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Charge Flow in KH_2PO_4 Lattice Structure by Using the Proton-Beam Irradiation.

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Abstract : The mechanism of charge flow has been probed by measuring the ^1H chemical shift on a proton-irradiated KH_2PO_4 (KDP) single crystal. The proton irradiation caused the increase in ^1H chemical shift. It can be interpreted as the electronic charge transfer from the proton to oxygen atom, accompanied with the proton displacement along the hydrogen bond. For the high resolution ^1H chemical shift measurement, CRAMPS (Combined Rotation And Multiple Pulses) technique is utilized.
Keywords: KH_2PO_4 (KDP) crystals, Nuclear magnetic resonance, Proton-beam irradiation, Electronic instabilities

INTRODUCTION

The ferroelectric/ferroelastic phase transitions related to the atomic level phenomena of the KH_2PO_4-type ferroelectrics have been debated for a long time. The local ferroelastic strain effect on the proton ordering was reported in squaric acid. Below T_c, the protons are ordered anti-ferroelectrically and the squarate units are distorted simultaneously[1]. Observation of coexisting order-disorder and displacive behaviors in these ferroelectrics is considered to be very peculiar case[2-4] of the anti-ferroelectric and the ferroelastic co-transition (T_c=T_c'). In the proton-lattice coupling model, the proton is associated with the

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molecular moiety (PO_4) motion.[5] In this work, we reported the high-resolution CRAMPS measurement of the hydrogen nucleus in the O-H...O hydrogen bond networks in KDP crystals. The results reveal the change of σ_{iso}, induced by the proton beam irradiation leading to a charge flow and a charge redistribution around hydrogen atoms. The purpose of our investigation was to provide experimental evidence of the proton displacement features associated with the electronic instabilities in the hydrogen bonds.

EXPERIMENTALS

A KDP single crystal, supplied by the Crystal Bank at Pusan National University, was irradiated with 1-MeV protons at a dose of $10^{15}/cm^2$. A powder sample of KDP was investigated with a 200-MHz Varian Nuclear Magnetic Resonance (NMR) spectrometer in the temperature range of 290-380 K. This NMR unit is equipped with a 1-kW output radio-frequency (*rf*)-amplifier on the 1H channel, which is necessary to generate a very short pulse width for 90-pulse length. The various glitches of the multiple pulse technique are known to be minimized with a shorter pulse[6]. The variable temperature experiments were performed with nitrogen gas to avoid any condensation of water vapor from the drive gas of sample spinning and also the ambient gas for temperature control. A special combined rotation and multiple pulse spectroscopy (CRAMPS) probe is designed to have a good *rf*-homogeneity and a short ringing time of less than 2 μs. These hardware requirements should be met to obtain a good CRAMPS results. The CRAMPS NMR measurements for KDP were made at Larmor frequency of 200 MHz with spinning frequency of 2 kHz. The chemical shifts were measured relative to a solution of tetramethylsilane (TMS). The BR24 pulse sequence was chosen for the CRAMPS experiments, as shown in Fig. 1.[7] The experimental CRAMPS conditions are as follows: 10 sec. recycle delay, 1.2-μs 90 degree pulse width, 256 acquisition data points, and 256 number of acquisitions. The sample was grinded to a fine powder for spinning stability. The rotor was made of glass, which assured no background ^{1}H-signal from the rotor material. So far, the CRAMPS technique has achieved the highest dipolar line narrowing compared to other multiple pulse techniques and even with the ultra-fast magic angle spinning (MAS) techniques.[8]

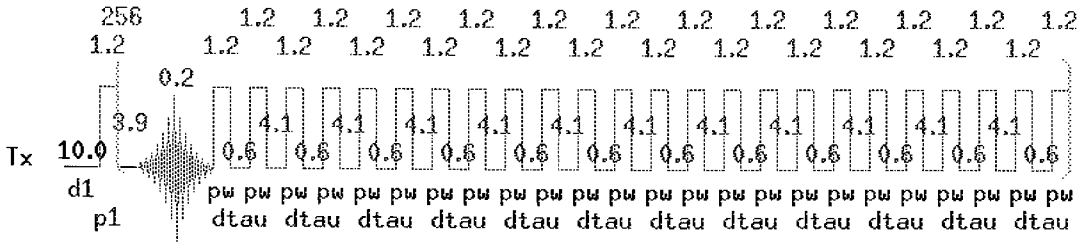

Fig. 1. A typical pulse sequence diagram for ^{1}H CRAMPS NMR. The 90 degree pulse width was 1.2 μs. A single data point is acquired after every 24 pulse train. Each acquisition requires minimal 200 ns acquiring event. In this study, 256 data sampling is used. More details of various variables can be found in references given in the text.

RESULTS and DISCUSSION

Multiple pulse sequence technique, based on the average Hamiltonian theory, was devised to remove the dipolar interaction. Its basic idea is to let the spin system align along the X, Y and Z axes repeatedly by applying the multiple pulses so that the spins are rotated around the magic angle by the *rf*-pulses. [6-7, 9-11]. In MAS experiment, powder sample is rotated along an axis of 54.7 degree tilted from the external magnetic field. The MAS removes the anisotropy of the chemical shift anisotropy (CSA) tensor. Thus, the dipolar line broadening and the CSA are averaged out with the CRAMPS technique.

In an effort to elucidate the microscopic effect of the proton-beam irradiation on the KDP lattice, ^{1}H CRAMPS NMR measurements is utilized. The room-temperature ^{1}H CRAMPS spectrum in Fig. 2, shows an isotropic chemical-shift toward high frequencies after proton irradiation. The peak was observed at 14.5 ppm corresponding to the hydrogen bonds observed in the room-temperature structure of KH_2PO_4. Previously, our X-ray diffraction pattern showed the main peak shifted to the higher angles after proton irradiation. No noticeable changes in the lineshape were observed, indicating the defect formation was negligible.[12] This may readily be understood by considering that the irradiation of $10^{15}/cm^2$ corresponds to only about $1/10^7$ KDP lattice sites. Nonetheless, the relative effect observed

with ^{1}H CRAMPS in hydrogen bond, is ascribed to the 10^5 secondary electrons that are produced by the irradiating proton.[13]

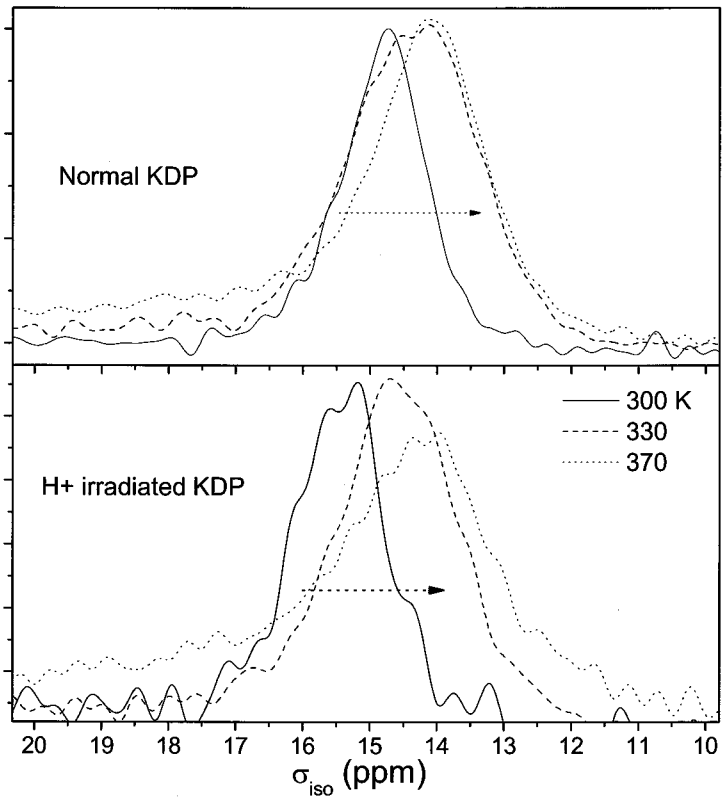

Fig. 2. The changes of CRAMPS spectrum for KDP crystal at various temperatures after the proton-beam irradiation.

The ^{1}H spectrum was well fitted with Lorentzian lineshape representing hydrogen-bonded proton between two oxygen atoms. The change of the isotropic chemical shift before and after the proton irradiation is $\Delta\sigma_{iso} \sim 0.66$ ppm. The change in the isotropic chemical shift and the line broadening is attributed to deformation of the O-H…O hydrogen bonds.[14]

Figure 2 shows the temperature dependence of the ^{1}H isotropic chemical shift. After the proton irradiation, the isotropic chemical shift is moved toward high frequencies in paraelectric phase. The shifted resonance frequency ω, depends on the local field of the crystal and is related to the resonance frequency ω_o, by a relation of $\omega = \omega_o(1- \sigma)$. The

chemical shielding tensor depends on the electronic charge distribution around the proton nucleus. The increase of the ^1H chemical shift after the proton irradiation corresponds to an enhanced deshielding. The down-field component of the shielding turns out to lie along the O-H...O direction, which is the direction of the lowest electron density.[15] In previous results, the decrease in the ^{31}P chemical shift corresponds to an electron density increase around the phosphorous nucleus along the P-O bond's direction.[12] Our observation suggests there is a displacement of charge distribution toward the phosphorous nucleus from hydrogen after proton irradiation. The phase transition temperature was shown to increase about 5 K, from 192 K to 197 K after irradiation, indicating a geometrical change in the hydrogen bonds in the DKDP crystal.[16] Our ^1H CRAMPS measurements, thus indicate the proton-beam irradiation treatment can modify the lattice configuration along the hydrogen bond's direction and the local structure of O-O bond. The $2R$, oxygen separation ($2R_{O...O}$), consequently gives rise to a charge redistribution.[17] The charge transfer from proton to oxygen is accompanied by the proton-lattice coupling term H_{TL}. H_{TL} is modeled by Morse potentials V^M between protons and its neighboring PO_4 moieties. The Morse potential is approximately given by

$$V^M(|\vec{X}|) = D[e^{(2-\alpha|\vec{X}|)} - 2e^{(-\alpha|\vec{X}|)}] \qquad \text{e.g.[1]}$$

where D, α, R_o are parameters which are listed in table 1.[14]

$$|\vec{X}| = \sqrt{(R-R_o)^2+1} \qquad \text{e.g.[2]}$$

The $2R$ is being the equilibrium distance between the neighboring PO_4 groups.

Table 1. Morse potential parameters used for KDP.

	R_o [Å]	α [Å^{-1}]	D [eV]
KDP	1.119	4.68	2.94

The temperature dependent Morse potential is shown in figure 4. The observed ^{1}H-CSA tensor is related to atomic position, accounting for a charge transfer and a displacive effect around oxygen atom. After the proton beam irradiation, the potentials are increased due to charge redistribution of O-O bonds. In previous ^{1}H spin-lattice relaxation time (T_1) measurements, the activation energies before and after proton irradiation were 0.42 eV and 0.28 eV, respectively with the paraelectric phase.[18] The thermally-activated proton energy under a double-well potential can be controlled by using proton irradiation, indicating different local environments in the hydrogen-bond networks.

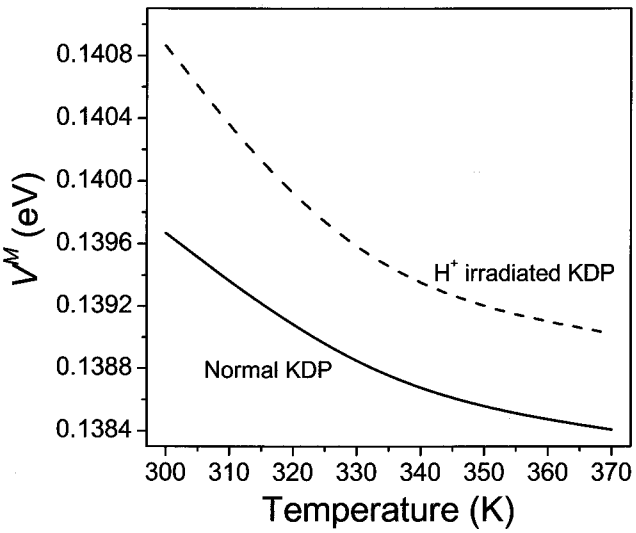

Fig. 3. Temperature dependence of the calculated Morse potential.

In summary, we have studied the effect of proton-beam irradiation on a single crystal of KH_2PO_4, which is a typical hydrogen-bonded ferroelectric system. The isotropic chemical shift of ^{1}H after proton-irradiation was measured with the ^{1}H CRAMPS technique. The increase of the Morse scalar potentials is explained with a distance change between adjacent oxygens. It can be interpreted as modification of electronic charge distribution in hydrogen bond.

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