Journal of the Physical Society of Japan
Vol. 70, No. 8, August, 2001, pp. 2327–2332

X-Ray Structural Study of Ferroelectric KH_2AsO_4 and KD_2AsO_4

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(Received April 11, 2001)

In order to understand systematically the relationship between the crystal structure and phase transition in tetragonal KH_2PO_4 (KDP) family, the structures of KH_2AsO_4 (KDA) and KD_2AsO_4 (DKDA), which are the end members concerning the transition temperature T_c, have been studied by X-ray diffraction at room temperature and at $T_c + 5$ K (110 K and 171 K, respectively). It was revealed that the hydrogen-bond distances R_{OO} for KDA and DKDA are longer than those for KDP and DKDP, respectively. These results smear the linear R_{OO} vs T_c relation found earlier in the tetragonal KDP family, contrary to our expectation. The temperature dependence of the bond lengths and angles in KDA and DKDA are compared with those in other members in the family and similarity and difference are discussed.

KEYWORDS: X-ray diffraction, KDP-type crystal, hydrogen-bonded ferroelectrics, transition temperature, isotope effect

§1. Introduction

Tetragonal KH_2PO_4 (KDP) type crystals (Fig. 1) constitute a group of typical hydrogen-bonded ferroelectrics. The member crystals belonging to this MH_2XO_4 family (M = K, Rb, Cs, NH_4; X = P, As) have the following characteristics: (1) they are isomorphous, with the space group $I\bar{4}2d$ in the room temperature phase and (2) the protonated compounds exhibit a large isotopic upward shift (~ 100 K) of the transition temperature T_c when deuterium is substituted for hydrogen.[1)] The origin of this remarkable isotope effect and phase transition mechanism have attracted much interest and extensive experimental and theoretical studies have been devoted to elucidate them.[2–4)] This group of crystals, which includes many isomorphous members, is exceptional in ferroelectric compounds since a crystal often changes its structure by changing part of the constituent atoms. Tetragonal KDP-type crystals therefore offer a unique opportunity to investigate systematically the relationship between phase transition and structure. The crystal structure of the KDP family, in particular KDP and DKDP, has been extensively investigated by X-ray diffraction as well as neutron diffraction.[5,6)] It is known that the transition temperature is affected by the change of atoms at the M and X sites, although the deuteration effect is the most remarkable (*e.g.* ref. 7).

KH_2AsO_4 (KDA) and KD_2AsO_4 (DKDA) also belong to the tetragonal KDP family and have the lowest transition temperature among the members (97 K and 162 K, respectively).[1)] The structure of KDA, however, has been studied much less than that of KDP[8)] and the structure of DKDA has not yet been reported. Due to these circumstances the structures of KDA and DKDA have been determined by X-ray diffraction at room temperature and at $T_c + 5$ K (110 K and 171 K respectively) in order to study systematically the relationship between crystal structure and phase transition in the tetragonal KDP family. The purpose of this paper is to report these results and to discuss the temperature dependence of the bond lengths and angles in comparison with those in other members of the family.

§2. Experimental

KH_2AsO_4 was synthesized by the reaction $K_2CO_3 + As_2O_4 + 2H_2O \rightarrow 2KH_2AsO_4 + CO_2$. Single crystals were grown by cooling the saturated solution around 313 K. KD_2AsO_4 crystals were similarly obtained from cooling the saturated D_2O solution. As-grown crystals with well developed natural faces were selected as specimen. All faces of the specimen were indexed and the distances to each face from the origin placed at an intersecting point of three faces were measured. The maximum origin to face distance of the specimen was 0.15 mm for KH_2AsO_4 and of 0.25 mm for KD_2AsO_4. Intensity data were collected using Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) on a Huber/Stoe/Aracor four-circle diffractometer equipped with a 400 mm χ-circle and two-stage closed-cycle helium refrigerator.[9)] The data collection was done over one hemisphere of the reciprocal space. The other experimental details are given in Table I.

It was necessary to know T_c of the specimen used to collect the data just above T_c, since T_c depends on the crystal quality as well as the deuterium content in the case of deuterated crystals. T_c of the sample was estimated from an average of the highest transition temperature on cooling and the lowest transition temperature on heating during several thermal cyclings, since tetragonal KDP family is known to exhibit a first-order transition. The transition temperature was judged from the peak-splitting of the intensity profiles due to the formation of ferroelectric domains below T_c. The estimated T_c was 105(1) K for KH_2AsO_4 and 166(1) K for KD_2AsO_4. Thus the temperature at $T_c + 5$ K for

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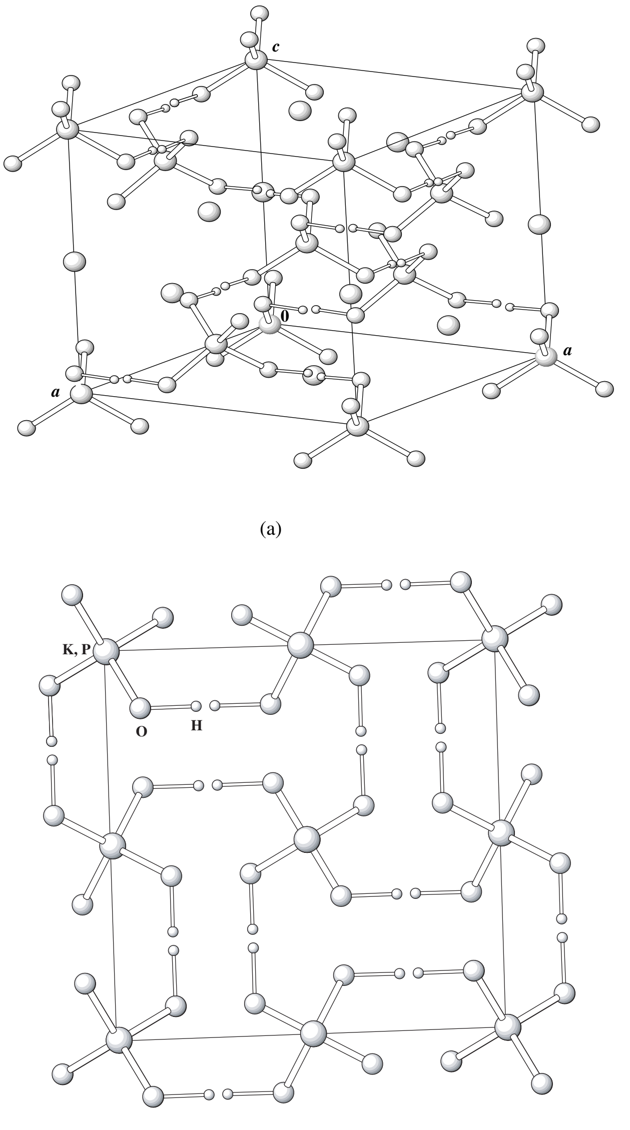

Fig. 1. Structure of tetragonal KH_2PO_4 (KDP). (a) perspective view and (b) projection along the *c*-axis.

Table I. Experimental details of the data collection, the number of reflections used in the calculations and discrepancy factor $R(F^2)$ of KDA and DKDA. The h, k, and l denote the range of the indices covered in the data collection.

	KDA (297 K)	KDA (110 K)	DKDA (296 K)	DKDA (171 K)
Number of reflections measured	3273	4599	7078	7145
$2\theta_{\max}$	102°	105°	106°	106°
$\frac{\sin(\theta_{\max})}{\lambda}$	1.09345	1.11625	1.12368	1.12368
h	0 to 14	−16 to 0	−17 to 17	−17 to 17
k	0 to 14	−16 to 11	−17 to 7	−17 to 7
l	−14 to 14	−15 to 15	−15 to 15	−16 to 16
Number of reflections used	2505	3649	5337	5479
$R(F^2)$ (%)	2.43	4.05	4.48	3.52

Table II. Lattice constant determination of KDA and DKDA.

	KDA (297 K)	KDA (110 K)	DKDA (296 K)	DKDA (171 K)
Number of reflections measured	49	48	39	48
$2\theta_{\max}$	67.89°	68.17°	68.84°	68.93°
$2\theta_{\min}$	60.74°	61.02°	52.35°	47.62°
a (= b) (Å)	7.6228(3)	7.5973(4)	7.6343(5)	7.6237(7)
c (Å)	7.1547(4)	7.0966(5)	7.1583(5)	7.1163(7)
V (Å^3)	415.74(3)	409.61(4)	417.21(6)	413.60(7)

KH_2AsO_4 was set at 110 K and for KD_2AsO_4 at 171 K. The estimated T_c of KH_2AsO_4 and KD_2AsO_4 of our specimen is 8 K and 4 K, respectively, higher than the earlier values.[1)]

Lattice parameters have been determined using 2θ values of high angle reflections. Details are given in Table II. Intensity measurements were carried out in the ω–2θ scan mode. Six standard reflections were measured every 240 min. The intensities were corrected for the time variation of the standard reflections by the method of MacCandlish *et al.*[10)] The data set was corrected for background effect and Lorentz, polarization and absorption effects, which were calculated by numerical integration from the face indices and distances between the faces of the specimen.

All calculations were performed using the program system described by Lundgren.[11)] Atomic scattering factors and mass attenuation coefficients were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV).

§3. Analysis and Results

All measured reflections were used in the least-squares analysis. Function minimized in the refinements was $w(F_o^2 - F_c^2)^2$ with $w = 1/\sigma^2(F^2)$, where $\sigma^2(F^2)$ was estimated from counting statistics and the scatter of the standard reflections. The extinction effect was corrected by a type I isotropic extinction parameter with Lorentzian distribution.[12)]

Fractional atomic coordinates and anisotropic displacement parameters are given in Table III, where the results by Nakano[8)] is also given for comparison. The values of our results of KDA at 297 K agree within three times the combined standard deviations with those at 293 K by Nakano. Selected bond lengths and angles are given in Table IV. It must be remembered that the distances involving hydrogen are not true internuclear distances, but correspond to distances between the maxima of the electron densities (as X-rays have been used). $R(F^2)$ is expressed by

$$R(F^2) = \frac{\Sigma_{\boldsymbol{H}}\left||sF_o(\boldsymbol{H})|^2 - |F_c(\boldsymbol{H})|^2\right|}{\Sigma_{\boldsymbol{H}}|sF_o(\boldsymbol{H})|^2} \qquad (1)$$

where $\boldsymbol{H}$ denotes the reciprocal lattice vector and s is the scale factor.

Table III. Fractional coordinates and displacement parameters of KDA and DKDA.

		KDA (297 K)	KDA (110 K)	DKDA (296 K)	DKDA (171 K)	KDA[8] (293 K)
K	u^{11} ($= u^{22}$)	0.02268(4)	0.00920(4)	0.02320(4)	0.01331(3)	0.0224(6)
	u^{33}	0.01815(6)	0.00699(6)	0.01816(6)	0.01029(4)	0.0178(5)
As	u^{11} ($= u^{22}$)	0.01464(3)	0.00624(3)	0.01549(3)	0.00940(2)	0.0131(4)
	u^{33}	0.01789(4)	0.00853(4)	0.01896(4)	0.01324(3)	0.0164(3)
O	x	0.15962(5)	0.16066(6)	0.15983(5)	0.16072(4)	0.1610(5)
	y	0.08542(6)	0.08582(6)	0.08437(6)	0.08403(4)	0.0867(5)
	z	0.13540(6)	0.13620(6)	0.13539(6)	0.13608(4)	0.1336(7)
	u^{11}	0.01863(14)	0.00761(15)	0.01953(15)	0.01154(11)	0.0180(9)
	u^{22}	0.02022(15)	0.00902(16)	0.02031(16)	0.01218(11)	0.0203(11)
	u^{33}	0.02672(15)	0.01157(16)	0.02756(16)	0.01658(11)	0.0281(16)
	u^{12}	0.00228(12)	0.00024(13)	0.00269(12)	0.00125(9)	0.0034(9)
	u^{13}	−0.00763(14)	−0.00322(14)	−0.00769(14)	−0.00457(10)	−0.0049(12)
	u^{23}	−0.00592(13)	−0.00231(15)	−0.00578(15)	−0.00305(10)	−0.0068(12)
H/D	x	0.1611(9)	0.1605(9)	0.1602(7)	0.1626(16)	
	y	0.1979(8)	0.1961(8)	0.1878(6)	0.1951(5)	
	z	0.1044(9)	0.1095(11)	0.1163(8)	0.1199(7)	

Table IV. Selected bond lengths and angles of KDA and DKDA.

	KDA (297 K)	KDA (110 K)	DKDA (296 K)	DKDA (171 K)
Distances (Å)				
$O\cdots O^{i}$ (R_{OO})	2.5135(9)	2.4998(10)	2.5333(9)	2.5355(7)
As–O	1.6861(4)	1.6879(5)	1.6861(4)	1.6880(3)
K–O	2.9511(4)	2.9292(5)	2.9523(4)	2.9357(4)
$K–O^{ii}$	2.7980(4)	2.7792(5)	2.7986(4)	2.7854(4)
O–H(D)	0.886(6)	0.859(6)	0.802(5)	0.855(4)
$H\cdots O^{i}$	1.653(6)	1.657(6)	1.739(5)	1.684(4)
$H–H^{i}$	0.847(12)	0.848(12)	0.957(9)	0.840(7)
Angles (°)				
θ	61.85(2)	61.89(2)	62.17(2)	62.46(1)
$O–As–O^{iii}$ (α_1)	109.86(3)	110.13(3)	109.83(3)	109.99(2)
$O–As–O^{iv}$ (α_2)	109.28(1)	109.14(2)	109.21(1)	109.24(1)
$O–H\cdots O^{i}$	163.0(6)	166.2(8)	170.6(6)	173.6(6)

Symmetry codes: (i) $x, \frac{1}{2}-y, \frac{1}{4}-z$; (ii) $-y, \frac{1}{2}-x, \frac{1}{4}+z$; (iii) $-x, -y, z$; (iv) $-y, x, -z$.

§4. Discussion

From a structural point of view, the basic unit of tetragonal KDP-type crystals MH_2XO_4 consists of alkaline metal M, tetrahedron XO_4, and hydrogen bond $O–H\cdots O$ connecting two XO_4 ions (Fig. 1). As shown in Fig. 2 in more detail, geometrical parameters characterizing the tetragonal KDP-type structure are thus (1) the ionic radius of the M atom, (2) the size, distortion, and rotation angle θ of the XO_4 ions around the c-axis, and (3) hydrogen-bond distance R_{OO}. The distortion of the tetrahedron XO_4 can be expressed by using Baur's distortion indices[13] which are defined by the average deviations of X–O lengths, O–X–O angles, and O–O edge from their means:

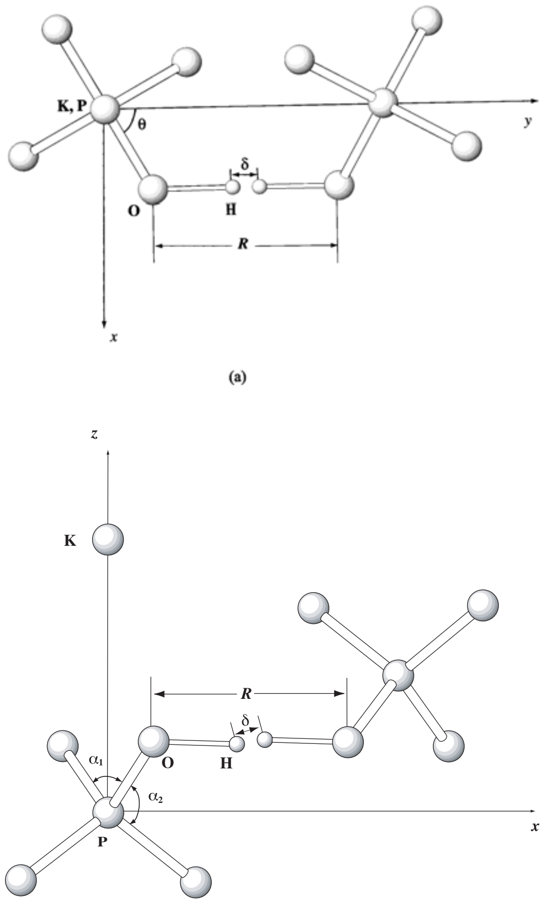

Fig. 2. Part of the structure of tetragonal KH_2PO_4 (KDP) and some structural parameters. (a) view along the c-axis and (b) view along the b-axis.

$$\mathrm{DI(XO)} \equiv \sum_{i=1}^{4} \frac{|\mathrm{XO_i} - \mathrm{XO_m}|}{4\mathrm{XO_m}} \tag{2}$$

$$\mathrm{DI(OXO)} \equiv \sum_{i=1}^{6} \frac{|\mathrm{OXO_i} - \mathrm{OXO_m}|}{6\mathrm{OXO_m}} \tag{3}$$

$$\mathrm{DI(OO)} \equiv \sum_{i=1}^{6} \frac{|\mathrm{OO_i} - \mathrm{OO_m}|}{6\mathrm{OO_m}}. \tag{4}$$

where $\mathrm{XO_i}$ stands for the individual X–O distances, $\mathrm{OXO_i}$ for the individual angles O–X–O, $\mathrm{OO_i}$ for the individual tetrahedral edges O–O and m signifies the mean value.

Since there is no difference in the X–O lengths in the KDP-type structure in the tetragonal phase (space group $\mathrm{I\bar{4}2d}$) above T_c, the distortion is simply expressed by the distortion indices DI(OXO) [or equivalently DI(OO)]. Furthermore, if we take into consideration that

(1) in a $\mathrm{XO_4}$ ion with the site symmetry $\bar{4}$, there are two O–X–O angles α_1 with two *up* (*down*) O atoms and four O–X–O angles α_2 with one *up* and one *down* O atom [see Fig. 2(b)],
(2) the relation that $\alpha_1 > \langle\alpha\rangle_{av} > \alpha_2$ is valid for KDP-type crystals, where $\langle\alpha\rangle_{av}$ is the mean value $((\alpha_1 + 2\alpha_2)/3)$, and
(3) $\langle\alpha\rangle_{av}$ is known to be kept constant (109.4°) for various $\mathrm{PO_4}$[13,14] and $\mathrm{AsO_4}$[15] groups,

then eq. (3) becomes

$$\mathrm{DI(OXO)} = \frac{1}{3\langle\alpha\rangle_{av}} (\alpha_1 + \langle\alpha\rangle_{av} - 2\alpha_2) \tag{5}$$

Expressing α_2 by α_1 and $\langle\alpha\rangle_{av}$, we get

$$\mathrm{DI(OXO)} = \frac{2}{3} \frac{\alpha_1 - \langle\alpha\rangle_{av}}{\langle\alpha\rangle_{av}} \tag{6}$$

Through this equation, there exists one to one correspondence between α_1 and DI(OXO); i.e. the distortion increases with increasing α_1. The magnitude of α_1 can thus be regarded as a measure of the distortion of the $\mathrm{XO_4}$ ion. We will therefore use α_1 in stead of DI(OXO) hereafter.

4.1 Hydrogen-bond distance R_{OO}

The temperature dependence of the hydrogen-bond distance R_{OO} in KDA and DKDA is shown in Fig. 3 together with other tetragonal KDP-type compounds. The most remarkable result is that R_{OO} of KDA and DKDA just above T_c are larger than those of KDP and DKDP, respectively, although T_c of the former are lower than those of the latter. This smears out the linear relation T_c vs R found earlier in tetragonal KDP-type compounds.[16] This seems to indicate that some structural parameters other than R_{OO} also affect T_c.

R_{OO} of KDA decreases with decreasing temperature similarly to KDP. On the other hand, no decrease in R_{OO} with decreasing temperature could be seen in DKDA, but instead an increase. This is unexpected since R_{OO} usually decreases with a decrease of the lattice constant a. However, the decrease in R_{OO} in DKDP is very small.

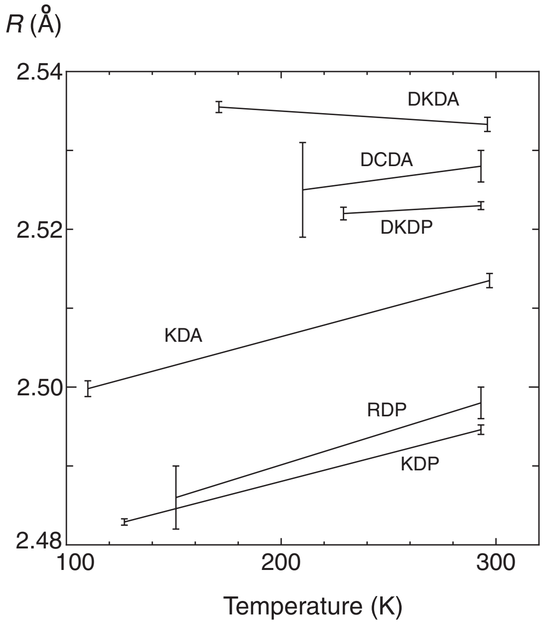

Fig. 3. Temperature dependence of the hydrogen-bond distances R_{OO} in some tetragonal KDP-type compounds: KDP: $\mathrm{KH_2PO_4}$; DKDP: $\mathrm{KD_2PO_4}$; RDP: $\mathrm{RbH_2PO_4}$; KDA: $\mathrm{KH_2AsO_4}$; DKDA: $\mathrm{KD_2AsO_4}$; DCDA: $\mathrm{CsD_2AsO_4}$.

4.2 Rotation angle θ around the c-axis

The temperature dependence of the rotation angle θ around the *c*-axis is shown in Fig. 4. The θ value in both KDA and DKDA is the largest among the family members shown. The θ value in KDA shows almost no temperature dependence, but the θ value in DKDA exhibits a clear increase with decreasing temperature, similarly to DKDP. This may probably be interpreted as

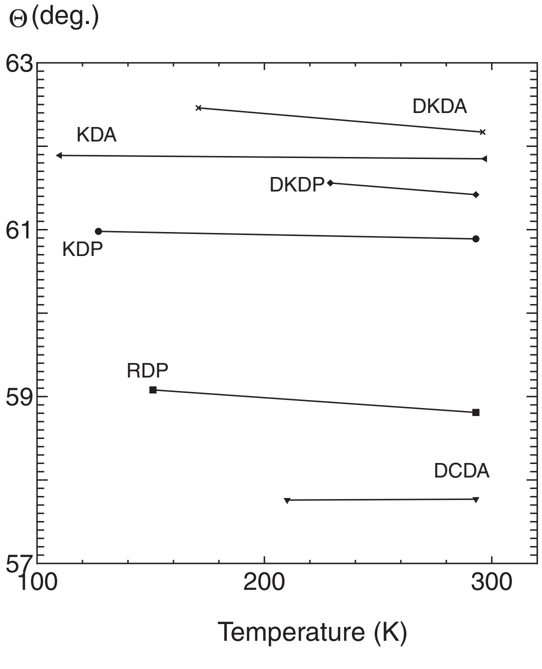

Fig. 4. Temperature dependence of the rotation angle θ around the *c*-axis in some tetragonal KDP-type compounds. The notations for the compounds are the same as in Fig. 3.

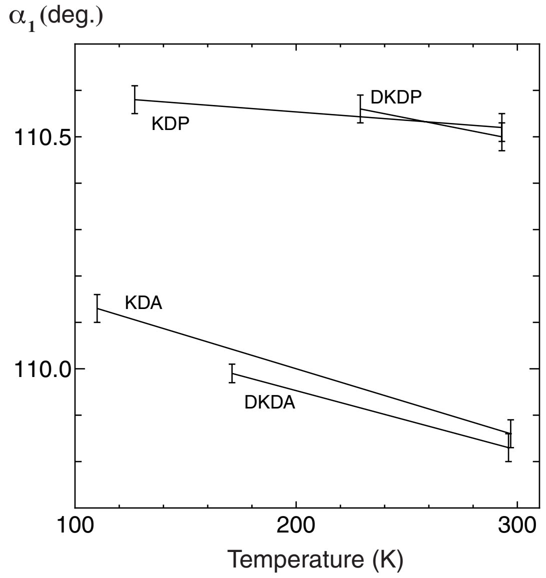

Fig. 5. Temperature dependence of the OXO angle α_1 in the XO_4 tetrahetron in some tetragonal KDP-type compounds. The notations for the compounds are the same as in Fig. 3.

that a contraction of the lattice constant a in DKDA result in an increase of the XO_4 rotation angle. A general trend in the family is that the θ angle has a tendency to increase with decreasing temperature.

4.3 OXO angle α_1 in the XO_4 tetrahedron

The temperature dependence of the OXO angle α_1 of the XO_4 tetrahedron in KDA and DKDA is shown in Fig. 5 together with KDP and DKDP. It can be generally stated that the α_1 value appears to increase with decreasing temperature, although more accurate data are needed to draw definite conclusions. Furthermore, the α_1 value shows almost no change on deuteration. These results indicate that the distortion of the XO_4 tetrahedron increases with decreasing temperature in general. The α_1 value in KDA is smaller than that in KDP, indicating that the distortion of the tetrahedron is less in KDA than in KDP. This conclusion is consistent with that derived from Raman spectra of KDA.[17)]

4.4 Displacement parameters of K and As atoms

The temperature dependence of the displacement parameters u^{ii} of the K and As atoms in KDA and DKDA are shown in Fig. 6. It is clearly seen that only the y intercept of the u^{33}(As) line is definitely positive for both of H and D compounds, while the others are around 0. These facts are common to the other members of the tetragonal KDP family.[5)] The inequalities $u^{11}(\mathrm{K}) > u^{33}(\mathrm{K})$, $u^{11}(\mathrm{As}) > u^{33}(\mathrm{As})$ are also valid, as in other crystals of this family.

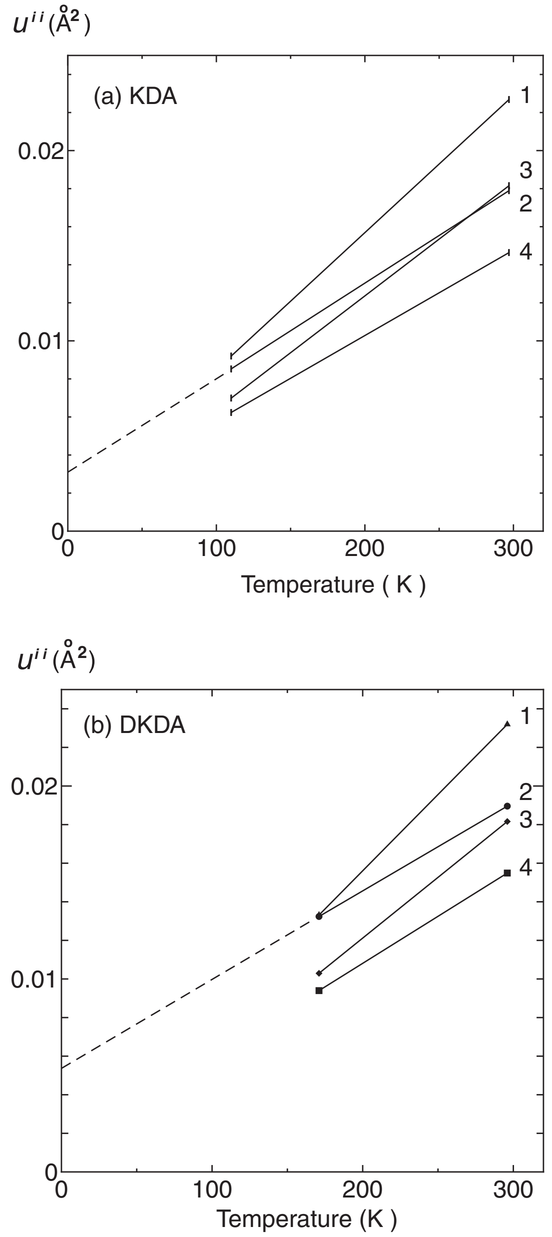

Fig. 6. Temperature dependence of the displacement parameters u^{ii} of K and As for (a) KDA (KH_2AsO_4) and (b) DKDA (KD_2AsO_4). 1: u^{11}(K); 2: u^{33}(As); 3: u^{33}(K); 4: u^{11}(As).

§5. Summary

(1) The hydrogen-bond distances R_{OO} in KDA and DKDA are longer than those in KDP and DKDP in spite of the fact that the transition temperatures of the former are lower than of the latter. This smears out the linear relation T_c vs R_{OO} found earlier in tetragonal KDP-type compounds.[16)] The distance R_{OO} in KDA decreases with decreasing temperature similarly to other members of the tetragonal KDP family. However, no obvious decrease in R_{OO} with decreasing temperature could be seen in DKDA.

(2) The θ value in both of KDA and DKDA is the largest among the family members shown, which may suggest the existence of an inverse correlation of T_c with θ.

(3) The α_1 value in KDA is smaller than that in KDP, indicating that the distortion of the XO_4 tetrahedron is less in KDA than in KDP, which is consistent with Raman spectra of KDA.

These new facts seem to imply the existence of subsidiary structural parameters other than the primary parameter R_{OO}. The results of the investigation of the correlations between certain structural parameters and the transition temperature will be published elsewhere.[18)]

Acknowledgment

We thank Hilding Karlsson for his skilled assistance in the data collection.

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