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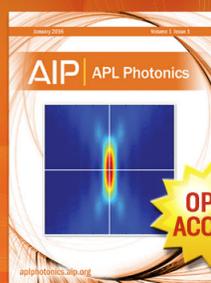
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^{17}O NQR study of the antiferroelectric phase transition in TiH_2PO_4

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The temperature dependence of the ^{17}O NQR spectra in TiH_2PO_4 has been measured using a proton- ^{17}O nuclear quadrupole double resonance technique. The results show that the protons in the short one-dimensionally linked $\text{O}_1\text{-H}_1\text{-O}_1$ and $\text{O}_2\text{-H}_2\text{-O}_2$ hydrogen bonds are moving between two equilibrium sites above T_c and freeze into one of the off-center sites below T_c . The protons in the asymmetric $\text{O}_3\text{-H}_3\text{-O}_4$ hydrogen bonds are static and ordered above and below T_c .

I. INTRODUCTION

TiH_2PO_4 (TIDP) undergoes¹⁻³ a slightly discontinuous antiferroelectric phase transition at $T_c = 230$ K. At room temperature,⁴ the primitive cell is monoclinic^{4,5} with the dimensions $a = 14.308(5)$ Å, $b = 4.518(6)$ Å, $c = 6.516(5)$ Å, and $\beta = 91.76(1)^\circ$. The space group is $P2_1/a$, and there are four formula units per primitive cell. The phase transition³ is associated with a doubling of the primitive cell along the a and b axes.

There are three types of the O-H-O hydrogen bonds in the structure. The hydrogen bonds $\text{O}_1\text{-H}_1\text{-O}_1$ [$R(\text{O}_1\text{-O}_1) = 2.43(1)$ Å] and $\text{O}_2\text{-H}_2\text{-O}_2$ [$R(\text{O}_2\text{-O}_2) = 2.47(1)$ Å], which form zig-zag chains along the c axis, are effectively symmetric above T_c . The protons are either dynamically disordered between the two equilibrium sites or are sitting at the center of the H bond. The hydrogen bonds $\text{O}_3\text{-H}_3\text{-O}_4$ [$R(\text{O}_3\text{-O}_4) = 2.50(1)$ Å] are asymmetric—with the proton in an off-center position—above T_c .

The strong deuteration effect on the transition temperature T_c ¹ as well as on the pressure dependence of it, dT_c/dp ,⁶ suggests that the O-H-O bonds play an important role in the phase transition.

Structural studies³ suggest that the phase transition in TIDP is, similarly as in the related monoclinic CsH_2PO_4 , connected with a pseudo-one-dimensional proton ordering in the hydrogen bonded chains along the c axis.

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

II. EXPERIMENTAL RESULTS

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

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

where the energy $E = xA$ and $A = e^2qQ/4I(2I - 1)$. Here eQ is the nuclear quadrupole moment, $eq = V_{ZZ}$ is the largest eigenvalue ($|V_{ZZ}| \geq |V_{YY}| \geq |V_{XX}|$) of the electric field gradient (EFG) tensor at the nuclear site and $\eta = (V_{XX} - V_{YY})/V_{ZZ}$ is the asymmetry parameter of the EFG tensor. For each chemically inequivalent oxygen site

we thus obtain three ^{17}O NQR frequencies $\nu_{1/2 \leftrightarrow 3/2} \leq \nu_{3/2 \leftrightarrow 5/2} < \nu_{1/2 \leftrightarrow 5/2} = \nu_{1/2 \leftrightarrow 3/2} + \nu_{3/2 \leftrightarrow 5/2}$. The asymmetry parameter η is calculated from the ratio $\nu_{1/2 \leftrightarrow 3/2} / \nu_{3/2 \leftrightarrow 5/2}$. When η is known the quadrupole coupling constant e^2qQ/h can be calculated from any NQR frequency.

The ^{17}O NQR spectra in naturally abundant (0.037% ^{17}O) TIDP samples have been measured by means of ^1H - ^{17}O nuclear quadrupole double resonance^{7,8} based on magnetic field cycling.

The temperature dependence of the ^{17}O NQR frequencies $\nu_{1/2 \leftrightarrow 3/2}$ and $\nu_{3/2 \leftrightarrow 5/2}$ is shown in Fig. 1. The corresponding quadrupole coupling constants and asymmetry parameters are shown in Figs. 2 and 3. Above T_c we observe three sets of lines corresponding to three chemically inequivalent oxygen sites. The lines corresponding to the ^{17}O nuclei with the intermediate quadrupole coupling constant are approximately twice as intense as the other lines. According to the previous ^{17}O NQR studies of KH_2PO_4 -type systems^{9,10} the ^{17}O quadrupole coupling constant increases with decreasing O-H distance. We can therefore safely assume that the largest quadrupole coupling constant corresponds to the oxygen O_3 —i.e., to the shortest O-H distance—and that the smallest quadrupole coupling constant corresponds to the oxygen O_4 , i.e., to the largest O-H distance. The intermediate quadrupole coupling constant corresponds to the oxygens O_1 and O_2 , i.e., to the two effectively symmetric H bonds $\text{O}_1\text{-H}_1\text{-O}_1$ and $\text{O}_2\text{-H}_2\text{-O}_2$. Here, in fact, two quadrupole coupling constants should be observed since the oxygens O_1 and O_2 are chemically inequivalent. The reason that within the experimental resolution (20 kHz) the $^{17}\text{O}_1$ NQR lines are not separated from the $^{17}\text{O}_2$ NQR lines is probably due to the fact that in disordered rather short O-H-O bonds of KH_2PO_4 -type systems⁹⁻¹¹ the ^{17}O NQR frequencies depend only slightly on the O-O distance.

Below T_c we observe six quadrupole coupling constants which can be divided into two sets. The three larger quadrupole coupling constants correspond to the “close” proton sites with the short O-H distances while the three smaller quadrupole coupling constants correspond to the “far” proton sites with the long O-H distances. In addition it was observed that the width of the ^{17}O NQR lines—which is due to proton- ^{17}O dipolar coupling—increases with increasing ^{17}O quadrupole coupling constant thus supporting the above

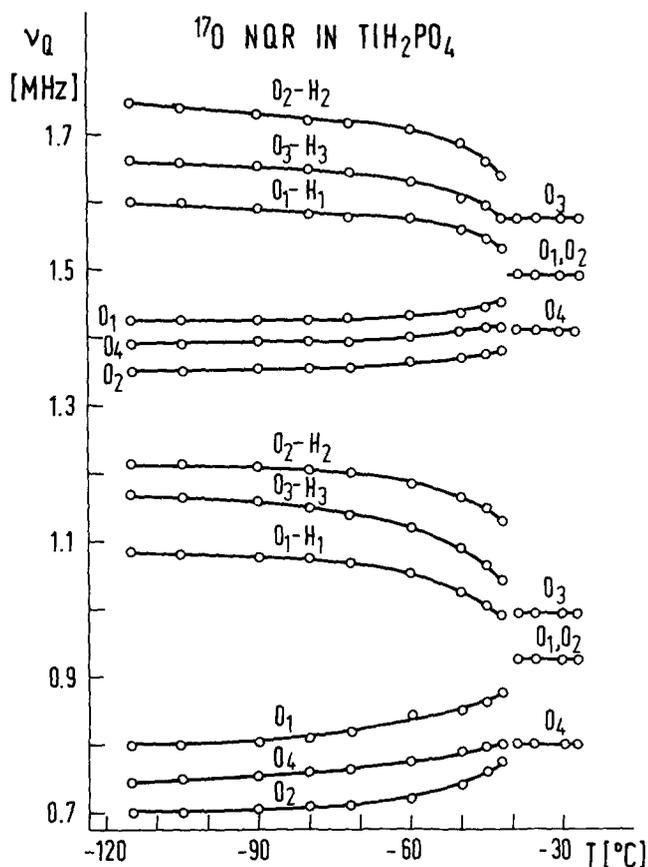


FIG. 1. Temperature dependence of the ^{17}O NQR frequencies in TIDP. The assignment procedure is given in the text.

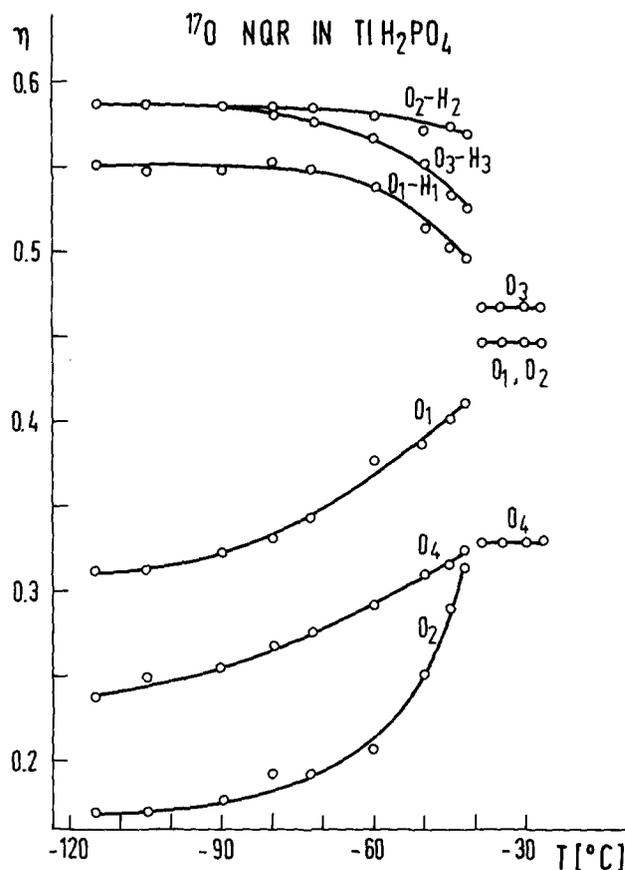


FIG. 3. Temperature dependence of the ^{17}O asymmetry parameters η in TIDP.

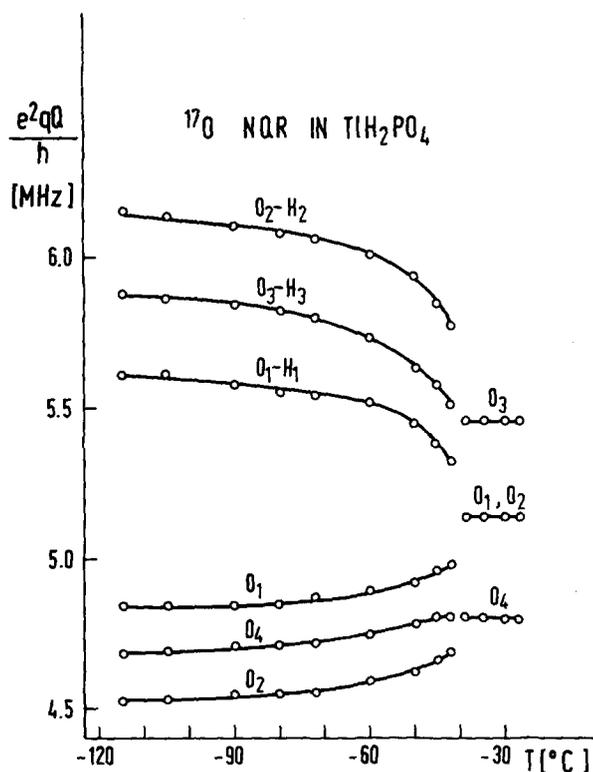


FIG. 2. Temperature dependence of the ^{17}O quadrupole coupling constants e^2qQ/h in TIDP.

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 studies⁵ these two quadrupole coupling constants correspond to the oxygens O_3 and O_4 .

A recent ^{17}O NQR study¹² of the phase transition in diglycine nitrate has shown that the separation between the two equilibrium proton positions in a short $\text{O}-\text{H}-\text{O}$ bond is much smaller than in longer $\text{O}-\text{H}-\text{O}$ bonds. If we assume that the same is true here we may assign the largest and the smallest quadrupole coupling constant to the sites $^{17}\text{O}_2-\text{H}-\text{O}_2$ and $\text{O}_2-\text{H}_2-^{17}\text{O}_2$.

III. DISCUSSION

The ^{17}O NQR data show that the hydrogens H_1 and H_2 are above T_c effectively in the centers of the hydrogen bonds. Below T_c they freeze into off-center positions. The displacement of one of them (supposedly H_1) is much smaller than the displacement of another one (H_2). The hydrogen H_3 is ordered already above T_c in a general position. Below T_c it displaces closer to the oxygen O_3 .

The near temperature independence of the ^{17}O NQR frequencies of ^{16}O and ^{20}O in the paraelectric phase and the fact that the corresponding EFG tensors above T_c are approximate, the averages of the EFG tensors below T_c seem to show that an order-disorder transition of $\text{O}_1-\text{H}-\text{O}_1$ and $\text{O}_2-\text{H}-\text{O}_2$ is more likely than a displacive transition. This

would mean that the protons in the O_1-H-O_1 and O_2-H-O_2 bonds are moving above T_c between two off-center sites and that this motion freezes out below T_c .

Measurements of the dipolar fine structure^{9,10} of the ^{17}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.

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