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NMR SPIN LATTICE RELAXATION STUDY OF $\text{Cs}_{1-x}(\text{NH}_4)_x\text{H}_2\text{PO}_4$

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Abstract Spin-lattice relaxation time T_1 for ^{31}P was measured as a function of temperature at 28.2 MHz in a powder sample of $\text{Cs}_{1-x}(\text{NH}_4)_x\text{H}_2\text{PO}_4$ (CADP) crystallized from a solution with a molar ratio $x = 0.2$. This crystal has the same structure as CsH_2PO_4 (CDP), which exhibits a low-temperature pseudo-one-dimensional ferroelectric phase transition at 159 K and a superionic transition at 504 K on heating. The measured temperature dependence is explained in terms of hydrogen bond dynamics.

INTRODUCTION

Crystals which contain mixtures of ferroelectrics and antiferroelectrics have interesting properties due to the frustration resulting from the opposing orderings. Many questions remain about the spatial and temporal behavior of domains and coexistence in such crystals. Cesium dihydrogen phosphate (CDP) is known to have “one-dimensional” ferroelectric order below¹ 159 K and a superionic transition at 504 K on heating,² whereas ADP is antiferroelectric below 148 K. In addition, their paraelectric phases have different structures. In the PE phase CDP is monoclinic ($P2_1/m$) with two units per unit cell. In the FE phase hydrogens along the b -axis order in one of the two off-center sites in the O-H...O bonds. The related shift of the Cs^+ and PO_4^{3-} groups the b -axis yields a spontaneous polarization along the b -axis.³

EXPERIMENT

We sought to learn about the rates of the hydrogen motions in CADP by observing the dipolar interaction between the phosphorus and the nearest hydrogen atoms.

Solutions of CsH_2PO_4 (CDP) and $\text{NH}_4\text{H}_2\text{PO}_4$ (ADP) were prepared by the reaction: $\text{P}_2\text{O}_5 + \text{X}_2\text{CO}_3 + n \text{H}_2\text{O} \rightarrow 2 \text{XH}_2\text{PO}_4 + \text{CO}_2 + (n-2) \text{H}_2\text{O}$, $\text{X} = \text{NH}_4, \text{Cs}$.

The two solutions were then vacuum desiccated before combining them in the fixed molar ratio of 1 mole of ammonium to four moles of cesium. The powders were combined and dissolved in H_2O . The resultant mixture was stirred for more than 24 hours in order to ensure spatial randomness of the NH_4^+ and Cs^+ ions in solution. The solution was crystallized at room temperature by slow (several weeks) evaporation of the solution. In order to maximize the fill factor of the NMR sample coil, several crystals were pulverized. They were then desiccated at 60°C for several days.

We measured the phosphorus (^{31}P) spin-lattice relaxation time T_1 as a function of temperature at 28.2 MHz in a $\text{Cs}_{1-x}(\text{NH}_4)_x\text{H}_2\text{PO}_4$ (CADP) crystal. The results for $x=0.2$ are shown in Fig. 1. There is no evidence for any phase transition in the observed temperature range. The magnetization recovery follows a two-exponential curve indicating a different local environment at the phosphorus site: if the cesium atoms occupy all the neighboring positions (site I), the relaxation is very slow (similar to the pure CDP case), whereas an ammonium group in the vicinity of the phosphorus site (site II) leads to a faster relaxation. From the T_1 minima one can estimate characteristic times of the proton motion.

NMR RELAXATION ANALYSIS

The primary mechanism for T_1 relaxation in our sample is dipolar coupling between the hydrogen and phosphorus nuclei in the lattice. Frequently even minute amounts of paramagnetic impurities will provide the dominant relaxation mechanism. However, the relatively long relaxation times suggest that the level of paramagnetic impurities in the sample was quite low.

FIGURE 1 Temperature dependence of the ^{31}P spin-lattice relaxation time: T_{1S} (circles), T_{1L} (triangles).

Spin $1/2$ ^{31}P has magnetic dipolar relaxation, caused by local magnetic field fluctuations from:

- A. spin diffusion to paramagnetic impurities;
- B. NH^{4+} ion hindered rotation;
- C. proton jumps between $\text{N-H}\dots\text{O}$ and/or $\text{O-H}\dots\text{O}$ bonds (ionic conductivity mechanism)
- D. proton jumps within $\text{O-H}\dots\text{O}$ bonds.

In CADP there is an important difference between the ^{31}P sites with ammonium ion in vicinity (site II) and those without it (site I). Mechanisms A and D are effective at all ^{31}P sites, whereas mechanism B is absent at sites I. Mechanism C is stronger at sites II, where protons jump between both $\text{N-H}\dots\text{O}$ and $\text{O-H}\dots\text{O}$ bonds, than at sites I where $\text{N-H}\dots\text{O}$ bonds are missing. Thus a two-exponential spin-lattice relaxation is expected. The relaxation at sites I and II is described by a longer value T_{1L} and a shorter value T_{1S} , respectively.

The most important contributions to the phosphorus relaxation rate in CADP are determined by the fluctuations of the proton-phosphorus magnetic dipolar interaction Hamiltonian⁴

$$H = \sum_{i < j} \sum_q F_{ij}^{(q)} A_{ij}^{(q)}, \quad (1)$$

where $F_{ij}^{(q)}$ are functions of the relative positions of the two spins and $A_{ij}^{(q)}$ are spin operators. Spin-lattice relaxation rate for the process A has a weak temperature dependence and for the processes B, C, D it is given by⁴

$$T_1^{-1} \propto J^{(0)}(\omega_H - \omega_P) + 18 J^{(1)}(\omega_P) + 9 J^{(2)}(\omega_H + \omega_P), \quad (2)$$

where the spectral density $J^{(q)}(\omega)$ - $q=0,1,2$ - for a relaxation process characterized by a single correlation time τ is proportional to⁴

$$J^{(q)}(\omega) \propto \tau / (1 + \omega^2 \tau^2). \quad (3)$$

The temperature dependence of the short component of the spin-lattice relaxation time T_{1S} shows two minima typical for thermally activated processes. The minimum observed at 328 K with activation energy $E_a \approx 0.35$ eV most probably corresponds to the proton interbond motion because it is observed also for the long component of the spin-lattice relaxation time T_{1L} . The other dip at 162 K is in the right temperature range for NH_4^+ ion hindered rotation, with $E_a \approx 0.16$ eV. These activation energies E_a are estimated from the correlation time τ at the T_1 minimum.

CONCLUSION

The minima obtained in the temperature dependence of spin-lattice relaxation time indicate the existence of different thermally activated processes of the proton motion. We observed the NH_4^+ ion hindered rotations. There is also some evidence for proton jumps between N-H...O and O-H...O bonds and for a better understanding of this mechanism a dielectric and conductivity study of CADP is planned.

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