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^{1}H–^{17}O nuclear-quadrupole double-resonance study of random fields in $K_{0.5}(NH_4)_{0.5}H_2PO_4$

J Seliger and V Žagar

J Stefan Institute, University of Ljubljana, Jamova 39, 61000 Ljubljana, Slovenia

Abstract. The second moment $\langle p^2 \rangle$ of the local polarization distribution $W(p)$ has been measure in $K_{0.5}(NH_4)_{0.5}H_2PO_4$ as a function of temperature by a ^{1}H–^{17}O nuclear-quadrupole double-resonance technique. The temperature variation of $\langle p^2 \rangle$ is well described by a dynamic disorder of randomly asymmetric O–H...O hydrogen bonds. The variance Δ of the Gaussian distribution of random fields which induce the asymmetry of the O–H...O hydrogen bonds is equal to $(k_B \times 54 \text{ K})^2$.

1. Introduction

Proton and deuteron pseudo-spin glass [1–3] are characterized by a random freeze out of the hydrogen and deuterium motion between the two possible positions in the O–H...O hydrogen bonds. This situation occurs in the solid solutions of KH_2PO_4-type ferroelectrics and antiferroelectrics. In spite of many investigations it is still not completely clear whether these systems undergo pseudo-spin-glass transitions of the Ising type driven by randomly frustrated competing interactions or just a strong random-field-type single-particle freezing [4, 5]. Neither is it completely understood which structural parameters influence the intensities of random fields and random interactions and are thus directly related to the occurrence of the glass phase.

The proton and deuteron pseudo-spin glasses are characterized by the Edwards–Anderson order parameter q_{EA} which is in fact the second moment $\langle p^2 \rangle$ of the average probability distribution function $W(p)$ of the local polarization p. The Edwards–Anderson order parameter has no macroscopic conjugate field. It is therefore hard to measure directly. It was recently shown that NMR, NQR and EPR techniques offer the possibility of a direct experimental determination of q_{EA}.

In deuteron glasses deuterium represents a local probe which directly probes the polarization of an O–D...O hydrogen bond [5], that is, its quadrupole-perturbed NMR frequency depends linearly on the local polarization p. The second moment of the quadrupole-perturbed deuterium NMR line is thus proportional to $\langle p^2 \rangle$, i.e. to the Edwards–Anderson order parameter. Deuterium NMR measurements in $Rb_{0.56}(ND_4)_{0.44}D_2PO_4$ show that in this substance the random-bond-type pseudo-spin-glass transition is smeared by the presence of quenched random fields [4, 5]. The nominal glass transition temperature is $T_g = 90$ K whereas the random-field contribution is $T_f = 53$ K.

In undeuterated $Rb_{1-x}(NH_4)_x H_2 PO_4$ (RADP) the static and dynamic features of the glass transition have been studied by Tl^{2+} EPR in Tl-doped substances [6]. The static

features can be described by a random-field smearing of a random-bond Ising pseudo-spin-glass transition with a nominal glass transition temperature of $T_g = 30$ K and the random field contribution of $T_f = 60$ K. The dynamic features show up as a slowing down of the proton intra-O–H...O bond motion.

Another local probe which directly probes the polarization of an O–H...O hydrogen bond is ^{17}O. It appears at a rather low natural concentration of 0.037% but it can be easily detected by a highly sensitive ^{1}H–^{17}O nuclear-quadrupole double-resonance (NQDR) technique [7]. The second moment of a ^{1}H–^{17}O NQDR line can be directly related to the second moment $\langle p^2 \rangle$ of the average local polarization distribution function [8, 9]. The ^{1}H–^{17}O NQDR measurements in the solid solution $Rb_{1-x}Tl_xH_2PO_4$ (RTlDP) show [8] that in this substance also the random-bond Ising pseudo-spin-glass transition is smeared by the presence of quenched random fields. The nominal glass transition temperature is $T_g = 210$ K whereas the random field contribution is $T_f = 130$ K. In $Rb_{0.5}(NH_4)_{0.5}H_2PO_4$ the ^{1}H–^{17}O NQDR measurements were performed far above T_g for experimental reasons [9]. The nominal glass transition temperature was not determined precisely ($T_g \cong 50$ K) but the random field contribution $T_f = 100$ K was determined with a higher precision.

The solid solution $K_{1-x}(NH_4)_xH_2PO_4$ (KADP) of ferroelectric KH_2PO_4 (KDP) and antiferroelectric $(NH_4)H_2PO_4$ (ADP) undergoes a ferroelectric phase transition when $x < 0.17$ or an antiferroelectric phase transition when $x > 0.85$ [10]. In the intermediate concentration range dielectric anomalies occur [10, 11]. These dielectric anomalies are similar to the dielectric anomalies observed in the proton glass $Rb_{1-x}(NH_4)_xH_2PO_4$, which suggests that KADP shows glassy behaviour. The results of an x-ray diffraction study of KADP [12] show that the thermal parameters U_{11} for K, P and O atoms are not proportional to absolute temperature at around 110 K. These anomalies are understood as the result of random and static displacements of K, P and O atoms. The low-temperature lattice dynamics of KADP has been studied using high-resolution inelastic neutron scattering [13]. The results show that the mean square displacements of hydrogen-bonded acid protons are larger in the glass phase than in the ordered ferroelectric and antiferroelectric phases.

In order to determine the Edwards–Anderson order parameter q_{EA} in KADP and to relate the temperature variation of q_{EA} to the distribution of random fields we decided to perform a ^{1}H–^{17}O NQDR study of $K_{0.5}(NH_4)_{0.5}H_2PO_4$.

2. Experimental details

^{17}O has a spin 5/2 and thus three doubly degenerate quadrupole energy levels in zero magnetic field. The energies of the three nuclear-quadrupole energy levels are the solutions X of the secular equation

$$X^3 - 7(3 + \eta^2)X - 20(1 - \eta^2) = 0 \tag{1}$$

multiplied by $eQV_{ZZ}/40$. Here eQV_{ZZ}/h is the quadrupole coupling constant and η is the asymmetry parameter of the electric-field-gradient tensor at the site of the nucleus. None of the three nuclear-quadrupole-resonance (NQR) transitions is forbidden, except for $\eta = 0$, and the three NQR frequencies are named as

$$\nu_{5/2-1/2} > \nu_{5/2-3/2} \geqslant \nu_{3/2-1/2}. \tag{2}$$

In a symmetric O–H...O hydrogen bond the two oxygen positions are equivalent and only three ^{17}O NQR frequencies are observed. In an asymmetric O–H...O hydrogen bond the two oxygen positions are inequivalent and two sets of three ^{17}O NQR frequencies are observed.

In KH_2PO_4-type systems with the O–H...O bond lengths of 0.25 nm the three ^{17}O NQR frequencies corresponding to a symmetric hydrogen bond are approximately $\nu_{3/2-1/2} = 0.98$ MHz, $\nu_{5/2-3/2} = 1.48$ MHz and $\nu_{5/2-1/2} = 2.46$ MHz. When the bond becomes asymmetric each of the three NQR lines splits into two lines: a broad line corresponding to a ^{17}O–H site and a narrow line corresponding to a ^{17}O...H site. The second moment of the part of the ^{17}O NQR spectra covering both the broad and the narrow NQR line corresponding to the same NQR transition may be related to the square of the local polarization. If we are dealing with a proton glass then the second moment M_2 of the ^{17}O NQR line corresponding to a given NQR transition is related to the Edwards–Anderson order parameter q_{EA} [8, 9] as

$$q_{EA} = [M_2 - (M_2)_{dip}]/\nu_1^2. \tag{3}$$

Here $(M_2)_{dip}$ is the contribution of the rather strong proton–oxygen dipole–dipole interaction to the second moment of the ^{17}O NQR line and ν_1 is the linear expansion coefficient in expanding the ^{17}O NQR frequency in powers of the local polarization p. In the case of the 5/2–3/2 NQR transition $(M_2)_{dip} = 1300$ kHz^2 and $\nu_1^2 = 20\,000$ kHz^2.

The ^{17}O NQR frequencies have been measured by a highly sensitive ^1H–^{17}O NQDR technique based on adiabatic demagnetization and irradiation of the sample in zero static magnetic field by a strong phase-modulated rf magnetic field [7].

3. Results and discussion

The ^1H–^{17}O NQDR spectra corresponding to the 5/2–3/2 transition are shown in figure 1 for paraelectric KDP, paraelectric ADP and $K_{0.5}(NH_4)_{0.5}H_2PO_4$ (KADP). The NQR line of pure KDP is centred at 1450 kHz whereas the NQR line of pure ADP is centred at 1460 kHz. The two lines are of nearly the same width with the second moments of $(M_2)_{dip} = 1300$ kHz^2. The ^1H–^{17}O NQDR lines corresponding to the 5/2–3/2 NQR transition in KADP are shown for three temperatures: 56 °C, 23 °C and −10 °C. It is clearly seen that the NQDR lines in the solid solution are broader than the NQDR lines in pure substances. The width of the NQDR line in KADP increases with decreasing temperature. The second moment M_2 at 56 °C is equal to 1800 kHz^2 whereas at −10 °C it is equal to 2100 kHz^2. The Edwards–Anderson order parameter q_{EA} as calculated from equation (3) is as a function of temperature shown in figure 2. It increases from the value of 0.025 at 56 °C to the value of 0.040 at −10 °C. The temperature dependence of q_{EA} is the consequence of ordering of the O–H...O hydrogen bonds in random fields caused by the random distribution of K^+ and $(NH_4)^+$ over the cation sites. The Edwards–Anderson order parameter $q_{EA} = q$ in the random-bond random-field model [5] is calculated from the self-consistency equation

$$q = (2\pi)^{-1/2} \int_{-\infty}^{\infty} \exp(-z^2/2) \tanh^2[\beta \tilde{J}(q + \tilde{\Delta})^{1/2} z] \, dz. \tag{4}$$

Here $J = k_B T_g$, $\beta = 1/k_B T$, $\tilde{\Delta} = \Delta/\tilde{J}^2$ and Δ is the variance of the Gaussian distribution of random fields which may be expressed as $\Delta = (k_B T_f)^2$. At high temperatures when $T \gg T_g$ equation (4) simplifies to

$$q = (2\pi)^{-1/2} \int_{-\infty}^{\infty} \exp(-z^2/2) \tanh^2[(T_f/T)z] \, dz. \tag{5}$$

The temperature dependence of q_{EA} is consistent with expression (5) when $T_f = 54 \pm 5$ K.

The value of T_f as observed in KADP by the present technique is close to the value $T_f = 53$ K as observed in deuterated RADP by deuterium NMR [4]. It is also close to the
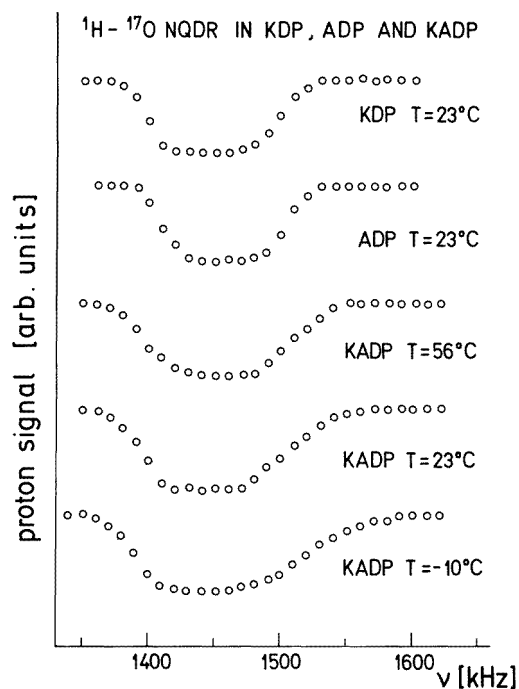
Figure 1. ^1H–^{17}O NQDR spectra at the 5/2–3/2 NQR transition in KDP, ADP and KADP.
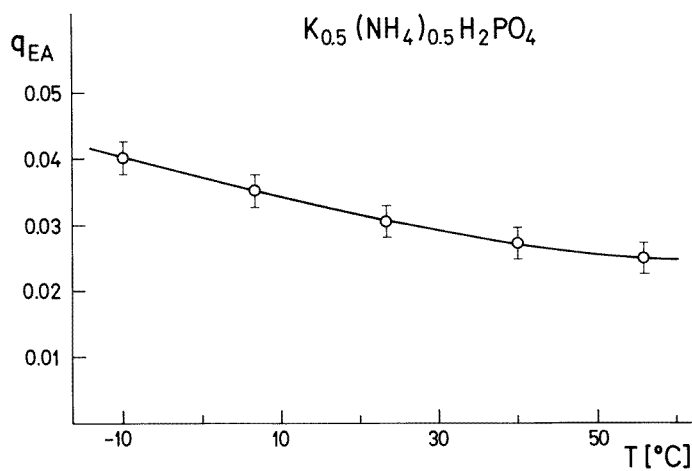

Figure 2. The temperature dependence of the Edwards–Anderson order parameter in KADP. The solid line represents a fit to expression (5) with $T_f = 54$ K.

value $T_f = 60$ K as observed in RADP by Tl^{2+} EPR [6]. The ^{17}O NQR in RADP [9] give, in contradiction with the EPR data, a higher value of $T_f = 100$ K. This discrepancy is not yet understood. In RTlDP the competition of two different crystal structures of the parent compounds is expected to increase the variance of the distribution of random fields. The ^1H–^{17}O NQDR data [8] which give $T_f = 130$ K agree with this expectation.

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