Novel Applications of the Variable Temperature Probe for the 900 MHz Wide Bore Magnet : First Evidence From ^{1}H MAS of the Coexistence of Order-Disorder and Displacive Features at the Paraelectric-Antiferroelectric Phase Transition of $NH_4H_2AsO_4$

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Introduction

Using the newly designed VT probe for the Wide bore 900 spectrometer, we report the first ^{1}H NMR evidence of the coexistence of order-disorder and displacive features at the antiferroelectric phase transition in $NH_4H_2AsO_4$ (ADA). ADA exhibits a paraelectric (PE) to antiferroelectric (AFE) phase transition at T_N ~ 216 K whose mechanism remains unclear. Employing the high-field, high resolution ^{1}H MAS NMR at 900 MHz, we measured the temperature dependence of the isotropic chemical shift as well as spin-lattice relaxation times of the O-H…O (acid) and NH_4^+ protons individually to probe the roles of both sets of protons. Our data reported herein strongly suggest that the AFE transition in ADA contains characteristics of both an order-disorder and a displacive transition. This result is significant since it shows that an equilibrium phase transition can be both 'order-disorder' and 'displacive' type, a novel concept in this field [1].

Experimental

A small piece of ADA single crystal was packed in a 3.2 mm MAS rotor and used for ^{1}H MAS NMR lineshape and spin-lattice relaxation time (T_1) measurements on a ultra-wide bore 900 MHz magnet equipped with a Bruker Avance III NMR console using a spinning speed of 13.5 kHz. The low temperature variable-temperature (VT) experiments on the 900 UWB magnet were carried out using an NHMFL-designed and fabricated 3.2 mm double resonance MAS probe with cooling both the bearing and VT channels.

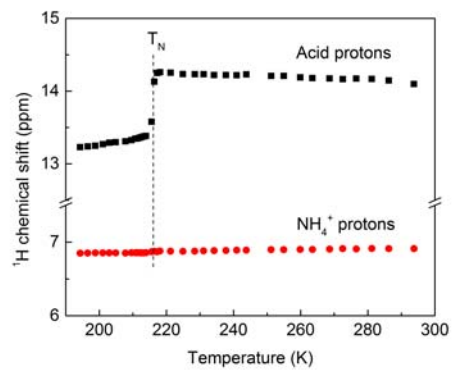

Fig. 1. Temperature dependence of ^{1}H δ_{iso} in ADA showing anomaly at T_N for acid protons.

Results and Discussion

Fig. 1 shows the temperature dependence of the isotropic chemical shift (δ_{iso}) on cooling through T_N. The δ_{iso} of the O-H…O (acid) protons undergoes a significant abrupt change around the T_N, implying the presence of a displacive character for the acid protons. On the other hand, the δ_{iso} of NH_4^+ protons remains unchanged through the T_N, showing that the NH_4^+ groups execute an order-disorder and not a displacive character. Using the E_a and τ_0 values yielded from the BPP fitting of the spin-lattice relaxation rates ($1/T_1$), the calculated correlation times (τ_c) of both protons (Fig. 2) are found to increase by one order of magnitude in going from the PE to the AFE phase (below T_N). The motional parameters of all the protons are essentially equal. The motion slows down anomalously across the T_N and thus seems to be the mechanism of the AFE phase transition.

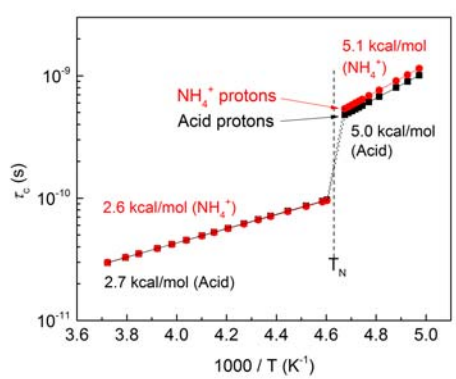

Fig. 2. Temperature dependence of correlation times in ADA; showing sharp break at T_N.

Conclusions

The 900 MHz ^{1}H MAS NMR measurements enable us to study the mechanism of the PE-AFE phase transition in ADA, using as probes both the acid (O-H…O) and NH_4^+ protons. The transition exhibits simultaneously features of both order-disorder and displacive type, a long sought-after feature.

Acknowledgement

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Reference

[1] Kweon, J.J., *et al.*, submitted to J. Phys. Chem. C (2014).