearly isotropic and is close to 2. The \mathbf{A} -tensor, however, is axial and shows a systematic variation in going from ADP to RDP through RADP (figure 2). This observation leads to a useful parameter in characterizing the mixed phase even at room temperature:

$$A_{\text{RADP}} = (1 - x)A_{\text{RDP}} + xA_{\text{ADP}}$$

Another important observation is the m_I -dependence of the linewidths of the hyperfine quartet in RADP. In pure RDP and ADP there are small differences in the linewidths

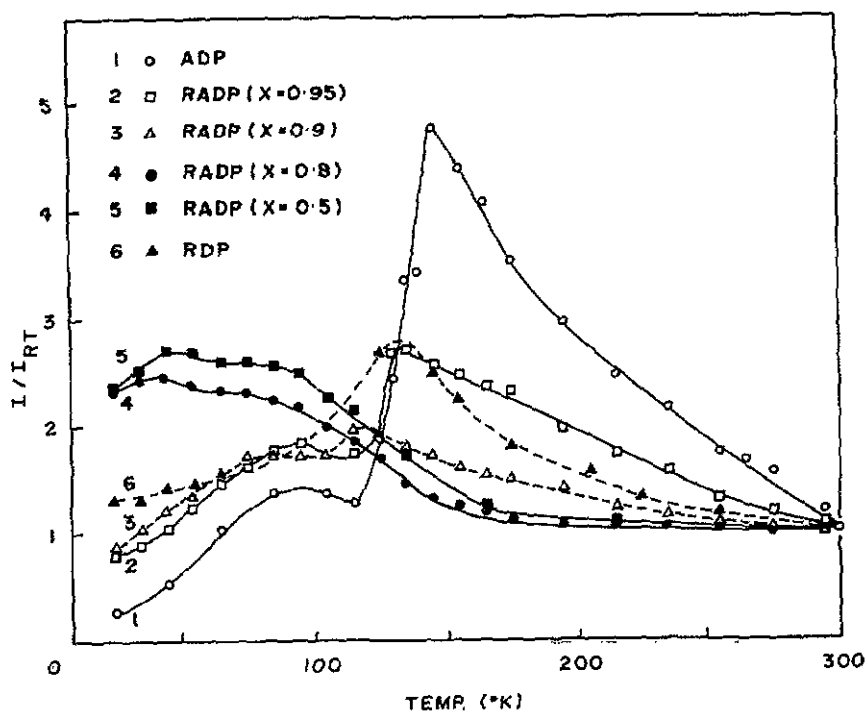


Figure 3. The temperature dependence of the intensity of EPR spectra of AsO_4^{3-} in ADP (curve 1), RADP ($x = 0.95$) (curve 2), RADP ($x = 0.9$) (curve 3), RADP ($x = 0.8$) (curve 4), RADP ($x = 0.5$) (curve 5) and RDP (curve 6). It may be noted that the anomalous changes observed in the vicinity of the respective phase transitions in ADP, RDP and RADP ($x = 0.95$ and 0.9) are absent for RADP ($x = 0.8$ and 0.5).

Table 1. Room-temperature spin-Hamiltonian parameters for the AsO_4^{3-} centre in mixed RADP crystals for the various compositions shown.

System	A_{\parallel} (MHz)	A_{\perp} (MHz)	A_{iso} (MHz)	g_{\parallel}	g_{\perp}
ADP	3281 ± 2	2946 ± 2	3057 ± 2	2.001 ± 0.001	2.001 ± 0.001
RADP ($x = 0.95$)	3276 ± 2	2945 ± 2	3055 ± 2	1.999 ± 0.001	2.001 ± 0.001
RADP ($x = 0.9$)	3275 ± 2	2941 ± 2	3053 ± 2	2.001 ± 0.001	2.002 ± 0.001
RADP ($x = 0.8$)	3272 ± 2	2939 ± 2	3050 ± 2	2.000 ± 0.001	2.001 ± 0.001
RADP ($x = 0.5$)	3262 ± 2	2934 ± 2	3043 ± 2	2.000 ± 0.001	2.002 ± 0.001
RDP	3231 ± 2	2922 ± 2	3025 ± 2	2.001 ± 0.001	2.003 ± 0.001

of the hyperfine lines. However, in the mixed phase a marked m_f -dependence is seen in the linewidths. This also suggests the presence of fluctuations affecting the $I \cdot AS$ term in the Hamiltonian [16].

3.2. Temperature dependence of EPR spectra

3.2.1. Ammonium dihydrogen phosphate. The experimental findings are as follows.

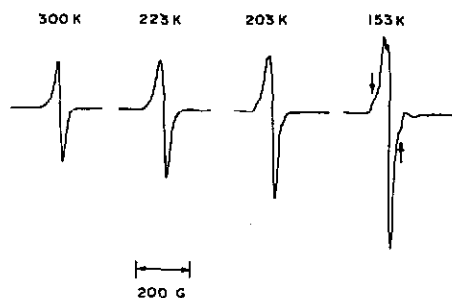


Figure 4. The temperature dependence of the high-field line of AsO_4^{3-} in RDP. The evolution of the ^1H SHFS at 203 K and below may be observed. The satellites appearing on either side of the line are shown by arrows. The asymmetry in the pattern is probably due to the magnetic hyperfine interaction of Rb isotopes.

(i) Above room temperature the AsO_4^{3-} spectra in ADP show a resolved quintet SHFS because of four equivalent protons.

(ii) As the temperature is lowered, the quintet structure changes to a triplet structure at around 273 K, which is well above the AFE transition temperature. This has been ascribed [10] to a slowing of the hydrogen-bond motion well above the transition temperature of 148 K. This results in the formation of AFE clusters, as monitored by paramagnetic AsO_4^{3-} even at 273 K.

(iii) On further cooling, the hyperfine lines split at the transition temperature, 148 K, and their intensity decreases drastically. The intensity of the lines plotted as a function of temperature shows (figure 3) a sudden drop at T_c as the temperature was lowered. With the AsO_4^{3-} probe this feature is unique for it is the only parameter in the EPR spectrum of AsO_4^{3-} which shows a drastic change at $T_c = 148$ K, unlike the ^1H SHFS which changes at $T^* = T_c + 125$ K. This feature has been used in the present work to monitor the 'smearing out' of ordered phase as the Rb concentration is increased from the NH_4 -rich side of the phase diagram. This will be discussed in section 3.2.3.

3.2.2. *Rubidium dihydrogen phosphate.* The experimental findings, given in the same order as in 3.2.1, are as follows.

(i) In RDP the ^{75}As hyperfine lines do not show resolved SHFS because of acid protons at room temperature unlike the case of ADP.

(ii) On cooling, the ^{75}As hyperfine lines start to show asymmetric and partially resolved structure below 203 K (figure 4). This temperature is 56 K above T_c . It is likely that the structure is due to acid protons, which becomes observable following the quintet-to-triplet transition. $T^* = T_c + 56$ K in the case of RDP may be compared with $T^* = T_c + 125$ K in ADP. Further, the clear asymmetry in the unresolved structure suggests possible magnetic interactions due to Rb isotopes with $I = \frac{5}{2}$ and $\frac{3}{2}$.

(iii) On further cooling, the temperature dependence of the intensity shows a marked decrease, from the expected Curie law, at T_c . This is included in figure 3 together with similar data on ADP. This is presumably due to the increased dielectric constant and associated decrease in Q of the cavity.

3.2.3. *Mixed rubidium ammonium dihydrogen phosphate.* The mixed crystals do not show resolved SHFS at room temperature. For $x = 0.95$ a poorly resolved structure has been observed and it becomes less resolved with further decrease in x . This feature for the high-field line of AsO_4^{3-} in ADP, RDP ($x = 0.95, 0.9, 0.8$ and 0.5) and RDP, is shown

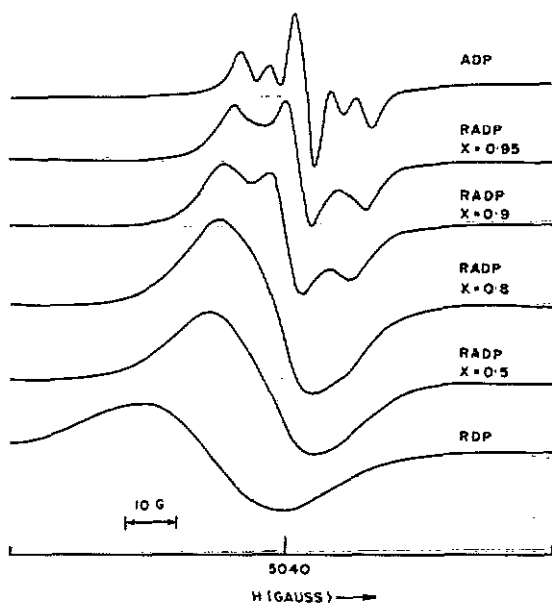


Figure 5. The high-field line of AsO_4^{3-} in ADP, RADP ($x = 0.95, 0.9, 0.8$ and 0.5) and RDP at room temperature, with $H \parallel c$. The quintet-to-triplet transition as 5% Rb was added to ADP clearly illustrates the effect of RDP in slowing down the O-H...O dynamics. In the concentration range $x \leq 0.8$, the ^1H SHFS is completely washed out because of the FE \leftrightarrow AFE fluctuation (see text).

in figure 5. This figure illustrates clearly the effect of Rb on the slowing down of acid protonic motion and also the shift in the resonance field of $m_l = \frac{3}{2}$ (high-field) line with increased Rb concentration. EPR measurements were carried out for RADP, with all the compositions mentioned, in the 25–425 K temperature region. Above room temperature the quintet structure was observed for $x = 0.95$ and $x = 0.9$ at 315 K and 360 K, respectively. This is shown in figure 6. The temperature dependence in the temperature range below room temperature has been investigated to examine the effects at PE \rightarrow AFE-glass phase transitions. Although both RDP and ADP show splitting of the As hyperfine lines at low temperatures, no splitting was observed in RADP with $x = 0.5$ and 0.8 down to 25 K. However, in RADP with $x = 0.95$ and $x = 0.9$, splitting was observed at around 125 K and 105 K, respectively, and the line intensity also reduced sharply at this temperature. These features are also included in figure 3 together with similar data for samples with $x = 0.8$ and 0.5 . These temperatures for $x = 0.95$ and $x = 0.9$ correspond to the PE \rightarrow AFE transition as seen from the phase diagram given by Courtens [3]. For $x \leq 0.8$, this feature was not observable down to 25 K, suggesting that even at $x = 0.8$ the RADP system does not go into an ordered state.

3.3. Discussion

The important experimental findings of the present investigation may be summarized as follows.

(i) The ^{75}As hyperfine coupling constant becomes averaged between the FE and AFE regions scaled by the respective concentrations of RDP and ADP in RADP (figure 2).

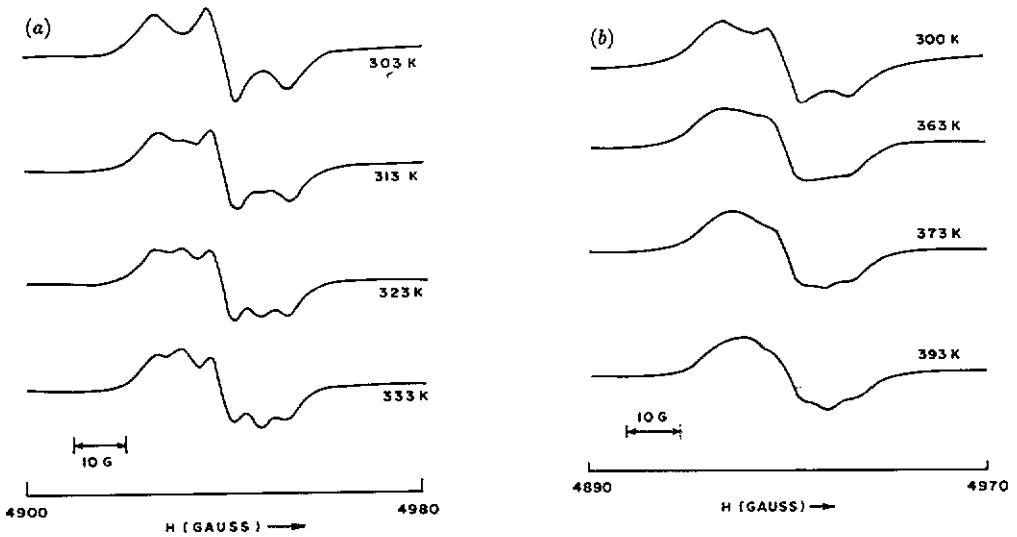


Figure 6. (a) The high-field line of AsO_4^{3-} in RADP ($x = 0.95$) for $H \parallel c$ at the different temperatures shown. The quintet-to-triplet transition takes place at around 313 K. (b) The high-field line of AsO_4^{3-} in RADP ($x = 0.9$) for $H \parallel c$ at the different temperatures shown. The quintet-to-triplet transition takes place at around 363 K.

(ii) The ^{75}As hyperfine quartet exhibits a prominent m_I -dependence of linewidths in RADP ($x = 0.5$), particularly when $H \parallel a, b$ (figure 1).

(iii) The quintet ^1H SHFS observed in pure ADP at room temperature is also observed in RADP with $x = 0.95$ and 0.9 above room temperature. The quintet transforms into a triplet in RADP, at around room temperature, as the amount of Rb is progressively increased up to 10%; even this structure disappears in RADP for $x = 0.8$ and below.

(iv) The splitting of lines and reduction in intensity observed at T_c in ADP were absent in mixed crystals for $x < 0.9$ and this feature can, therefore, be used for monitoring the absence of AFE ordering in the NH_4 -rich side of the phase diagram.

The difference in the ^{75}As hyperfine coupling constants in KDP-type hydrogen-bonded FES and AFES was explained by Dalal *et al* [13] as due to the difference in cationic sizes. The differences between the ^{75}As hyperfine structures of ADP (AFE) and RDP (FE), which have cations of the same size, we believe, arise primarily owing to differences in the respective Slater configurations and can practically be used for monitoring the FE and AFE clusters in RADP, as the differences in hyperfine constants are significant. The first two findings mentioned above, therefore, clearly show that fluctuations exist between FE and AFE ordering when the concentration of NH_4^+ decreases below 0.9 in RADP. Furthermore, these observations give a clear way of identifying the formation of a mixed phase even at room temperature. This has become possible because of the unique nature of the $(\text{H}_2\text{AsO}_4)^{2-}$ centre in ADP and ADP-like systems wherein it takes the local FE and AFE ordering at temperatures much higher than the bulk transition temperatures. The fluctuation becomes averaged if its characteristic time τ is shorter than $(A_{\text{FE}} - A_{\text{AFE}})^{-1}$ in frequency units.

An important question addressed by us is whether these fluctuations are artefacts of the slowing down of $\text{O}-\text{H} \cdots \text{O}$ protonic motion presumably [5, 8] associated with glass

formation or whether they are different. The observation of the triplet structure at room temperature in RADP ($x = 0.95$ and 0.9), as mentioned in finding (iii) above, in contrast with the quintet structure in ADP at room temperature (see figure 5) clearly gives direct EPR evidence of slowing down the O–H . . . O dynamics in the mixed crystal. In RADP ($x = 0.95$) the quintet structure was observable only above 315 K, whereas in RADP ($x = 0.9$) this temperature rose further to 360 K (figure 6). This clearly establishes that the unusual slowing down of the O–H . . . O motion is more a characteristic of mixed RADP crystal, which may or may not form a glass. On the other hand, the ^1H SHFS (with triplet or quintet) was completely washed out in RADP ($x \leq 0.8$) throughout the temperature range investigated (up to 423 K). This feature is observable only in the Rb– NH_4 composition range, $x \leq 0.8$, facilitating glass formation. This implies the existence of another fluctuation ‘washing out’ the ^1H SHFS in this range of compositions of RADP. This observation, together with the concentration dependence of A (^{75}As) (see figure 2) is a strong pointer towards the existence of FE–AFE fluctuations. This clearly suggests that the fluctuations causing averaging between local FE and AFE configurations is intrinsic to the glass formation and is distinguishable from that causing polarization fluctuations arising because of slowing down of the hydrogen motion in the O–H . . . O bond. Furthermore, the characteristic frequency of this fluctuation, 30–50 MHz, is nearly equal to that of the close proton hyperfine structure of 33 MHz, explaining the ‘washing out’ of this structure in RADP. Therefore, we believe that the present results give strong evidence for the existence of a fluctuation between FE and AFE configurations of $(\text{H}_2\text{AsO}_4)^{2-}$ with characteristic frequency 30–50 MHz ($T = 3 \times 10^{-8}$ s).

Muller [15] has discussed in detail the nature of the slow dynamics of AsO_4^{4-} centres in hydrogen-bonded FEs and its coupling to the local soft modes. His analysis clearly established the Halperin–Varma (HV) [17] nature of the AsO_4^{4-} centre, with local probe dynamics modifying the protonic soft mode dynamics, leading to dynamic central peak in these materials. This coupling is proportional to the concentration of the defects. The HV centre reorients slowly with its characteristic time, $\tau = \tau_0 \exp(E/kT)$, with $\tau = 10^{-8}$ s and $E = 0.2$ eV. It was shown by Binder [18] that these HV centres have zero critical dimensionality and no true freeze-out can occur, with the system jumping between the two states $\pm \langle S_p^z(T) \rangle$ with temperature-dependent activation energy. We believe that this formalism aptly describes the present experimental results with the states $\pm \langle S_p^z(T) \rangle$ corresponding to the local FE and AFE states of the system, resulting in the effective ^{75}As hyperfine coupling constant as the weighted average of FE and AFE constituents. In pure KDP and ADP-like systems the behaviour of AsO_4^{4-} essentially served as premonition of what was to happen at lower temperatures, and hence a similar behaviour is expected in RADP. Therefore, we conclude by stating that slow fluctuation between FE and AFE clusters with a characteristic time of the order of 10^{-8} s plays an important role in the glass formation of RADP.

4. Conclusions

We have given EPR evidence for slowing down the O–H . . . O dynamics in RADP even for $x = 0.95$ and 0.9 , which do not exhibit a glass transition. This proves that this O–H . . . O slowing down is more a characteristic of the ‘mixed crystal’ than of glass formation. Furthermore, we have shown that there exist fluctuations between the FE and AFE configurations of $(\text{H}_2\text{AsO}_4)^{2-}$, with a characteristic frequency 30–50 MHz in RADP ($x \leq 0.8$). This may be identified with the expected behaviour of HV type of centres

having a fluctuation between two Ising-like states (FE and AFE configurations) down to very low temperatures.

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