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The Hydrogen Position in Tin(II) Hydrogen Phosphate by Nuclear Magnetic Resonance

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Abstract The crystal structure of SnHPO_4 has been studied by X-ray and neutron diffraction independently. Re-examination of the hydrogen position by means of proton and phosphor NMR second moments shows that measured second moments, 1.80 ± 0.03 and 2.14 ± 0.05 in 10^{-8}T^2 , for proton and phosphor respectively, are well understood by assuming linear O-H-O bond.

Introduction

The crystal structure of tin(II) hydrogen phosphate, SnHPO_4 , has been studied by A. F. Berndt and R. Lamberg¹⁾ using single crystal X-ray diffraction and by L. W. Schroeder and E. Prince²⁾ using single crystal neutron diffraction. Although there are some discrepancies in structures determined by these authors and the former did not mention the position of the hydrogen atom, both studies have shown that the unit cell which contains four molecular units is monoclinic, the space group is $\text{P}2_{1/c}$, and HPO_4^{2-} ions are linked together to form dimeric $(\text{HPO}_4^{2-})_2$ ion by a pair of hydrogen bonds. Projection of the contents of the unit cell determined by Schroeder and Prince²⁾ is illustrated in Fig. 1. Two hydrogen bonds in each dimer are related by an inversion symmetry.

Neutron diffraction study²⁾ showed that the hydrogen atom lies nearly on the line joining two bonded oxygen atoms and the shorter O-H distance in the bond is 1.017 Å, while O-O distance and OHO angle are 2.560 Å and 178.1° respectively.

To confirm the hydrogen position, second moments of nuclear magnetic resonance (NMR) absorption lines of proton and phosphor nucleus of the powdered crystal were measured by means of Fourier transformation of free induction decay (FT-FID) following 90° pulse³⁾.

The FT-FID method which has been extensively used in the high resolution NMR

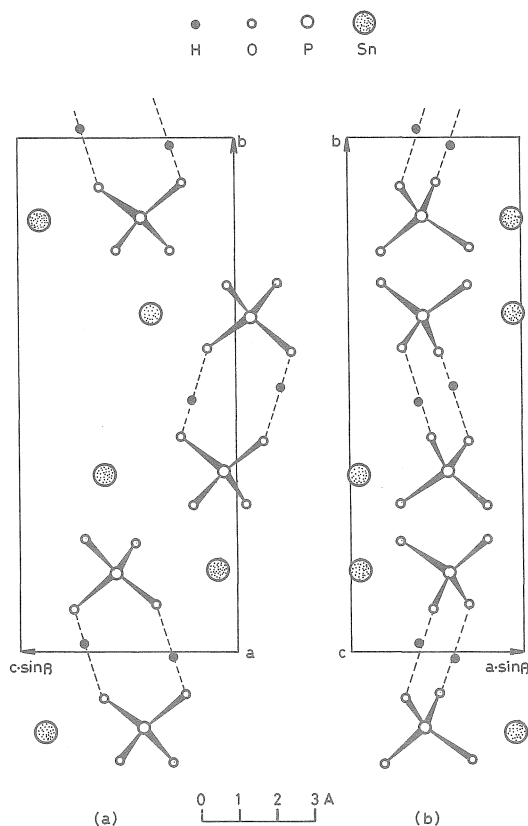


Fig. 1. Projection diagrams of a unit cell of SnHPO_4 .²⁾
 (a) Projection down the a -axis. (b) Projection down the c -axis. The dashed lines illustrate the hydrogen bonds.

gives the line shape free from any distortions inevitable in a steady state slow sweep NMR. Results of NMR were analyzed by assuming a linear hydrogen bond.

Experimental Procedures

Powdered SnHPO_4 precipitated when hot SnSO_4 solution was added to extra amount of hot 40% H_3PO_4 solution. Precipitates which were washed by distilled water and then dried at 80°C for 2 days, were tested by X-ray diffraction. Measured diffraction angles of 16 lines among 30 resolved diffraction lines agreed with the angles estimated from the structure factors reported¹⁾.

The compressed sample to cylindrical shape of 5 mm diameter and 7 mm length, was used in NMR measurements.

Second moments of proton and phosphor nucleus were obtained by integrating the

cosine Fourier transformed FID signal. FID signals produced by a homemade pulse apparatus* operating at 24 MHz were recorded by an 8 bit transient recorder, Kawasaki Electronica TR-1610, with sampling rate of $1 \mu\text{S}$ and 1024 sampling points. Sampled data were transferred to a microcomputer, TEAC PS-80, via PIO interface. This computer carried out the signal-to-noise enhancement by accumulating subsequent FID's under the control of programs written in BASIC language. Numerical treatments, for example signal conditioning or fast Fourier transformation, were carried out by the same computer.

The static field was stabilized by means of NMR field lock system resonated to Na^{23} nucleus in NaBr solution. Long term stability of the field better than 1 ppm was effective to accumulation of many times over long period.

All NMR measurements were made at room temperature.

Results and Discussion

Proton NMR

In Fig. 2 is shown the FID signal of proton which was obtained by numerically subtracting the long tail due to presence of protons in residual free water from accumulated 25 FID's. In Fig. 2, the initial portion of the FID signal which was missing due to a finite instrumental recovery time, about $4 \mu\text{S}$, was completed by adding the initial portion of a half of solid echo. The peak of the solid echo appeared after the recovery time was over and it was recorded under the same conditions as FID's but a

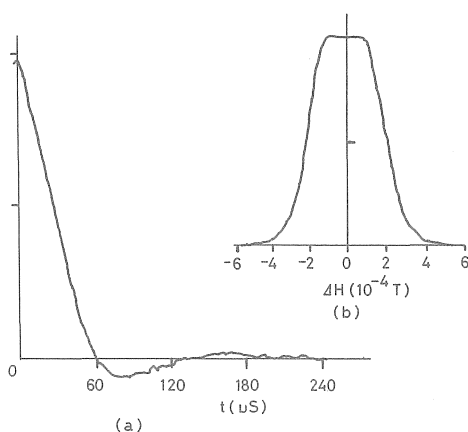


Fig. 2. (a) Corrected FID signal (see text) and (b) the cosine Fourier transformed FID signal of proton.

* To be submitted elsewhere.

$90^\circ - \tau - 90^\circ_{90}$ sequence was used.

The half solid echo (HSE) is given by P. Mansfield⁴⁾ as follows:

$$HSE(t) = FID(t) + M_{2e}^1 \tau(t + \tau) + M_{4e1}^1 \tau^3(t + \tau) + M_{4e2}^1 \tau^2(t + \tau)^2 + M_{4e3}^1 \tau(t + \tau)^3 + \dots, \quad (1)$$

where M_{2e}^1 is Van Vleck's second moment-like term and M_{4ei}^1 ($i=1,2,3$) are fourth moment-like terms. In the present measurements, τ is equal to $10 \mu\text{S}$ and t is smaller than $24 \mu\text{S}$, while M_{2e}^1 and M_{4ei}^1 's are estimated to be of the order of 10^8 Hz^2 and 10^{15} Hz^4 respectively. Little algebra shows that the initial portion of the FID agrees with the initial portion of the HSE.

Measured proton second moment is $(1.80 \pm 0.03) \times 10^{-8} \text{ T}^2$ where $1 \text{ T} = 10^4 \text{ gauss}$. Estimated error was introduced by ambiguous choice of cut-off of the wing in the transformed FID.

To check the validity of the present FT-FID method, proton second moment and width of maximum slopes of absorption spectrum were measured by a steady state frequency sweep NMR. The steady state measurement gives second moment of $(1.8 \pm 0.1) \times 10^{-8} \text{ T}^2$ and width of maximum slopes of $(3.8 \pm 0.4) \times 10^{-4} \text{ T}$. The present FT-FID also gives width of maximum slopes of $(3.90 \pm 0.03) \times 10^{-4} \text{ T}$. The agreement is quite well.

Phosphor NMR

Fig. 3 shows the phosphor FID signal obtained by accumulating 100 FID's over about 2 hours. In this case, the initial portion of FID signal was not corrected, because

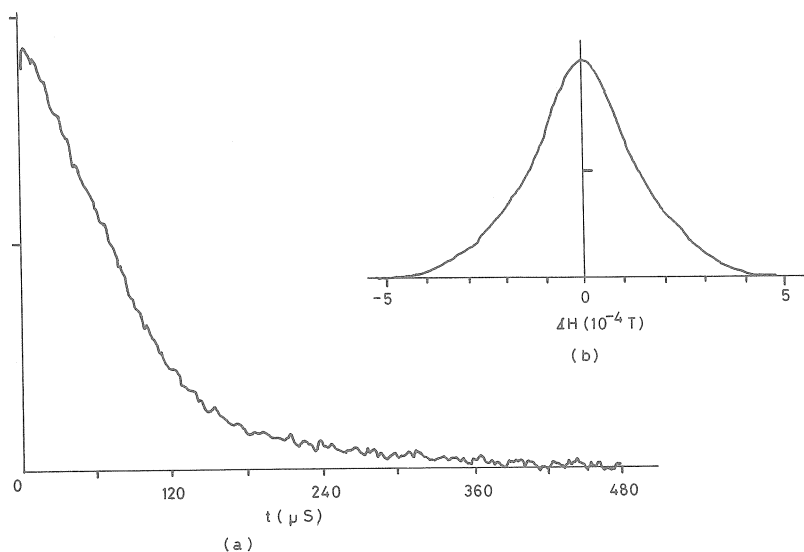


Fig. 3. (a) FID signal and (b) the cosine Fourier transformed FID signal of phosphor.

the instrumental recovery time was not a significant fraction of the FID, not as in the proton case. FT-FID gives the phosphor second moment of $(2.14 \pm 0.05) \times 10^{-8} \text{T}^2$. Estimated error was introduced by the same reason as in the proton case.

Second Moment Considerations

To determine the hydrogen position, measured second moments of proton and phosphor nucleus are compared with ones calculated by assuming hydrogen locations in an arrangement of all other magnetic nuclei.

It has been shown⁵⁾ by many investigators that the hydrogen atom in O-H-O hydrogen bond shorter than about 2.55 Å lies nearly on the straight line joining two bonded oxygen atoms. Since observed bond lengths are 2.50 Å¹⁾ or 2.560 Å²⁾, it is reasonable to assume that the hydrogen atom lies on the line joining two bonded oxygen atoms.

The second moment of powdered crystal is given by⁶⁾

$$\begin{aligned} \langle \Delta H^2 \rangle = & (3/5) \gamma_I^2 \hbar^2 I(I+1) (1/N) \sum_j^N \sum_k \gamma_{jk}^{-6} \\ & + (4/15) \sum_m \gamma_m^2 \hbar^2 S_m(S_m+1) (1/N) \sum_j^N \sum_{k'}^{N_m} \gamma_{jk'}^{-6}, \end{aligned} \quad (2)$$

where I is spin of the resonant nucleus, m runs over all non-resonant nuclear species of which spins are denoted by S_m 's, and the other quantities are usual ones.

In SnHPO₄, magnetic species are ¹H, ³¹P, ¹¹⁵Sn, ¹¹⁷Sn, and ¹¹⁹Sn. Taking account of a stochastic distribution of tin isotopes on tin atomic positions, the second moments of proton and phosphor in 10^{-8}T^2 are given by following equations, where r_{jk} 's are in Å.

Proton second moment :

$$\begin{aligned} \langle \Delta H^2 \rangle = & 89.54 \sum \sum_{j \neq k} r_{jk}^{-6} + 6.52 \sum_j \sum_{k'} \gamma_{jk'}^{-6} \\ & + 0.88 \sum_j \sum_{k''} \gamma_{jk''}^{-6}, \end{aligned} \quad (3)$$

where j runs over four protons in a unit cell, k over all protons except j , and k'' over all phosphor and tin nuclei respectively.

Phosphor second moment :

$$\begin{aligned} \langle \Delta H^2 \rangle = & 14.68 \sum_{j \neq k} \gamma_{jk}^{-6} + 39.79 \sum_j \sum_{k'} \gamma_{jk'}^{-6} \\ & + 0.88 \sum_j \sum_{k''} \gamma_{jk''}^{-6}, \end{aligned} \quad (4)$$

where j runs over four phosphor nuclei in the unit cell, k over all phosphor nuclei except j , k' and k'' over all protons and tin nuclei respectively.

In actual computation, summations were confined up to fifth nearest unit cells. Small corrections due to outer nuclei were estimated by continuum approximation.

Fig. 4 shows the calculated second moments of proton and phosphor as a function of various hydrogen positions on the assumed linear O-H-O bond. The present NMR data are well understood if the hydrogen atom is located on the linear bond in the crystal lattice of Schroeder and Prince²⁾ and the shorter O-H length in the bond is 0.95 ± 0.03 Å. This length is shorter than the reported value of 1.017 Å.

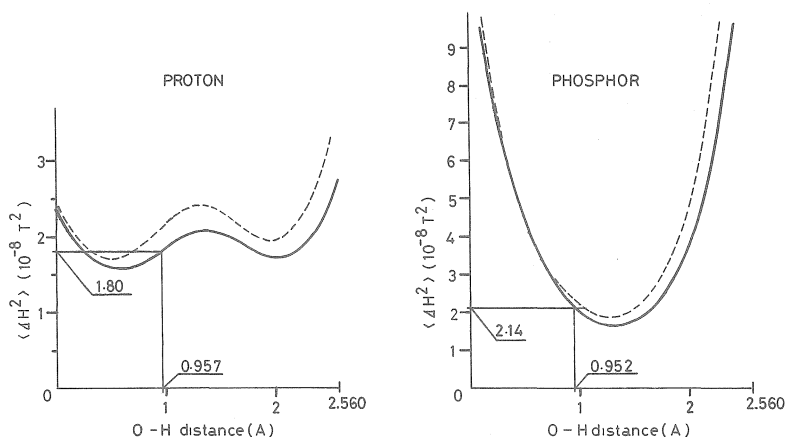


Fig. 4. Calculated second moments of proton and phosphor nucleus for various locations of the hydrogen atoms on the assumed O-H-O bonds in the crystalline lattices of Berndt and Lamberg¹⁾ (dashed lines) and of Schroeder and Prince²⁾ (solid lines). Experimental values obtained by the present NMR measurements are shown by horizontal lines and figures.

For the structure determined by Schroeder and Prince, $2.21 \times 10^{-8} T^2$ was calculated for the proton second moment. This value is much greater than the present experimental value of $(1.80 \pm 0.03) \times 10^{-8} T^2$. Since the experimental second moment of proton does not significantly increase at liquid nitrogen temperature, the present experimental second moment is considered to be the one of the rigid lattice. According to Eq. (3), proton second moment is sensitive to the interval between the nearest protons. The interval between two protons in a dimer is 2.631 A by Schroeder and Prince, while it is 2.673 A in the present linear bond model.

The hydrogen position determined by Schroeder and Prince gives the phosphor second moment of $1.76 \times 10^{-8} T^2$. This value is smaller than the present experimental value of $(2.14 \pm 0.05) \times 10^{-8} T^2$. The interval between phosphor atom and proton in a dimer is 2.202 A by Schroeder and Prince, while it is 2.156 A in the present linear bond model.

It is concluded that carefully measured second moments of powdered crystal present good criterion for the crystal structure.

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