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Neutron-diffraction study of polycrystalline H_2SO_4 and H_2SeO_4

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Polycrystalline H_2SO_4 and H_2SeO_4 were studied by powder neutron-diffraction techniques at temperatures near the melting points and at 10 K. This work was undertaken to determine hydrogen positions and to search for order-disorder transitions in the hydrogen-bond networks. Rietveld refinement located the hydrogen positions and established that the hydrogen atoms are ordered at the temperatures studied (i.e., no ordering transitions). The other atom positions were found to be consistent with those determined in earlier x-ray single-crystal analyses of the H_2SO_4 and H_2SeO_4 crystal structures.

I. INTRODUCTION

Although anhydrous H_2SO_4 and H_2SeO_4 crystallize in different space groups (monoclinic $C2/c$ and orthorhombic $P2_12_12_1$, respectively), both form layered structures with hydrogen bonding occurring only within the layers.[1,2] The hydrogen-bond networks in the layers can be regarded as two-dimensional versions of the well-known KH_2PO_4 (KDP) structure,[3] and the question arises as to whether hydrogen-bond ordering transitions might be observed in these structures. We report here the results of exploratory neutron-diffraction studies, undertaken with this question in mind, on polycrystalline samples of H_2SO_4 and H_2SeO_4 at temperatures of 240 and 330 K, respectively, and at 10 K. No deviations from the published space-group symmetries are evident in any of the diffraction patterns, and Rietveld refinements[4-6] indicate also that the hydrogen bonds are ordered in these cases. Diffraction data were also collected at 290 K for H_2SeO_4.

Apart from providing information on the possibility of phase transitions in these materials, these neutron-diffraction results confirm the heavy-atom positions determined in the earlier x-ray analyses of the H_2SO_4 and H_2SeO_4 crystal structures,[1,2] and they extend the results of those analyses by determining the ordered hydrogen positions in these structures. An unusual element in this work is the use of Rietveld refinement when high background due to incoherent scattering is present.[7]

II. SAMPLE PREPARATION AND EXPERIMENTAL DETAILS

Solid H_2SO_4 was prepared from reagent-grade (95–98 %) sulfuric acid. To eliminate water the reagent was heated until it reached a constant boiling temperature, 603 K. Further dehydration was accomplished by a fractional crystallization procedure performed in a dry box. The method takes advantage of the existence of a eutectic in the H_2O-H_2SO_4 phase diagram occurring at approximately 72 mol % H_2SO_4. The freezing point of this eutectic is near 233 K, about 50 K below that of anhydrous H_2SO_4. Crystallites of H_2SO_4 were grown slowly from the liquid in a quartz test tube suspended over liquid nitrogen. When the material was about 80% solidified the remaining (low melting point and thus water-rich) liquid was discarded. This crystallization procedure was repeated several times. While sizable crystals were often obtained, these were found to be badly twinned and, consequently, unusable for a single-crystal investigation. Next, the sample was transferred to a platinum dish in a refrigerated (253 K) helium-atmosphere glove box where the solid H_2SO_4 was ground into small crystallites. This "powder" sample was loaded into a standard aluminum sample holder 6 mm in diameter and sealed with an indium *O* ring. The process of loading this sample holder into a closed-cycle He refrigerator was accomplished without allowing the sample to approach the melting temperature.

Published methods were used as a basis for the preparation procedure for solid H_2SeO_4.[8,9] H_2SeO_4 was synthesized from SeO_2 (99%) dissolved in water, to which 30% H_2O_2 was added. When this solution was heated above about 50 °C in an oxygen atmosphere, an exothermic reaction occurred, producing a greenish aqueous solution of selenic acid. This was dehydrated using, simultaneously, a P_2O_5-dried oxygen stream and a partial vacuum. Since selenium precipitated from solution when the sample came into contact with some metals and plastics, only glass was used where direct contact was involved, joints were sealed with silicone grease, and modified polyvinyl chloride (PVC) tubing was used for the gas supply line. The sample, when dried, was loaded into a 6-mm i.d. fused silica tube and sealed off without exposure to air.

The neutron-diffraction experiments were carried out at the Brookhaven National Laboratory high flux beam reactor. H_2SO_4 was studied at two temperatures. The scan parameters are listed in Table I.

Two separate experimental setups were used for the study of H_2SeO_4, with parameters also listed in Table I. Except for the second run at 290 K (290 #2), which was performed with the sample outside the cryostat, scattering from Al is present. In all runs there remains background scattering due to the presence of the silica sample container, as well as a sizable background due to the incoherent component of the hydrogen scattering. To mini-

TABLE I. Parameters for neutron-diffraction scans. In all cases the step size was 0.05°. Pyrolytic graphite (PG) filters and PG(002) monochromators were utilized. Analyzers used were PG(002) for 1.55-Å data, PG(004) for other cases. Collimation figures are, respectively, for in-pile, monochromator sample, sample analyzer, and analyzer detector.

Sample	Temperature (K)	λ (Å)	2θ range (deg)	Collimation (min)
H_2SO_4	10	2.34	20–120	20-40-40-20
H_2SO_4	240	2.34	20–120	20-40-40-20
H_2SeO_4	10	1.55	14–112	10-60-40-20
H_2SeO_4	290 #1	2.46	10–112	20-30-40-10
H_2SeO_4	290 #2	2.46	20–107	20-30-40-10
H_2SeO_4	330	1.55	14–105	10-60-40-20

mize possible effects of preferred orientation, the H_2SeO_4 sample was rotated about the axis of the cylindrical sample holder.

III. RESULTS

A. H_2SO_4

Neutron-diffraction scans of H_2SO_4 revealed that, to the limits of detection, the sample was single phase with monoclinic symmetry at both 10 and 240 K. In spite of an unfavorable typical peak to background ratio of 1:2, Rietveld profile refinement[4–6] was successfully performed for the $C2/c$ structure at both temperatures. Lattice parameters were initially estimated. Heavy-atom positional parameters were taken from the earlier structural study[1] while hydrogen positions were initially chosen to lie midway between the oxygen positions. One isotropic temperature factor, B_H, was defined for hydrogen atoms and

TABLE II. Parameters from Rietveld refinement of H_2SO_4. U, V, and W are halfwidth parameters (Refs. 4 and 5). R_I, R_{WP}, and R_E are R factors described elsewhere (Ref. 6 and 7) for integrated intensities, weighted profile, and statistical or expected values. Estimated standard deviations (e.s.d.'s) are given in parentheses based on least significant figures. Fixed values have no e.s.d.'s. E.s.d.'s quoted for lattice parameters do not take into account uncertainty in wavelength. Two isotropic temperature factors were refined, one for H atoms (B_H), the other for S and O (B).

	Parameter	$T=240$ K	$T=10$ K
H	x	−0.140 (2)	−0.133 (2)
	y	0.346 (4)	0.327 (3)
	z	0.374 (2)	0.365 (1)
S	x	0	0
	y	0.028 (6)	0.092 (4)
	z	$\frac{1}{4}$	$\frac{1}{4}$
O_1	x	−0.023 (2)	−0.020 (2)
	y	0.280 (2)	0.268 (1)
	z	0.375 (1)	0.387 (1)
O_2	x	0.168 (1)	0.159 (1)
	y	−0.089 (3)	−0.091 (2)
	z	0.326 (1)	0.322 (1)
	B_H (Å^2)	3.5 (4)	1.3 (4)
	B (Å^2)	5.8 (3)	0.8 (2)
	a (Å)	8.1310 (14)	8.1824 (11)
	b (Å)	4.7673 (8)	4.6549 (6)
	c (Å)	8.6335 (14)	8.5015 (10)
	β (deg)	111.081 (8)	111.521 (5)
	U (deg^2)	0.55 (9)	0.78 (6)
	V (deg^2)	−1.13 (15)	−1.40 (12)
	W (deg^2)	0.77 (6)	0.85 (5)
	R_I (%)	23.0	14.0
	R_{WP} (%)	38.9	25.8
	R_E (%)	31.5	20.4

TABLE III. Some bond lengths (Å) and angles (deg) for H_2SO_4. Oxygen-oxygen distances are within the hydrogen bonds. See the text for a discussion of uncertainties and errors.

	$T=240$ K	$T=10$ K
O_1—O_2 (Å)	2.47	2.52
O_1—H (Å)	1.00	0.91
$O_2 \cdots$ H (Å)	1.49	1.65
O_1—S (Å)	1.54	1.48
O_2—S (Å)	1.40	1.49
H-bond θ (deg)	163	175

another, B, was defined for all other atoms. Refined parameters and reliability (R) factors defined previously[6,7] are shown in Table II. The weighted profile R_{WP}'s compare favorably with the statistical, or expected, R_E's.[6,7] The profile fit and difference plot for Rietveld refinement of 10-K data are plotted in Fig. 1. Table III shows some bond lengths and angles. An additional refinement in the *Cc* space group resulted in negligible improvement.

The principal conclusion from the refinement is that the hydrogens are ordered at both temperatures studied. In addition, the parameters of the other atoms are qualitatively consistent with the x-ray single-crystal studies, but the e.s.d.'s in Table II seem to be unrealistically low. An indication of the degree to which the e.s.d.'s of the positional parameters may be underestimated is provided by an examination of bond lengths listed in Table III. Furthermore the calculated e.s.d.'s for the bond lengths in Table III derived from the positional parameter e.s.d.'s are about 0.01 Å. Normally, when there is no phase change, the covalent O_1—H bond length is independent of temperature to a level of about ±0.002 Å. However, we see an apparent discrepancy of 0.05—0.10 Å. This suggests that the true e.s.d.'s are no better than about 0.05 Å.

Several factors may contribute to the underestimate of the e.s.d.'s within the refinement. Any inadequacy of the model results in errors not taken into account in the calculation of e.s.d.'s. For example the present calculations use isotropic temperature factors for simplicity, while the x-ray diffraction results[1] indicate that anisotropic factors would be more appropriate. Also, Sakata and Cooper[10] have noted that the Rietveld method tends to give unrealistically low estimates of the e.s.d.'s of positional parameters, especially in cases in which many peaks overlap.

As a check on the possibility of disordered bonds, the occupation values were refined (constraining the sum to be one H atom) for two partially occupied hydrogen positions determined as follows. One position is the refined position x,y,z. Naming the position of the bond center (midway between oxygen atoms) x_0,y_0,z_0, the hypothetical hydrogen is placed at $x_0-(x-x_0)$, $y_0-(y-y_0)$, $z_0-(z-z_0)$. Within the estimated accuracy of the refinements (less than about 0.2 H atom) the original H position fills while the hypothetical H position empties.

B. H_2SeO_4

Neutron-diffraction scans of H_2SeO_4 showed that, to within the limits of detection, the sample is single phase with orthorhombic symmetry at 10 K, at room temperature, and at 330 K. Rietveld refinement[4-6] of the orthorhombic structure was performed using estimated lattice parameters and heavy-atom positions from Ref. 2, as starting parameters. A plot of calculated and observed values for the 10-K data is shown in Fig. 2. The refined parameters for the 10- and 330-K data (wavelength 1.55 Å) are shown in Table IV. The weighted-profile R_{WP} factors compare favorably with the expected calculated statistical R_E's in each case. Refinements of two sets of 290-K data are not described here. The neutron wave-

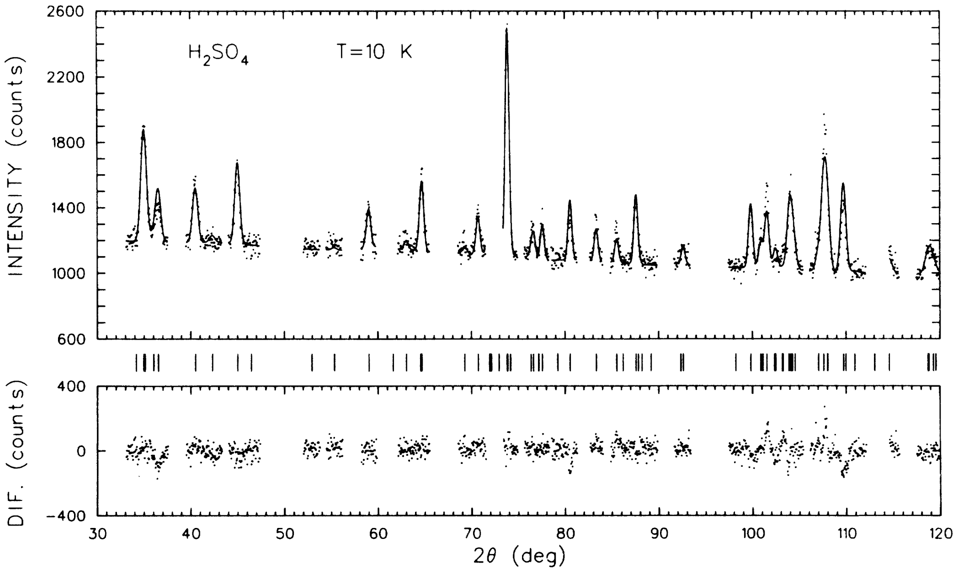

FIG. 1. Rietveld profile fit to 10-K H_2SO_4 data. Observed counts are data points. Calculated intensities are connected by the line. DIF. is the difference between observed counts and calculated counts. Neutron $\lambda=2.34$ Å. Calculated peak positions are marked below the main plot.

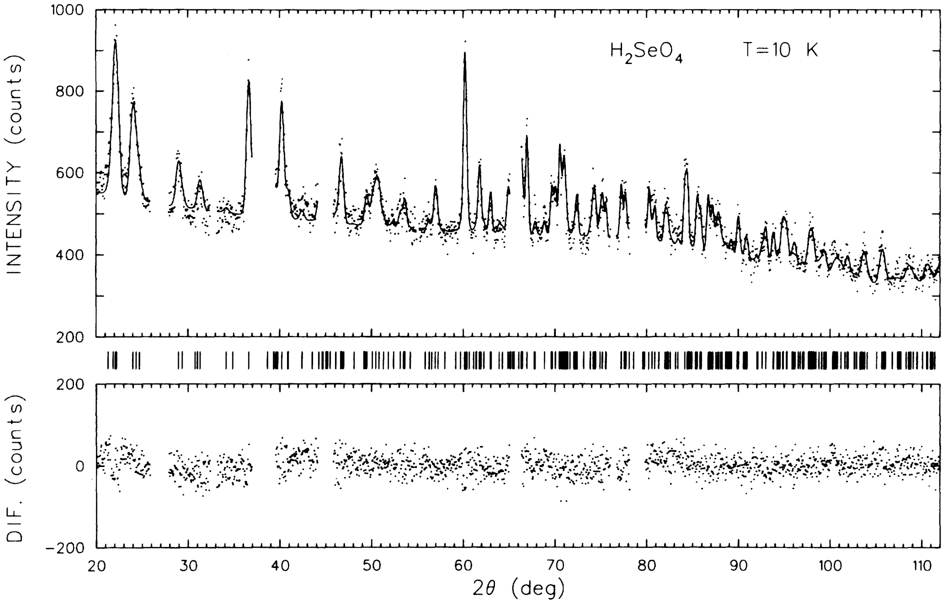

FIG. 2. Rietveld profile fit to 10 K H_2SeO_4 data. Observed counts are data points. Calculated intensities are connected by the line. DIF. is the difference between observed counts and calculated counts. Neutron $\lambda = 1.55$ Å. Calculated peak positions are marked below the main plot.

TABLE IV. Parameters from Rietveld refinement of H_2SeO_4. Parameter definitions are the same as those in Table II.

	Parameter	$T = 330$ K	$T = 10$ K
H_1	x	0.465 (4)	0.454 (3)
	y	0.478 (4)	0.479 (3)
	z	0.542 (8)	0.549 (7)
H_2	x	0.239 (3)	0.222 (3)
	y	0.208 (4)	0.195 (3)
	z	0.010 (7)	0.020 (6)
Se	x	0.368 (1)	0.367 (1)
	y	0.208 (1)	0.209 (1)
	z	0.575 (2)	0.577 (3)
O_1	x	0.514 (2)	0.517 (1)
	y	0.130 (2)	0.131 (2)
	z	0.723 (3)	0.716 (3)
O_2	x	0.290 (1)	0.289 (2)
	y	0.102 (2)	0.111 (2)
	z	0.313 (3)	0.305 (3)
O_3	x	0.236 (1)	0.231 (1)
	y	0.271 (2)	0.266 (1)
	z	0.818 (3)	0.806 (3)
O_4	x	0.415 (2)	0.413 (2)
	y	0.396 (2)	0.390 (2)
	z	0.416 (3)	0.410 (3)
	B_H (Å^2)	4.5 (5)	2.2 (4)
	B (Å^2)	1.8 (1)	0.0 (1)
	a (Å)	8.5416 (10)	8.3330 (10)
	b (Å)	8.1807 (10)	8.1286 (11)
	c (Å)	4.6233 (6)	4.5913 (6)
	U (deg^2)	0.94 (7)	1.09 (8)
	V (deg^2)	−1.52 (9)	−1.75 (11)
	W (deg^2)	0.69 (3)	0.81 (4)
	R_I (%)	20.4	17.1
	R_{WP} (%)	32.2	33.3
	R_E (%)	30.3	31.7

TABLE V. Some bond lengths (Å) and angles (deg) for H_2SeO_4. Oxygen-oxygen distances are within the hydrogen bonds. See the text for a discussion of uncertainties and errors.

	$T=330$ K	$T=10$ K
O_1—O_4 (Å)	2.61	2.67
O_4—H_1 (Å)	0.99	1.02
$O_1 \cdots H_1$ (Å)	1.66	1.66
H-bond θ_{14} (deg)	160	169
O_2—O_3 (Å)	2.71	2.66
O_3—H_2 (Å)	1.03	1.14
$O_2 \cdots H_2$ (Å)	1.70	1.58
H-bond θ_{23} (deg)	166	155
O_1—Se (Å)	1.56	1.54
O_2—Se (Å)	1.63	1.62
O_3—Se (Å)	1.67	1.62
O_4—Se (Å)	1.75	1.70

length, 2.46 Å, improved resolution in Q space relative to 1.55-Å data, but reduced the number of reflections by a factor of 4. In the present case this trade-off was unfavorable.

There are two crystallographically distinct hydrogen bonds in this structure. Each bond is positionally ordered at 330 and 10 K. As in the case of H_2SO_4, the positional parameters appear to be less well established by a factor of 3—4 than the uncertainty estimates calculated by the Rietveld method indicate. However, the general features of these hydrogen bonds are reasonable and consistent with an ordered bond in both cases. We can again compare the covalent bond lengths (O_4—H_1 and O_3—H_2) at low and high temperatures to estimate the reliability of the positional parameters determined in the refinement. As in the case of H_2SO_4 the covalent bond lengths are expected to be temperature independent to about ±0.002 Å. Here the refinement shows variations in bond length which indicate a true uncertainty of about ±0.05 Å. The data were tested for the presence of a statistically disordered bond. Refinement of the occupation of the two crystallographically distinct H bonds, each with two partially filled H positions (chosen as in the case of H_2SO_4) again produces the result that the original H position becomes fully occupied and the proposed position becomes vacant within the estimated accuracy of the profile technique.

IV. DISCUSSION

The major objectives for this neutron-diffraction study of H_2SO_4 and H_2SeO_4 were (1) to ascertain the positions of the H atoms in the crystal structures, and (2) to determine whether or not variation of temperature would affect the ordering of the hydrogen bonds.

Results for both compounds studied are consistent with the previously proposed heavy-atom positions.[1,2] The positions of hydrogen atoms in the bonds were also determined. Structure refinement yielded hydrogen-bond lengths and angles which are reasonably consistent with other hydrogen-bond structures. From a comparison of data collected at different temperatures, we conclude that there is no transition to a phase in which these hydrogen atoms are positionally disordered. It appears that the coupling energy between the asymmetric heavy atoms and the H positions is strong enough to overcome the entropy gain associated with disorder within the range of temperatures for which these crystals are stable.

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