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REPLY TO COMMENT

The existence of ferroelectric–antiferroelectric fluctuations in $\text{Rb}_{1-x}(\text{NH}_4)_x\text{H}_2\text{PO}_4$

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Abstract. By taking ^{75}As hyperfine coupling constants for AsO_4^{4-} in hydrogen bonded crystals of RbH_2PO_4 and $(\text{NH}_4)\text{H}_2\text{PO}_4$ as fingerprints of ferroelectric (FE) and antiferroelectric (AFE) phases respectively, it is shown that the variation of the coupling constant as a weighted average of Rb^+ and NH_4^+ concentrations in $\text{Rb}_{1-x}(\text{NH}_4)_x\text{H}_2\text{PO}_4$ clearly proves the existence of FE and AFE fluctuations in the mixed crystal.

We [1] have recently investigated the dipolar glass formation in $\text{Rb}_{1-x}(\text{NH}_4)_x\text{H}_2\text{PO}_4$ (abbreviated as RADP) by electron paramagnetic resonance (EPR) using an AsO_4^{4-} probe. An important outcome of our investigation is the evidence for the existence of ferroelectric (FE) and antiferroelectric (AFE) fluctuations in RADP, which are slowed down, resulting in the dipolar glass transition, at low temperatures. In arriving at this conclusion, we used the ^{75}As hyperfine (HF) coupling constant for AsO_4^{4-} in RbH_2PO_4 (RDP) and $(\text{NH}_4)\text{H}_2\text{PO}_4$ (ADP) as ‘fingerprints’ or ‘characteristics’ of FE and AFE ordering respectively in these hydrogen bonded crystals. Dalal *et al* [2] earlier investigated the cation dependence of the ^{75}As HF coupling constant for AsO_4^{4-} in a number of hydrogen bonded crystals of the KH_2PO_4 family. Their studies showed that the HF coupling constants varied smoothly with cation size in all FE crystals. The case of ADP was, however, found to be an exception to this behaviour. Though Rb^+ and NH_4^+ have almost the same size, the ^{75}As HF coupling constants were significantly different in these lattices. We attributed this difference to FE and AFE ordering in RDP and ADP respectively. It was clearly shown in our work [1] that, in RADP, the ^{75}As HF constant varied smoothly as the weighted average between pure RDP and ADP values. This is a well known ‘characteristic’ of dynamic averaging between two constituents or configurations. Without even referring to this important finding Kahol *et al* [3] found it appropriate to disagree with our conclusion on the existence of FE–AFE fluctuations and attributed the experimental features to a combination of strain broadening and motional broadening effects. Their efforts were solely concentrated on the effect of Rb HF coupling on the line width/shape. In understanding the RADP problem, mentioned above, our approach was to first identify the ‘fingerprints’ of FE and AFE phases, as the glass formation is believed to be caused by the frustration arising out of these competing interactions. As mentioned above, the ^{75}As HF structure was seen to hold the key information in this respect. This important aspect was not addressed by Kahol *et al* and hence their statement on the non-existence of FE–AFE fluctuations is not justified. They invoke the time-dependent $^{85,87}\text{Rb}$ and ^1H superhyperfine interactions to explain the line width/shape changes and the apparent

slowing down of AsO_4^{4-} motion. They attributed the broadening effects and quintet to triplet transition in RADP to lattice strains in combination with paramagnetic centres local dynamics. In RADP, Rb^+ and NH_4^+ have almost identical charge and size and are not expected to create significant lattice strains. If these existed and contributed to the slowing down of the probe dynamics, this should be seen in the occurrence of the quintet to triplet transition on different ^{75}As HF lines (different m_I values) at different temperatures. Both dynamic averaging and local strains contribute to m_I dependent line widths. However, the averaging of the HF coupling constant will occur only in the former case. We have shown this to be the case for AsO_4^{4-} in RADP. We also have clearly mentioned in our paper [1] the possible effects of Rb hyperfine coupling in RDP, resulting in the broadening of lines. We do not dispute the possible role of interplay of the local dynamics of the probe and the Rb superhyperfine interaction. This is, in fact, consistent with our interpretation, in which the local dynamics of the probe in RADP is associated with FE–AFE fluctuations. This is due to the fact that FE and AFE configurations basically depend only on the presence of Rb^+ and NH_4^+ ions in the immediate vicinity of $(\text{H}_2\text{AsO}_4)^-$ units.

In conclusion, we reiterate the existence of FE–AFE fluctuations in RADP as evidenced by the weighted average value of the ^{75}As HF coupling constant for AsO_4^{4-} in RADP between pure RDP and ADP values.

References

- [1] Babu Y, Sastry M D and Dasannacharya B A 1992 *J. Phys.: Condens. Matter* 4 1819–27
- [2] Dalal N S, Dickinson J R and McDowell C A 1972 *J. Chem. Phys.* 57 4254–65
- [3] Kahol P K, Lao X, Costello M B and Dalal N S 1994 *J. Phys.: Condens. Matter* 6 2971