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Citation: The Journal of Chemical Physics 88, 3260 (1988); doi: 10.1063/1.453921
View online: http://dx.doi.org/10.1063/1.453921
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**17O NQR study of the antiferroelectric phase transition in TiH₂PO₄**

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(Received 13 October 1987; accepted 13 November 1987)

The temperature dependence of the 17O NQR spectra in TiH₂PO₄ has been measured using a proton-17O nuclear quadrupole double resonance technique. The results show that the protons in the short one-dimensionally linked O₁–H₁–O₁ and O₂–H₂–O₂ hydrogen bonds are moving between two equilibrium sites above Tc and freeze into one of the off-center sites below Tc. The protons in the asymmetric O₁–H₁–O₂ hydrogen bonds are static and ordered above and below Tc.

I. INTRODUCTION

TiH₂PO₄ (TIDP) undergoes a slightly discontinuous antiferroelectric phase transition at Tc = 230 K. At room temperature, the primitive cell is monoclinic, with the dimensions a = 14.308(5) Å, b = 4.518(6) Å, c = 6.516(5) Å, and β = 91.76(1)°. The space group is P2₁/a, and there are four formula units per primitive cell. The phase transition is associated with a doubling of the primitive cell along the c axis.

There are three types of the O–H–O hydrogen bonds in the structure. The hydrogen bonds O₁–H₁–O₁, [R(O₁–O₁) = 2.43(1) Å] and O₂–H₂–O₂, [R(O₂–O₂) = 2.47(1) Å], which form zig-zag chains along the c axis, are effectively symmetric above Tc. The protons are either dynamically disordered between the two equilibrium sites or are sitting at the center of the H bond. The hydrogen bonds O₃–H₃–O₄, [R(O₃–O₄) = 2.50(1) Å] are asymmetric with the proton in an off-center position above Tc.

The strong deuteration effect on the transition temperature suggests that the O–H–O nuclei with the intermediate quadrupole coupling constant are approximately twice as intense as the other lines. According to the previous 17O NQR studies of KH₂PO₄-type systems, the 17O quadrupole coupling constant increases with decreasing O–H distance.

In order to elucidate the role of the protons in the antiferroelectric phase transition in TIDP we decided to measure the 17O NQR frequencies as a function of temperature.

II. EXPERIMENTAL RESULTS

17O (I = 5/2) has, in general, three doubly degenerate quadrupole energy levels. Their energies are obtained from the secular equation

\[ x^2 - 7(3 + \eta^2)x - 20(1 - \eta^2) = 0, \]  

where the energy \( E = \alpha x \) and \( \alpha = e^2qQ/4I(2I - 1) \). Here \( qQ \) is the nuclear quadrupole moment, \( \alpha = V_{zz} \) is the largest eigenvalue (\( |V_{zz}| > |V_{rr}| > |V_{xx}| \)) of the electric field gradient (EGF) tensor at the nuclear site and \( \eta = (V_{xx} - V_{rr})/V_{zz} \) is the asymmetry parameter of the EFG tensor. For each chemically inequivalent oxygen site we thus obtain three 17O NQR frequencies \( \nu_{1/2, \pm 3/2} \). The asymmetry parameter \( \eta \) is calculated from the ratio \( \nu_{1/2, - 3/2} / \nu_{1/2, + 3/2} = \eta. \)

The temperature dependence of the 17O NQR frequencies \( \nu_{1/2, \pm 3/2} \) is shown in Fig. 1. The quadrupole coupling constants and asymmetry parameters are shown in Figs. 2 and 3. Above Tc we observe three sets of lines corresponding to three chemically inequivalent oxygen sites. The lines corresponding to the 17O nuclei with intermediate quadrupole coupling constant are approximately twice as intense as the other lines. According to the previous 17O NQR studies of KH₂PO₄-type systems, the 17O quadrupole coupling constant decreases with increasing O–H distance.
assignment. Within each set of three quadrupole constants the NQR lines corresponding to the intermediate one are approximately twice as intense as the others. According to structural studies these two quadrupole coupling constants correspond to the oxygens O₃ and O₄.

A recent ¹⁷O NQR study of the phase transition in diglycine nitrate has shown that the separation between the two equilibrium proton positions in a short O–H–O bond is much smaller than in longer O–H–O bonds. If we assume that the same is true here we may assign the largest and the smallest quadrupole coupling constant to the sites O₂–H–O₂’ and O₂–H₂–O₂.

III. DISCUSSION

The ¹⁷O NQR data show that the hydrogens H₁ and H₂ are above Tₑ effectively in the centers of the hydrogen bonds. Below Tₑ they freeze into off-center positions. The displacement of one of them (supposedly H₁) is much smaller than the displacement of another one (H₂). The hydrogen H₂ is ordered already above Tₑ in a general position. Below Tₑ it displaces closer to the oxygen O₃.

The near temperature independence of the ¹⁷O NQR frequencies of ¹⁷O and ¹⁷O in the paraelectric phase and the fact that the corresponding EFG tensors above Tₑ are approximate, the averages of the EFG tensors below Tₑ seem to show that an order–disorder transition of O₁–H–O₁ and O₂–H–O₂ is more likely than a displacive transition. This
would mean that the protons in the $\text{O}_1$-$\text{H}$-$\text{O}_2$ and $\text{O}_2$-$\text{H}$-$\text{O}_2$ bonds are moving above $T_c$, between two off-center sites and that his motion freezes out below $T_c$.

Measurements of the dipolar fine structure$^{9,10}$ of the $^{17}\text{O}$ NQR lines—which could provide a direct proof of the order–disorder character of the transition—cannot be done at present due to the short proton spin–lattice relaxation time in zero magnetic field.
