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Application of CRAMPS for a Phase Transition in H⁺-ion irradiated TIH₂PO₄

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Abstract : We studied the hydrogen-bonded TIH₂PO₄ (TDP) ferroelectrics treated with the proton-beam bombardment. The TDP material was irradiated with 1-MeV proton beam at a dose of 10¹⁵/cm². In order to analyze the hydrogen environment in TDP, we carried out the ¹H high resolution nuclear magnetic resonance (NMR) - *i.e.*, Combined Rotation And Multiple Pulse Spectroscopy (CRAMPS) measurement. The isotropic chemical shift of hydrogen indicates its displacive property is related to the PO₄ lattice deformation which occurs throughout the antiferroelectric-, the ferroelastic- and the paraelastic-phase transitions. The temperature dependence of σ_{iso} reveals the electronic charge redistribution is induced by the proton-beam irradiation and the elastic property.

Keywords : CRAMPS, TIH₂PO₄, solid-state NMR, Proton beam irradiation

INTRODUCTION

It is well known that the phase transition of the hydrogen-bonded KH₂PO₄ (KDP) family occurs with the proton tunneling in the double well potential¹. The coupling between the proton tunneling

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and the lattice vibration mode induces a structural phase transition with the spontaneous polarization². The substitution of Tl in the place of K^+ cation makes TlH_2PO_4 (TDP) has three different crystallographic hydrogen bonds as determined by x-ray and neutron scattering³. The crystal structure of TDP has three inequivalent H sites. The lengths of two shorter bonds are 0.243 nm and 0.245 nm, respectively. The length of longer bond is 0.25 nm, which is asymmetric along the b -axis⁴ (fig.1). They are centrosymmetric and form zigzag chain along the c -axis. Whereas the ferroelectric and the ferroelastic transitions occur simultaneously in KDP, the antiferroelectric and the ferroelastic phase transitions in TDP occur at $T_C = 230$ K and at $T_C' = 357$ K, respectively^{5,6}. In fact, a recent *ab initio* calculation has shown the strong correlation between H and heavy ions and its role in the phase transition of the KDP system^{7, 8}. While the KDP-type crystals mostly undergo a ferroelectric transition, only a few of them undergo the antiferroelectric transition. Thus, the hydrogen-bonded antiferroelectrics are much less understood^{9,10}. The antiferroelectric transition has been reported to be associated with the lattice strain and some ferroelectrics exhibit antiferroelectric phases under an external pressure¹¹. The local ferroelastic strain effect on the proton ordering has been reported in squaric acid. Below T_C , the protons are ordered in antiferroelectric phase while the squarate unit is under strain simultaneously¹². Confirming the coexistence of the order-disorder and the displacive behaviors in these anti-ferroelectrics is a major advance in the theoretical framework for the hydrogen-bonded ferroelectrics study.^{2, 13, 14} The phase transition at T_C was explained by the proton order/disorder mechanism combined with the displacive feature of the lattice distortion detected by

the chemical shift NMR measurements. In the proton-lattice coupling model, the proton tunneling motion is coupled to the molecular moiety (PO_4) motions¹⁵. Thus, it is of considerable interest to investigate the state of the proton ordering and the ferroelastic shear strain at the two different transitions ($T_C \neq T_C'$) in TDP.

Generally, the solid materials have the strong dipolar interaction and anisotropic chemical shift which generate a featureless wide NMR spectrum. To detect the isotropic chemical shift of the hydrogen, the dipolar interaction and the chemical shift anisotropy (CSA) should be removed by the combination of rotation and multiple pulse sequence, often called as CRAMPS. Here we used BR24 as a multiple pulse sequence whose theoretical background is based on the average Hamiltonian theory¹⁶⁻²⁰. Here the multiple pulses remove the strong homo-dipolar interaction and the sample spinning removes CSA, which resulted in a high-resolution 1H spectrum. The BR24 has achieved the highest dipolar line narrowing compared to other techniques such as the Waugh-Huber-Haberlen (WHH4), the frequency- shifted Lee-Goldburg (FSLG), and even with the ultra-fast magic angle spinning (MAS) techniques²¹.

Compared to all previous works concentrated on heavy atoms in lattice, our focus is to detect the physical state of the hydrogen which is located in a double-well potential provided by the two tetrahedral PO_4 group. The 1H chemical shift of TDP gives the electronic information for proton environments around PO_4 tetrahedra transformed by the proton-irradiation. In this work, we discussed an experimental evidence of proton geometric displacement combined with the PO_4 tetrahedral

distortion at the ferroelastic phase transition under the proton beam bombardment. The results show the possibility that the proton-irradiation can be used to induce an internal stress inside the hydrogen-bonded materials

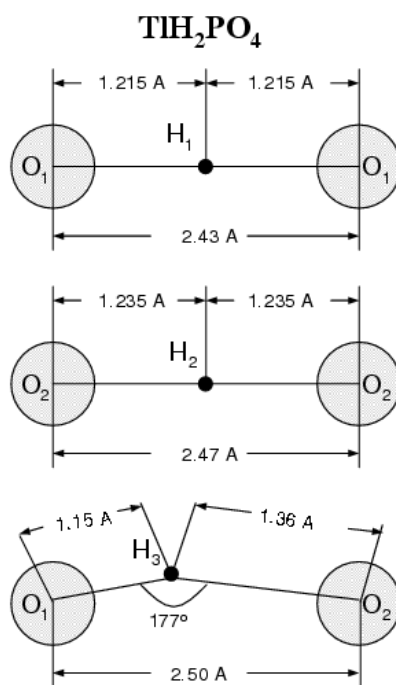


Figure. 1. Three independent hydrogen bonds of TIH₂PO₄ in Ref. 4.

EXPERIMENTAL

A TDP single crystal was irradiated with 1-MeV protons at a dose of 10^{15} /cm². Then a powdered sample was investigated by using the 4.7 T Unity Inova NMR. The NMR unit is equipped with the 1 kW output rf-amplifier on the ¹H -channel, which is necessary to generate a very short

pulse width of 90 pulse. The various glitches of the multiple pulse technique, is known to be minimized with the shorter pulse sequence²³. The variable temperature experiments are performed with the dry nitrogen gas. The special CRAMPS probe is designed to have a good rf -homogeneity as well as a short ringing time which is less than 2 μ s. The hardware requirements should be met to obtain a good CRAMPS result. The CRAMPS NMR measurements for TDP were made at the Larmor frequency of 200 MHz and the 2 kHz sample spinning. The chemical shifts were measured relative to a solution of tetramethylsilane (TMS). The experimental conditions of CRAMPS are as follows: recycle delay time 10 s, pw 90 1.2 μ s, acquisition data points 256, number of acquisitions 256. The sample is grounded to a fine powder for the spinning stability. The rotor is made of glass, which assures no background 1H NMR signal from the rotor material.

RESULTS AND DISCUSSION

In order to see an effect of proton-beam irradiation on the TDP lattice, we performed a high-resolution 1H CRAMPS measurement²⁴. The 1H CRAMPS NMR spectrum in fig. 2 shows the isotropic chemical shift before and after the proton irradiation at representative temperatures chosen by the relevant phase transition. In the temperature range of $T < T_C$ where the untreated TDP is in the antiferroelectric state. The linewidth and the isotropic chemical shift shows a negligible change. In the temperature range $T_C < T < T_C'$ where the untreated TDP is in ferroelastic state, the isotropic chemical shift also shows not much change. In the paraelastic region of $T > T_C$, however, the

spectrum for the untreated sample becomes more inhomogeneous. Since the strain is released in the paraelastic state, a disordered state in TDP should give the inhomogeneous line-broadening. The width of broad spectrum reflects a statistical distribution of the electronic states around the nucleus.

It is not the chemical shift anisotropy which is removed by the sample spinning. The irradiated sample in the antiferroelectric state shows no difference compared to the untreated sample. In the ferroelastic state, however, the treated sample shows high-field shift or more electron distribution around the hydrogen, compared to the untreated sample. More electron distribution around the hydrogen can be interpreted as an increase of the hydrogen bond length, which means a distance increase between the two oxygen atoms in PO_4 group.

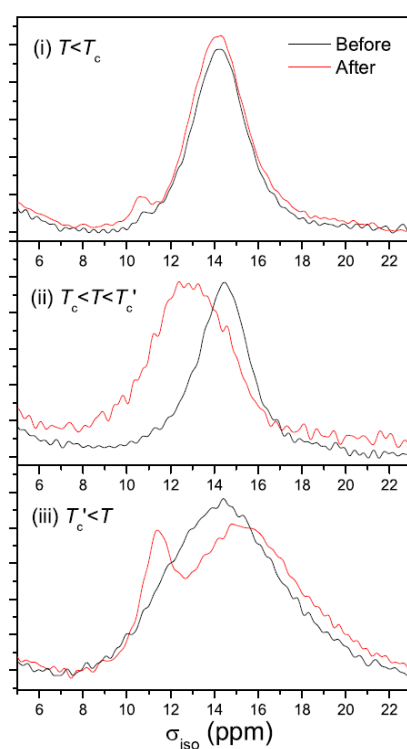


Figure. 2. Lineshapes of 1H CRAMPS NMR spectrum in TDP before and after the proton-beam irradiation at various temperatures. From the top to bottom, the data are obtained in the ferroelectric, the ferroelastic, and the paraelastic phases.

In the ferroelastic temperature range, the CRAMPS result shows the proton irradiation causes a structural change, which is manifested by the electronic state change around the hydrogen. In the paraelastic temperature range, the structural change is remarkable where two peaks appeared. Based on this observation, the irradiated TDP sample in paraelastic phase can be interpreted to have two regions resulted from the irradiation. A similar observation from the $T_{1\rho}$ measurements for the hydrogen was reported^{25, 26}.

Our 1H CRAMPS measurements, thus, indicate that the proton-beam irradiation can modify the lattice configuration along the direction of the hydrogen bond and the local structure of O-O bond. In other words, the oxygen separation ($2 R_{O\cdots O}$) is modified upon the proton irradiation, which determines the charge redistribution along the hydrogen bond [7]. In general, Morse potential V^M describes the interaction between the proton and the outer electronic shell of neighboring PO_4 ^{2,14,15}.

The Morse potential is given by

$$V^M(|\vec{X}|) = D[e^{(2-\alpha|\vec{X}|)} - 2e^{(-\alpha|\vec{X}|)}], \quad (1)$$

where D , α , and R_0 are parameters listed in Table 1,

$$|\vec{X}| = \sqrt{(R - R_0)^2 + 1} \quad (2)$$

where the $2R$ is the equilibrium distance between neighboring PO_4 groups and D is the well depth, and α indicates the width of the potential²⁷.

The oxygen separation can be calculated by using a conversion formula

$$\sigma_{\text{iso}}(\text{ppm}) = 79.05 - 255d(\text{O} - \text{H} \cdots \text{O})(\text{nm}) \quad (3)$$

suggested by Eckert *et al.* where $d(\text{O}-\text{H}\cdots\text{O})$ is the oxygen separation ($2R_{\text{O}\cdots\text{O}}$)²⁸. The hydrogen-bond length can be obtained from the ^1H high resolution chemical shift data.

Table 1. Morse potential parameters used for TDP.(ref. 2,4)

	$R_o[\text{\AA}]$	$\alpha [\text{\AA}^{-1}]$	$D [\text{eV}]$
TDP	1.23	4.68	2.94

In summary, the proton bombardment effect on the hydrogen-bonded ferroelectrics TDP was studied with the high-resolution ^1H NMR spectrum with variable temperatures. The phase transition behavior between the untreated sample and the irradiated sample shows quite a difference, which is due to a structural change induced by the bombardment. The chemical shift change is explained in terms of the interatomic distance between two oxygen atoms in PO_4 moieties. The distance extracted from the CRAMPS is used to estimate the Morse potential. The changes of the ^1H chemical shift undergoing the ferroelastic phase transition, is interpreted as the proton displacive feature as well as a distance change between the two adjacent oxygen atoms. The remnant ferroelastic property in the

paraelastic phase was similarly reported by previous results of $T_{1\rho}$ measurement²⁵, which imply two different dynamic states for 1H . The present chemical shift result for 1H gave the information about the relative displacement after the proton bombardment, which is the more direct evidence of the same structural change.

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