Journal of the Physical Society of Japan
Vol. 66, No. 1, January, 1997, pp. 270-271

Electron Distribution of Hydrogen and Deuteron in KH_2PO_4 and KD_2PO_4

Tadao HAYASHIDE and Yukio NODA

Faculty of Science, Chiba University, Yayoi, Inage, Chiba 263

(Received July 9, 1996)

KEYWORDS: KH_2PO_4, hydrogen bond, electron distribution

The ferroelectric phase transition temperatures in KH_2PO_4 (KDP) and KD_2PO_4 (DKDP) are almost 100 K different from each other, and the phenomenon is called an "isotope effect". To explain the phenomenon, geometrical effect was proposed.[1] In this model, the hydrogen-bond length R_{OO} are crucial, and the bond length in deuterated sample is longer than that in a hydrogen sample in general as an experimental evidence. In addition, the position of a hydrogen atom in the hydrogen-bond region is important, and amplitude of the splitting of a hydrogen or a deuterium atom (R_{HH}, R_{DD}) has a large correlation with the transition temperature T_c.[1]

Recently Noda and Kasatani offered a new idea[2] in connection with the geometrical model based on the precise X-ray structure analyses of $K_3H(SO_4)_2$ (KHS) and $K_3D(SO_4)_2$ (DKHS). They revealed that the electron number around the hydrogen atom is less than that around the deuterium atom. This result means that the hydrogen atom is more ionic compared with the deuterium atom. They also pointed out that the position of the proton nucleus slightly shifts from the center of the electron cloud of the hydrogen atom, and the hydrogen atom is polarized.[3] However, there are almost no other experiments to discuss the nature of the electron distribution in hydrogen-bonding. It seems important to investigate the electron distribution of hydrogen atoms in KDP and DKDP by high precision X-ray structure analysis, because these materials are considered to be the standard in a hydrogen-bonding family.

Usually, the study of the nature of hydrogen atoms is performed by neutron diffraction experiments. The reason is that the scattering amplitude of a deuterium is relatively large so that it is easy to pin down the position of hydrogen nucleus as structure parameters. Indeed, there are many reports concerning the structure analysis of KDP and DKDP by neutron experiments. On the other hand, the investigation of an electron distribution of a hydrogen atom by X-ray experiments is technically difficult, and the systematic error for the electron number is not so clear at the moment. Up to knowledge of the authors, there are no detail X-ray experiments to discuss the electron distribution of hydrogen atoms in KDP and DKDP. Only performed were conventional structure analysis by X-ray, in which positional parameters of K, P and O atoms were discussed. The standard deviation of parameters are usually estimated from the statistical nature of the set of intensity data. If one wants to discuss the nature of electron distribution such as electron number of a hydrogen atom in a hydrogen-bond area and the amplitude of the splitting of the electron cloud, it is very difficult to estimate the standard deviation of these values. This seems to be the reason why there is almost no report for the hydrogen atom in KDP by X-ray experiments. We consider further experiments are necessary from the statistical view point to investigate such a delicate problem. Namely, the results from a structure analysis, such as a bond length, an electron distribution etc., are well reproducible when one uses the same sample and the same reciprocal region with the same diffractometer. However, when the sample is different and the data are taken at the different reciprocal region, the structure parameters usually scatter over the standard deviation. In order to avoid such systematic errors, experiments with many samples and different reciprocal regions are necessary to test the geometrical effect in KDP. The purpose of the present experiments is to obtain the structure parameters of KDP and DKDP based on the statistical view point. Special attention was paid to detect the electron distribution of hydrogen and deuterium atoms and to evaluate the electron number.

Single crystals of KDP were grown from aqueous solution by slow evaporation at room temperature. DKDP powder sample was prepared by the evaporation of a solution in D_2O. Nominal concentration of deuteron was about 99 %. DKDP crystals grown at room temperature had a monoclinic unit cell as was reported. We grow the tetragonal DKDP at 2°C. Samples were shaped as sphere with a diameter about 350 μm. Three KDP and two DKDP crystals were used for the experiments.

Intensities of Bragg reflections were collected on a four-circle diffractometer. As an X-ray source, Mo $K\alpha$ radiation with Zr-filter was used with the power of 50 kV × 60 mA. All measurements were performed by a 2θ-ω scan method. The limit of 2θ in which intensity data were collected was 86.0°. Total number of collected data was about 1600 in a ($h \geq 0$, $k \geq 0$, $\pm l$) region. About 1100 data stronger than $3\sigma(F_{ob})$ is used for the structure analysis. We separated the data into an independent region from the view point of the crystal symmetry ; [a] ($h \geq k$, $+l$), [b] ($h \leq k$, $+l$), [c] ($h \geq k$, $-l$) and [d] ($h \leq k$, $-l$). We made a least square analysis to obtain positional parameters.

In Table I, we summarized the R-factors for each sample and each region in the reciprocal space. The final R-factors were about 2.2 %. The obtained positional parameters are essentially consistent with the reported values.[4] The hydrogen-bond lengths R_{OO} calculated from the positional parameters are tabulated in the table, and the average values are $R_{OO}(\mathrm{H}) = 2.502(3)$ Å and $R_{OO}(\mathrm{D}) = 2.526(2)$ Å. These values are well consistent with the reported ones.[5] Note that the standard deviation estimated from the intensity data (given in the parenthesis of each R_{OO}) is well consistent with the one obtained from the statistical method.

Fourier synthesis was executed with the obtained parameters. Electron density on the x-y plane at $z = 1/8$ for the data KDP1-c is shown in Fig. 1. Here, oxygen atoms connected by hydrogen atoms are seen. Large

Table I. Result of structure analysis.

sample	region	R_F %	R_{OO} Å	R_{HH} Å	n_e
KDP1	a	1.96	2.501(3)	—	0.84
	b	2.38	2.502(2)	0.73	0.46
	c	1.93	2.498(1)	0.84	1.06
	d	2.44	2.505(2)	0.81	0.45
KDP2	a	1.74	2.503(3)	0.68	0.72
	b	2.32	2.506(2)	0.86	0.78
	c	1.91	2.498(2)	0.90	0.72
KDP3	a	2.14	2.501(3)	0.66	0.82
	c	2.06	2.499(2)	0.76	0.78
Average		2.10	2.502(3)	0.78(9)	0.74(17)

sample	region	R_F %	R_{OO} Å	R_{DD} Å	n_e
DKDP1	a	2.21	2.526(3)	1.03	0.97
	b	2.47	2.528(3)	0.78	0.82
	c	1.35	2.527(3)	0.83	1.00
DKDP2	a	2.57	2.526(3)	1.13	0.81
	b	2.54	2.528(3)	1.04	0.86
	c	2.21	2.521(3)	0.87	0.87
	d	2.58	2.524(3)	0.73	0.76
Average		2.42	2.526(2)	0.92(13)	0.87(8)

peaks express electron density of oxygen atoms.

The so-called "difference Fourier synthesis" was carried out. The difference ΔF between the calculated structure factor F_c without hydrogen atoms and the observed one F_{ob} gives the contribution to the structural factor only by hydrogen atoms. Usually, ΔF at the higher value of $(h\ k\ l)$ tends to negligibly small so that we can expect to reduce the systematic errors such as the termination effect. In Fig. 2, we depicted the electron density of hydrogen atoms as the differential Fourier map. The area corresponds to the region enclosed with the gray square in Fig. 1. In the upper figure of Fig. 2, the electron density on the x-y plane at $z = 1/8$ is shown, while in the lower figure, the intersection at $x = 0.15$ is given. There are two peaks around $y = 0.18$ and 0.32. These peaks clearly mean that hydrogen atom is trapped in a double-minimum potential. The magnitude of the splitting of the hydrogen atom R_{HH} is evaluated from the differential Fourier map, and the results are summarized in Table I. For the data KDP1-a, the electron distribution was too broad so that we could not clearly determine the peak position. The average value of R_{HH} is 0.78(9) Å and R_{DD} is 0.92(13) Å. These should be compared with the data $R_{HH} = 0.365(3)$ Å and $R_{DD} = 0.446(1)$ Å obtained by neutron diffraction experiments.[5] Apparently, X-ray experiments look the distribution of electron around the hydrogen atoms, and neutron experiments look the distribution of proton nucleus. The above result suggests that the electron of hydrogen atom is polarized in a hydrogen-bond region.

The total electron number of hydrogen atom n_e is obtained by the accumulation of the electron density ρ_e shown in Fig. 2 and is tabulated in Table I. The average number of electron is 0.74(17) for a hydrogen atom and 0.87(8) for a deuteron atom. The electron number of a hydrogen atom seems slightly less than that of a deuteron atom, but the difference is very small. Our conclusion is so that there is almost no difference in the electron number between KDP and DKDP within an experimental error. This result seems to be different from the one for the KHS system. We are going to continue the similar experiments with other low dimensional hydrogen-bond system.

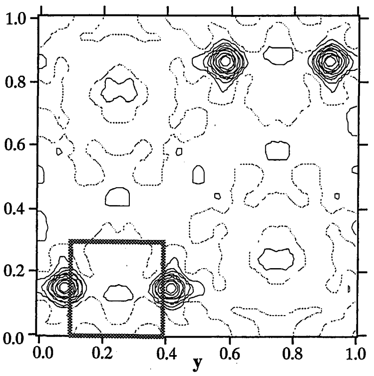

Fig. 1. Electron density map on $z = 1/8$ plane calculated from the Fourier synthesis of the data KDP1-c in Table I. Difference Fourier map of the gray square area is shown in Fig. 2.

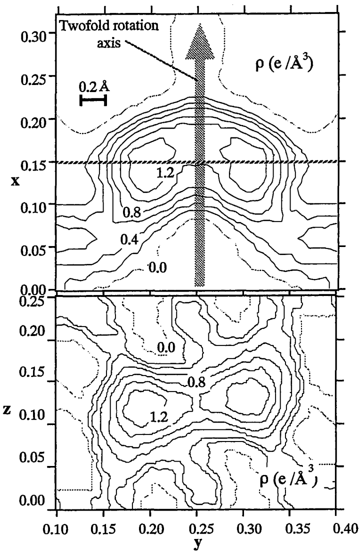

Fig. 2. Difference Fourier map of hydrogen atoms on $z = 1/8$ plane (upper), and on $x = 0.15$ plane (lower).

---

1) M. Ichikawa, K. Motida and N. Yamada: Phys. Rev. B **36** (1987) 874.
2) Y. Noda and H. Kasatani: J. Phys. Soc. Jpn. **60** (1991) 13.
3) Y. Noda: J. Korean Phys. Soc. Supl. **27** (1994) 156.
4) G. E. Bacon and R. S. Pease: Proc. Roy. Soc. **A220** (1953) 397.
5) R. J. Nelmes, G. M. Meyer and J. E. Tibballs: J. Phys. C **15** (1982) 59.