Hydrogen Atom of KH_2AsO_4 Determined by Neutron Diffraction Study

Tatsuki MIYOSHI, Tomoshi AKIMOTO, and Hiroyuki MASHIYAMA*

Faculty of Science, Yamaguchi University, Yamaguchi 753-8512, Japan

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The crystal structure of KH_2AsO_4 (KDA) is refined at room temperature by neutron single-crystal structural analysis. The distance R_{OO} between two oxygen atoms bonded by a hydrogen atom is slightly longer than that in KH_2PO_4 (KDP). A double-peak distribution of H with the splitting distance δ is visualized directly in the nuclear density map obtained by the maximum entropy method. The parameter δ of KDA is also larger than that of KDP, though the transition temperature of KDA is lower than that of KDP.

KEYWORDS: KDP family, hydrogen bonding, ferroelectrics, disordered proton, neutron diffraction, structure analysis

1. Introduction

Potassium dihydrogen arsenate (KH_2AsO_4, abbreviated KDA, hereafter) is an early discovered ferroelectric belonging to the potassium dihydrogen phosphate (KDP) family.[1,2] The spontaneous polarization and the dielectric constant of KDA are similar to those of KDP. In KDA, the ferroelectric transition takes place at 92 K, the lowest among the KDP-type pure crystals under atmospheric pressure. If H is replaced by D, T_c is elevated to 161 K, and this isotope effect is as prominent as that in KDP. The crystal structure is isomorphic to tetragonal KDP at room temperature, and takes the space group of $I\bar{4}2d$ with $Z = 4$.

In early studies, the disordered proton distribution was recognized in KDP, and the isotope effect on T_c was explained by the proton tunneling model.[3] Later, the chemical difference between proton and deuteron compounds was considered to be the origin of the isotope effect; the distance R_{OO} between two O atoms bonded by a H atom is decisive in T_c.[4] According to this idea of the geometric isotope effect, T_c becomes higher as R_{OO} lengthens. Such an empirical criterion appeared to be successful in many KDP-type ferroelectrics. Therefore, it was expected that the distance R_{OO} of KDA

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* E-mail address: mashi@yamaguchi-u.ac.jp

should be the shortest among the KDP family crystals, since T_c of KDA is the lowest. However, X-ray structural analysis demonstrated that R_{OO} of KDA is longer than that of KDP, but shorter than that of deuterated KDP (DKDP).[5)]

Thus the simplified idea of the geometric isotope effect was modified. Moreover, X-ray study is not suitable for the precise determination of the H position and its distribution. Therefore, we perform a neutron scattering experiment on the single crystal to refine the crystal structure and to discuss the structural parameters of H in KDA.

In the next section, experimental methods are explained, and the description of the analyzed structure follows. The comparison of KDA and KDP is discussed in the final section.

2. Experiment

By slow evaporation at room temperature, single crystals were grown from a water solution of the commercial chemical provided from WAKO. A platelet sample was cut from the bulk and the dielectric constant was measured. The tetragonal-to-orthorhombic transition was observed at $T_c = 93$ K from the peak position of the dielectric constant.

For the neutron diffraction experiment, a cubic with a dimension of 3 mm along the tetragonal axes was cut from the transparent part of the grown crystal. The sample was mounted on the four-circle diffractometer FONDER, installed in the guide hall of JRR-3M, JAEA, Tokai.[6)] The neutron wavelength was monochromated to 1.2384 Å, and the maximum 2θ was 156 °. The integrated intensities were collected at 298 K. The crystal data is summarized in Table I.

Table I

The observed structure factor F_o and its estimated standard deviation σF were reduced using a profile check program of FONDER..[6)] And the absorption and extinction correction programs, DABEXN and RADIELN, were applied.[7)] Starting from structural parameters obtained by X-ray analysis,[5)] we refined the parameters using a least-squares program and a Fourier synthesis programs of the AXS system.[8)] The coherent scattering lengths were 3.67, -3.739, 6.58, and 5.803 for K, H, As, and O, respectively. The Fourier maps of the atomic distribution in the unit cell were also estimated using the maximum entropy method (MEM) program PRIMA,[9)] and were visualized using VESTA.[10)] The pixel numbers for MEM were 128, 128, and 120 along the tetragonal axes. The calculations by PRIMA converged at $R_f = 0.0312$, which is almost the same level of the residual factor as $R_1 = 0.0324$ given by the least-squares calculations, when $1.5\sigma F$ is employed for PRIMA calculations.

3. Result

The refined atomic parameters are given in Tables II and III. The positional and the mean square displacement parameters of all atoms except for H are in good agreement with those determined by X-ray diffraction analysis.$^{5)}$ The distance R_{OO} between two O atoms bonded by H is determined to be 2.512(3) Å, which is in agreement with 2.5135(9) Å obtained in the previous X-ray study.$^{5)}$ The number in parentheses represents the estimated standard deviation (e.s.d.) of the parameter.

Table II

On the other hand, positional parameters of H are different between neutron and X-ray diffraction studies. The bond length r_{OH} between O and H atoms is determined to be 1.057(4) Å by the present neutron study, however, it was 0.886(6) Å in the previous X-ray study; $^{5)}$ such discrepancy seems to be a common situation of the O-H bonding observed using either neutrons or X-rays. The splitting distance δ between the double-peak H is 0.405(5) Å in the neutron study, while it is 0.847(12) Å in the X-ray study.

Table III

The atomic density (strictly speaking, the coherent scattering length representative of the nucleus) is estimated using the MEM program PRIMA. The density distribution is drawn in Fig. 1 at the surface level of 5. Between two O atoms, H has a double-peak distribution, in agreement with the disordered coordinates given in Table II.

Fig. 1

The contour maps of P and K at $z = 0$, and O and H at $z = 0.125$ are shown in Fig. 2. The contour lines are drawn every 5 density levels between -30 and 50. The peak values of the density were 77.5, -32, 244, and 107 for K, H, As, and O, respectively. The negative value for H is represented by broken lines in Fig. 2. The disordered distribution of H can be clearly recognized. If larger σF values were assigned in the PRIMA calculations, then we could obtain more rounded density distributions. The distribution of H became a single peak when $3\sigma F$ was assigned. The Fourier synthesis of F_{o} did not depend on σF, however, it gave only a single-peak distribution of H. The resolution of the traditional Fourier synthesis is limited by the optical resolution of 0.380 Å in the present experiment. The interatomic distances are summarized in Table IV.

Fig. 2

Table IV

4. Discussion

In this report, we determined the structure parameters of the H atom of KDA, using neutron diffraction data. The values of r_{OH} (the O-H bond length) and δ (the split distance of H) are somehow different from those determined by X-ray.5) As given in Table IV, those values are instead in agreement with that of KDP.11)

Recently, we reinvestigated the crystal structures of KDP and DKDP in wide temperature ranges by neutron diffraction study, and stressed the differences in R_{OO} and r_{OH}.12) Hereafter, we discuss the structural difference between KDA and KDP in detail.

Firstly, the physical properties of KDA are very similar to that of KDP; the magnitude of the spontaneous polarization and the transition temperature of KDA are about +20 and -20% those of KDP, respectively.2) The unit cell parameter ratio c/a=0.9385 of KDA is almost the same value as c/a=0.9359 of KDP.5,11)

Table IV gives interatomic distances of KDA and KDP at room temperature. Since the size of the As ion is larger than that of K, the As-O bond length is longer than that of P-O by 0.147 Å, which may expand the cell dimension by about 3.0%. Since the unit cell size of KDA is about 2.5% longer than that of KDP, the tilt angle of the AsO_4 tetrahedron and the interatomic distance between K and O should be arranged to reduce the cell dimension. In any case, the ion size difference between As and P is reduced and small differences exist in R_{OO}, r_{OH}, and δ.

We also note that the relation

$$\delta \cong R_{\mathrm{OO}} - 2r_{\mathrm{OH}} \tag{1}$$

is realized approximately, because the hydrogen bond is almost straight. In general, the transition temperature T_{c} is lower if the crystal has shorter R_{OO} in the crystal family of KDP.4) Thus it was surmised that R_{OO} of KDA is shorter than that of KDP, because T_{c} of KDA is the lowest among the pure crystals of the family at atmospheric pressure. However, that has been found to be untrue;5) the R_{OO} value of KDA is larger than that of KDP but shorter than the 2.523 Å of DKDP.11)

Referring to the X-ray study, the parameters r_{OH} and δ of KDA were estimated as 0.886(6) and 0.847(12) Å, respectively.5) Although the covalent electron in the O-H bond may exist between O and H, the proton is far from O, as determined by neutron studies.

The O-H distance r_{OH} = 1.057 Å of KDA is almost the same as that of KDP.

According to the quantum Ising model,[3,13)] the transition temperature is given by

$$T_{\mathrm{c}} = \frac{T_1}{\ln\dfrac{1+T_1/2T_0}{1-T_1/2T_0}} \approx \frac{T_0}{1+\dfrac{T_1{}^2}{12T_0{}^2}}, \tag{2}$$

where T_0 and T_1 represent the interaction energy and the energy gap of the two-level system, respectively. Comparing KDA with KDP, we can recognize that the H splitting distance δ of KDA is longer than that of KDP by an amount equal to the difference between R_{OO} and r_{OH}. This difference in δ crucially affects the proton tunneling frequency. For larger δ, T_1 is smaller, so that the transition temperature may increase. However, another factor is also important in the model; if the interaction strength between the order parameters becomes weak, T_0 becomes small. Then the transition temperature decreases rapidly.13)

A similar explanation holds if a quasi-harmonic phonon model is adopted, where the transition temperature is given by14,15)

$$T_{\mathrm{c}} = \frac{2\eta T_0}{\ln\dfrac{1+\eta}{1-\eta}} \approx \frac{T_0}{1+\dfrac{1}{3}\eta^2}, \tag{3}$$

where η is the quantum parameter, and the transition disappears at the quantum limit of η = 1, which corresponds to $T_1 = 2T_0$ in eq. (2). It is sometimes meaningless to distinguish between the quantum Ising and the quasi-harmonic cases.16)

It is widely accepted that the proton tunneling motion is coupled with the displacing motion of K and PO_4 in KDP-type crystals.17) In order to explain the T_{c}-pressure phase diagram, the mass of the quantum particle is estimated not as the proton mass but as the effective one, which is about half the mass of the H_2PO_4 molecule.15,18) This will be appropriate also for KDA. The heavy H_2AsO_4 may have low molecular-vibration frequencies, which may work to increase the transition temperature, but the large size of the tetragonal molecule may weaken the interaction to decrease the transition temperature. Therefore, we can image that the large As size makes R_{OO} large enough to cause two effects: on the one hand, the softening of the tunneling frequency and, on the other hand, the weakening of the proton-proton interactions as well as the AsO_4-AsO_4

(maybe dipole-dipole) interactions. Because of these competing mechanisms, T_c of KDA may become slightly lower than that of KDP.

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Table I. Crystallographic information of KDA at 298 K.

Crystal	KH_2AsO_4
Space group	$I\bar{4}2d$
Formula unit Z	4
a [Å]	7.635(4)
c [Å]	7.166(4)
Volume [Å ^{3}]	417.7(4)
Index range	$0 \leq h \leq 11$
	$0 \leq k \leq h$
	$0 \leq l \leq 11$
Scan range [°]	$2\theta < 156$
Total reflections	272
Unique reflections ($F > \sigma F$)	234
No. of parameters	23
R_1	0.0324
S	1.008
$(\Delta/\sigma)_{max}$	0.046

Table II. Atomic coordinates and equivalent displacement parameters of KDA at 298 K, with e.s.d.'s in parentheses.

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Atom	x	y	z	U_{eq} [Å ^{2}]
K	0	0	0.5	0.0224(8)
H	0.1587(5)	0.2237(5)	0.1221(9)	0.0311(11)
As	0	0	0	0.0157(3)
O	0.1594(1)	0.0857(2)	0.1350(2)	0.0217(2)

Table III. Atomic displacement parameters [Å ^{2}] of KDA at 298 K.

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Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
K	0.0243	-	0.0187	0	0	0
H	0.0279	0.0329	0.0324	-0.0006	-0.0026	-0.0064
As	0.0153	-	0.0166	0	0	0
O	0.0204	0.0203	0.0242	0.0029	-0.0070	-0.0041

Table IV. Interatomic distances [Å] of KDA at 298 K and of KDP taken from ref. 11. As-O should be read as P-O in KDP. The e.s.d.'s are given in parentheses. NN and NNN represent nearest-neighbor and next-nearest-neighbor positions, respectively.

Atom pair	Symbol	KDA	KDP
O-O	R_{OO}	2.513(2)	2.4946(6)
O-H	r_{OH}	1.057(4)	1.068(2)
H-H	δ	0.404(5)	0.365(3)
As-O		1.687(1)	1.5403(4)
K-O(NN)		2.805(2)	2.8274(3)
K-O(NNN)		2.958(2)	2.9000(8)

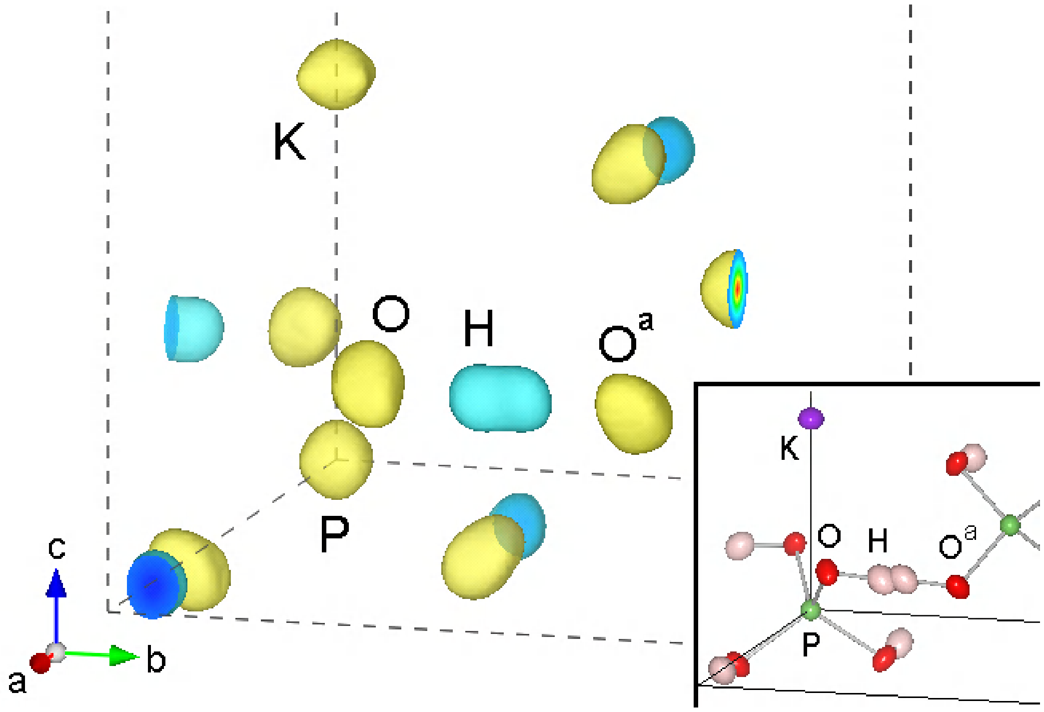

Fig. 1. (Color online) Atomic density distribution of KDA estimated by PRIMA. The isosurfaces of nuclear density level 5 are drawn using VESTA. The inset shows displacement ellipsoids and P-O and O-H bonds. The superscript a of O^a denotes symmetry codes of $x, 1/2-y, 1/4-z$.

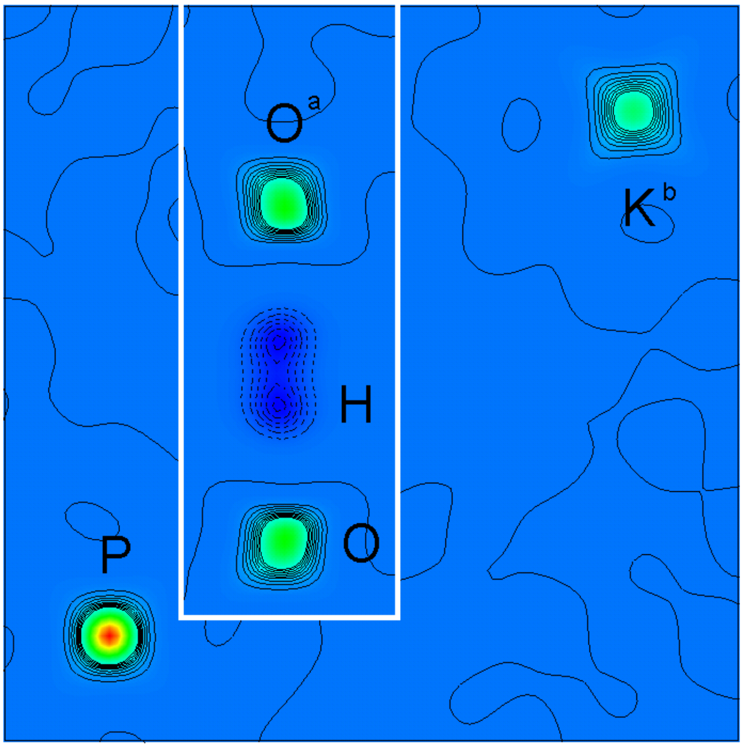

Fig. 2. (Color online) Contour map of P and K at $z = 0$, and O and H at $z = 0.125$. Contour lines are drawn every 5 level steps between -30 to 50; the broken lines for H are negative levels. The map range is $-0.1 < x,\ y < 0.6$. The superscripts a and b of O^a and K^b denote symmetry codes of $x, 1/2 - y, 1/4 - z$ and $1/2 + x, 1/2 + y, z - 1/2$, respectively.