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N Onoda-Yamamuro†‖, O Yamamuro†, T Matsuo†¶, M Ichikawa‡,
R M Ibberson§ and W I F David§

† Department of Chemistry, Graduate School of Science, Osaka University,
Machikaneyama-cho 1-1, Toyonaka, Osaka 560-0043, Japan
‡ Division of Physics, Graduate School of Science, Hokkaido University, Sapporo 060-0810,
Japan
§ ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire OX11 0QX, UK

E-mail: matsuo@chem.sci.osaka-u.ac.jp

Abstract. Neutron diffraction experiments on the room- and low-temperature phases of $K_3H(SeO_4)_2$ ($T_{trs} = 21$ K) and $K_3D(SeO_4)_2$ ($T_{trs} = 105$ K) have been performed using the time-of-flight high-resolution powder diffractometer HRPD at the ISIS pulsed neutron source. Data were collected at 2 and 30 K for $K_3H(SeO_4)_2$ and 2 and 130 K for $K_3D(SeO_4)_2$ over the d-spacing range 0.7–2.4 Å. The room-temperature phases of the crystals have monoclinic structure belonging to the space group $A2/a$. Rietveld refinement combined with the published dielectric and calorimetric studies reveals that H/D atoms are disordered over two symmetry-equivalent positions. The hydrogen bonds are non-linear with an O–H/D$\cdots$O angle of 175(1)°. The hydrogen bond length is 2.495(1) Å in $K_3H(SeO_4)_2$ and 2.533(2) Å in $K_3D(SeO_4)_2$. The separation between the half occupancy hydrogen positions is 0.32(1) Å for $K_3H(SeO_4)_2$ and 0.550(4) Å for $K_3D(SeO_4)_2$. The relation between these structural parameters and the isotope effect in the transition temperature is discussed. Diffraction patterns of the low-temperature phases indicated that the structure change accompanying the transition is very small.

1. Introduction

The isotope effect on the phase behaviour of the $M_3H(XO_4)_2$ type of crystals is remarkably large (M = K, Rb, X = S, Se). $K_3H(SeO_4)_2$ undergoes a phase transition at 20 K and $K_3D(SeO_4)_2$ at 103 K [1, 2]. $K_3H(SO_4)_2$ [3], $Rb_3H(SO_4)_2$ [3] and $Rb_3H(SeO_4)_2$ [4, 5] show no phase changes from room temperature down to the lowest temperature examined (typically 4.2 K), whereas their deuterated analogues undergo phase transitions at 70–100 K.

At room temperature, they share the same crystal symmetry of the monoclinic space group $A2/a$. For $Cs_3H(SeO_4)_2$ the structure is slightly different [6] but the isotope effect is equally large. Figure 1 shows the structure of $M_3H(XO_4)_2$ projected on the ac-plane. The crystals are formed by coulombic attraction between the M^+ ions and the dimers of two XO_4^{2-} ions connected by a short hydrogen bond. The proton may be situated on the inversion centre at the midpoint of the hydrogen bond or may be disordered over two symmetry-equivalent

‖ Present address: Department of Natural Sciences, College of Science and Engineering, Tokyo Denki University, Hatoyama, Hiki-gun, Saitama 350-0394, Japan.
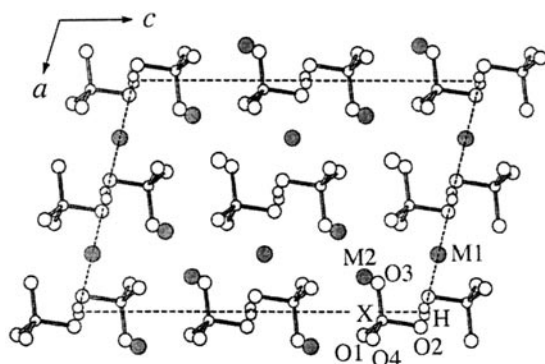¶ Author to whom any correspondence should be addressed.

Figure 1. A projection onto the (010) plane of the structure of $M_3H(XO_4)_2$ with the monoclinic space group $A2/a$. The H atom is placed on two symmetry-equivalent positions.

positions as shown in figure 1. The neighbouring dimer anions are separated from each other by cations (hence the appellation zero-dimensional hydrogen bond network sometimes attached to them). The disconnectivity makes the structure free from the ice rules [7] that impose strong correlation between the positions of the hydrogen atoms on the adjacent hydrogen bonds in ice and KH_2PO_4.

X-ray diffraction studies of $K_3H(SO_4)_2$ [8] and $K_3D(SO_4)_2$ [9] show that the H and D atoms are disordered at room temperature and only D atoms become ordered at the transition temperature [10]. A neutron diffraction study of $Rb_3H(SeO_4)_2$ reports that the H atoms are disordered even at 4 K [11]. For $K_3H(SeO_4)_2$, only the positions of heavy atoms were determined in a x-ray diffraction study [12].

In the present study, neutron powder diffraction experiments were carried out on the room- and low-temperature phases of $K_3H(SeO_4)_2$ and $K_3D(SeO_4)_2$. The purpose of the experiment was to determine the symmetry and structural parameters involved in the hydrogen bond. The comparison of the H and D crystals gives an important piece of structural information about the origin of the deuterium substitution effect. A recent calorimetric study has shown that $K_3H(SeO_4)_2$ becomes only marginally ordered at the lowest temperature as a result of the opposing effects of quantum fluctuation and ordering forces, while $K_3D(SeO_4)_2$ behaves in a classical way [2].

2. Experiment

The samples were prepared as described elsewhere [2]. Neutron powder data were collected on the time-of-flight (TOF) high-resolution powder diffractometer, HRPD [13], at the ISIS pulsed neutron source, Rutherford Appleton Laboratory, UK. The powders ($K_3H(SeO_4)_2$: 6.788 g, $K_3D(SeO_4)_2$: 6.836 g) were contained in a vanadium can under helium gas. Intensity data were recorded in the back-scattering geometry in a TOF range 32–117 ms, corresponding to a d-spacing range 0.66–2.43 Å. The resolution of the data ($\Delta d/d$) is $\sim 8 \times 10^{-4}$. The data were collected at 2 and 30 K for $K_3H(SeO_4)_2$, and 2 and 130 K for $K_3D(SeO_4)_2$, each for a period of 7–8 h. A standard data reduction was used; the spectral distribution of the incident neutron beam and the detector efficiency were normalized using a beam monitor spectrum and a vanadium standard. Rietveld refinement was carried out with the program TF12LS [14].

3. Results and discussion

3.1. Structure of the room-temperature phase

Figures 2 and 3 show the neutron powder diffraction patterns of $K_3H(SeO_4)_2$ at 30 K and $K_3D(SeO_4)_2$ at 130 K, respectively. The plus marks denote the observed intensities, and the solid lines those calculated as described below. The vanadium Bragg reflections from the sample environment were excluded from the refinement. Though the background level of the $K_3H(SeO_4)_2$ data is evidently higher than that of $K_3D(SeO_4)_2$ due to the incoherent scattering from the proton, the statistical quality of both sets of data was good enough for the Rietveld refinement.

The observed reflections were indexed fully with the space group $A2/a$ as reported [12]. The initial parameters of the refinement were taken from the literature as obtained by x-ray diffraction at 30 K [15]. We started the refinement with the H/D atom situated on the inversion centre at the midpoint of the hydrogen bridge and with isotropic displacement parameters for all atoms, and obtained a satisfactory convergence. In the next stage, we considered two models for the H/D atom; the H/D atom is situated on the inversion centre at the hydrogen bond with anisotropic displacement parameters (model 1) and the H/D atom is disordered in a double-minimum potential over two symmetry-equivalent positions with an isotropic displacement parameter (model 2). In refining with model 2, the H/D atom was initially placed at a position with the O(2)–H/D distance of 1.0 Å and the O(2)–H/D···O(2) angle of 180°. At this stage, a better fit was obtained with the χ^2-value decreasing from 1.79 to 1.75 for $K_3H(SeO_4)_2$ and from 2.55 to 2.28 for $K_3D(SeO_4)_2$. However, there was no significant difference between the refinements based on the two models, either in the refined structural parameters of the heavy atoms or in the χ^2-value. Low-temperature calorimetric study indicates that both protons and deuterons are disordered in a double-minimum potential [2] in better agreement with model 2. The diffraction intensities calculated from model 2 are shown by the solid line in figure 2 and 3. The tick marks represent the calculated peak positions and the curve below them represents the differences between the observed and calculated intensities. The final structural parameters of $K_3H(SeO_4)_2$ and $K_3D(SeO_4)_2$ are tabulated in tables 1 and 2, respectively. For $K_3H(SeO_4)_2$, all the refined structural parameters of the heavy atoms were in good agreement with those found by x-ray study [15]. The hydrogen bond length O(2)···O(2) of 2.495(1) Å agrees well with that of 2.497(2) Å at 30 K by x-ray diffraction. The hydrogen bond length of $K_3D(SeO_4)_2$, 2.533(2) Å, obtained here at 130 K is larger than that of $K_3H(SeO_4)_2$, 2.515(2) Å, at 297 K from x-rays [15]. With thermal expansion taken into account, the hydrogen bond length of $K_3D(SeO_4)_2$ is clearly longer than that of $K_3H(SeO_4)_2$ at least below room temperature. The alignment is clearly non-linear for both compounds, with an O(2)–H/D···O(2) angle of 175(1)° for both $K_3H(SeO_4)_2$ and $K_3D(SeO_4)_2$. The H···H distance of 0.32(1) Å in $K_3H(SeO_4)_2$ is unambiguously shorter than that of 0.550(4) Å in $K_3D(SeO_4)_2$. This, coupled with delocalization of the proton over to the two positions, may be the structural explanation of the strong isotope effect in the transition temperature.

Figure 4 shows the Fourier contour maps of the (110) plane around the hydrogen bond in $K_3H(SeO_4)_2$ and $K_3D(SeO_4)_2$. The inversion centre is located at the centre of the map. The H/D atom and the O atoms are sitting approximately in this plane. The map strongly suggests that the D atom is located on the two symmetry-equivalent positions in a double-minimum potential. In contrast, the H atom appears to be situated on the inversion centre at the midpoint of the hydrogen bond. In view of the phase transition found in dielectric and calorimetric experiments, the disorder model is more probable. However, the distinction between the disordered and truly centred structures may be subtle because the zero point
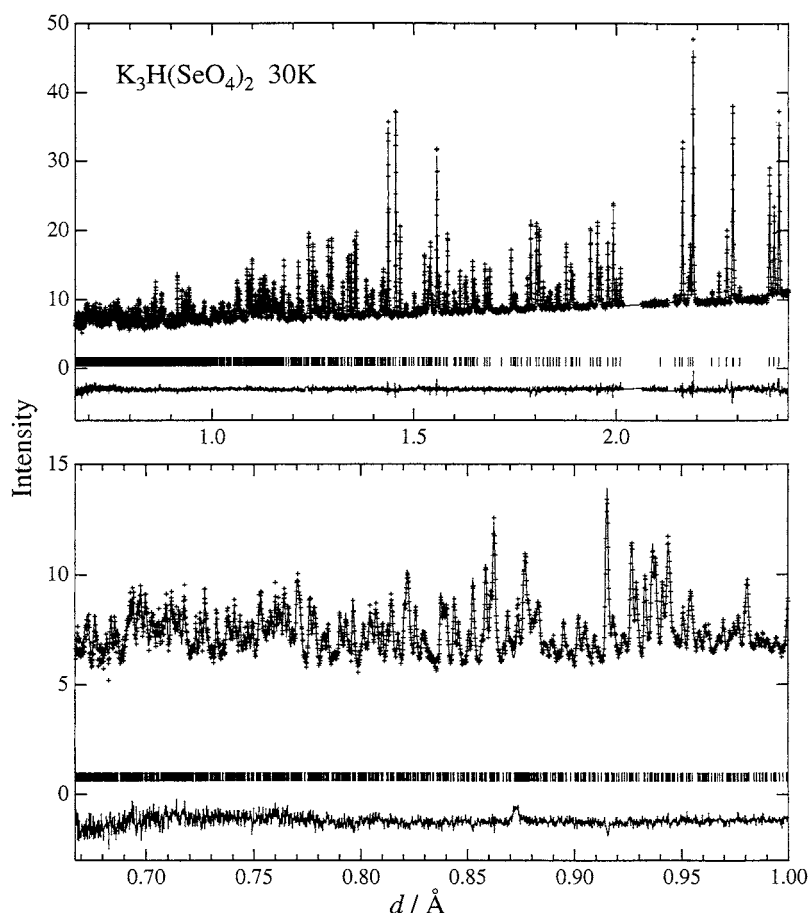
Figure 2. Neutron powder diffraction patterns of the room-temperature phase of $K_3H(SeO_4)_2$ recorded at 30 K. The plus marks denote the observed intensities and the solid line those calculated from the best-fit model of the Rietveld refinement. The tick marks represent the calculated peak positions and the curve below them represents the deviation between observed and calculated intensities.

amplitude is comparable with the separation between the two stable positions. Interestingly the two hydrogen positions in $Rb_3H(SeO_4)_2$ are separated by 0.34(3) Å [11], essentially the same distance as we found here, 0.32(1) Å, in the disordered phase of $K_3H(SeO_4)_2$. An interpretation of these structural parameters is that the proton tunnels between two potential minima with a more or less delocalized wave function having two maxima of amplitude centred at each of the potential minima. Drawing a distinction between the disordered structure and the intrinsic two-maximum case (the tunnelling ground state) may be a still subtler problem.

3.2. Structure of the low-temperature phase

New reflection peaks which are characteristic of a symmetry change were not found in the data taken at 2 K for either compound. The observed reflections in the diffraction patterns could again be indexed fully with the same space group of $A2/a$. In order to investigate the effect of the phase transition, Rietveld analysis based on the space group $A2/a$ was carried out using the
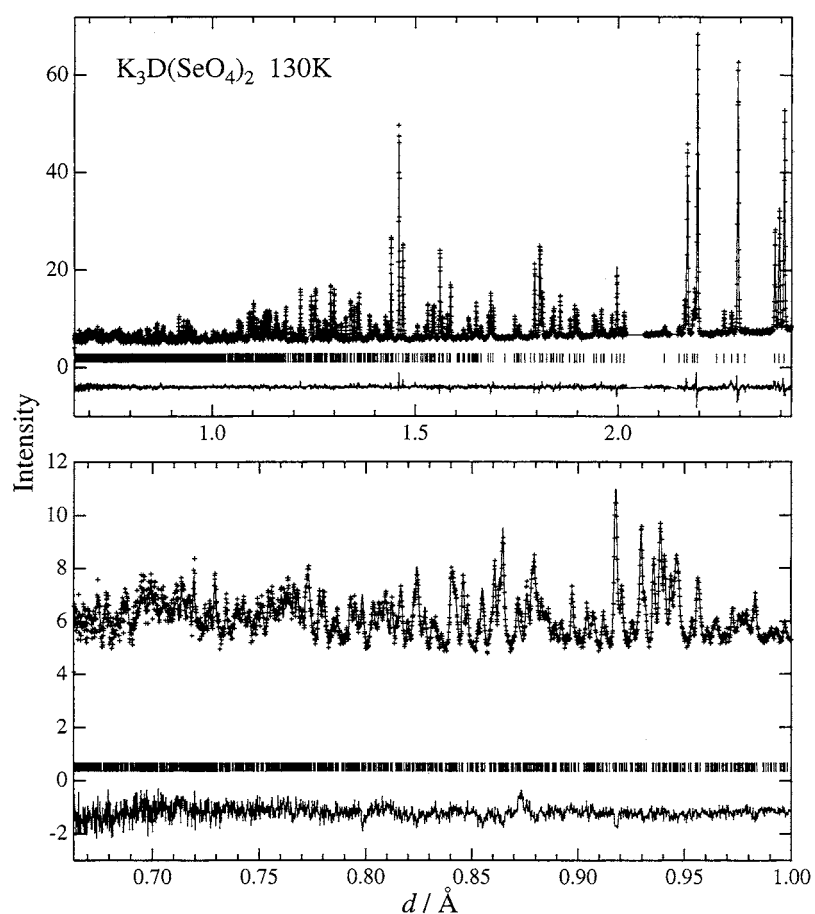
Figure 3. Neutron powder diffraction patterns of the room- temperature phase of $K_3D(SeO_4)_2$ recorded at 130 K. The meaning of the marks is the same as in figure 2.

Table 1. Final structural parameters for $K_3H(SeO_4)_2$ at 30 K. Space group $A2/a$ (No 15), $a = 10.049\,90(5)$ Å, $b = 5.859\,54(1)$ Å, $c = 14.829\,17(4)$ Å, $\beta = 103.6307(2)°$, $Z = 4$. $R_p = 1.86\%$, $R_{wp} = 2.10\%$, $R_{exp} = 1.59\%$ and $\chi^2 = 1.76$ for 6277 profile points and 46 variable parameters including 30 structure variables.

Atom	x	y	z	B_{iso}
K(1)	1/4	0.7608(4)	0	0.42(4)
K(2)	0.6518(2)	0.7367(3)	0.1961(1)	0.52(2)
H[a]	0.4896(7)	0.0205(12)	−0.0033(5)	1.19(7)
Se	0.460 27(7)	0.2327(1)	0.116 51(4)	0.28(1)
O(1)	0.3984(1)	0.0110(2)	0.158 65(7)	0.60(2)
O(2)	0.4347(1)	0.1806(2)	0.001 13(7)	0.56(2)
O(3)	0.625 36(4)	0.2501(2)	0.1546(1)	0.66(2)
O(4)	0.3813(1)	0.4671(2)	0.130 12(7)	0.54(3)

[a] Site occupancy 0.5.

final structural parameters for 30 K in $K_3H(SeO_4)_2$ and for 130 K in $K_3D(SeO_4)_2$ as the starting model. The χ^2-values were 2.94 for $K_3D(SeO_4)_2$ and 1.80 for $K_3H(SeO_4)_2$, respectively. The

Table 2. Final structural parameters for $K_3D(SeO_4)_2$ at 130 K. Space group $A2/a$ (No 15), $a = 10.08029(5)$ Å, $b = 5.87311(1)$ Å, $c = 14.86206(4)$ Å, $\beta = 103.6169(2)°$, $Z = 4$. $R_p = 2.67\%$, $R_{wp} = 3.07\%$, $R_{exp} = 2.01\%$ and $\chi^2 = 2.33$ for 6299 profile points and 46 variable parameters including 30 structure variables.

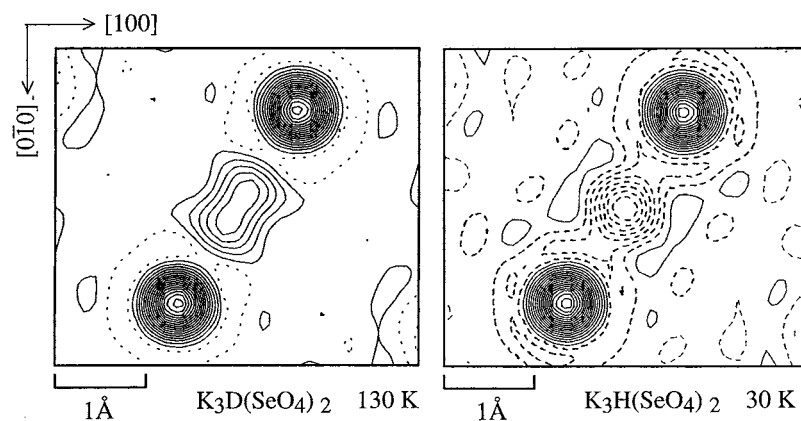| Atom	x	y	z	B_{iso}
K(1)	1/4	0.7594(2)	0	0.82(3)
K(2)	0.6524(2)	0.7377(5)	0.1968(2)	1.14(1)
D[a]	0.4850(5)	0.0394(9)	−0.0035(5)	4.40(6)
Se	0.4595(1)	0.2339(8)	0.1163(1)	0.57(2)
O(1)	0.3977(8)	0.0131(5)	0.1587(7)	1.09(3)
O(2)	0.4343(4)	0.1832(4)	0.0014(5)	1.16(6)
O(3)	0.6251(4)	0.2495(6)	0.1546(3)	1.12(8)
O(4)	0.3821(2)	0.4675(8)	0.1304(1)	1.10(9)

[a] Site occupancy 0.5.

Figure 4. Fourier contour maps (F_{obs}) of the nuclear density for the (110) plane around the hydrogen bond in $K_3H(SeO_4)_2$ and $K_3D(SeO_4)_2$. The inversion centre is located at the centre of the map. The H (or D) atom and the O atoms are sitting approximately on this plane.

small χ^2-values indicate that the structural rearrangements in the crystal resulting from the phase transition are very small for $K_3H(SeO_4)_2$. For $K_3D(SeO_4)_2$, however, the χ^2-value is larger than that for 130 K. The atomic displacement parameter for the D atom is anomalously large (3.7 Å^2), indicating that the model is inadequate. This is evidence to suggest that the D atom is ordered in the low-temperature phase. For a similar sulphate $K_3D(SO_4)_2$, the space group of the low-temperature phase has been determined to be $A2$ with a quadrupled unit cell of $a \times 2b \times 2c$ by the use of the Weissenberg photograph [10]. The new reflections were reported to be extremely weak. A single-crystal neutron diffraction study may be required in order to reveal unambiguously the deuteron distribution in the low-temperature phase.

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