Chem. Mater. **2007,** *19,* 270−279

Entropy Evaluation of the Superprotonic Phase of $CsHSO_4$: Pauling's Ice Rules Adjusted for Systems Containing Disordered Hydrogen-Bonded Tetrahedra

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Received August 31, 2006. Revised Manuscript Received October 26, 2006

The entropy of the superprotonic transition (phase II → phase I) of $CsHSO_4$ is evaluated both experimentally and theoretically. Calorimetric measurements reveal a value of 14.75(22) J mol^{-1} K^{-1}. Under the assumption that the entropy is entirely configurational, arising from both sulfate group orientational disorder and disorder in the hydrogen-bond network, we evaluated several structural models of $CsHSO_4$ for their consistency with the measured entropy. For a structure in which hydrogen-bond disorder is independent of sulfate-group orientational disorder, simple methods of calculating the number of structural configurations are inadequate. Thus, the configurational entropy of the superprotonic, disordered phase of $CsHSO_4$ is evaluated using an approach similar to that employed by Pauling to describe the residual entropy of ice at 0 K. Analogous to ice and the so-called ice rules, superprotonic $CsHSO_4$ is assumed to obey a set of structural rules. Key among these are that there is only one proton per sulfate tetrahedron and only one proton per hydrogen bond. Defects are argued to make a negligible contribution to the transition entropy. The transition entropy obtained from this model, 14.9 J mol^{-1} K^{-1}, is in excellent agreement with the measured value. Such a match between theoretical and experimental values suggests that of all published Phase I structures, the structure proposed by Jirak[2] more correctly describes the arrangements of the sulfate tetrahedra and protons attached to them. The assumption of a low defect concentration implies that the jump in proton conductivity at the transition is due to an increase in the mobility of charge carriers rather than their concentration.

Introduction

Several acid salt or solid acid compounds with stoichiometries $MHXO_4$, $M_3H(XO_4)_2$ ($M = Cs$, Rb, NH_4; $M = S$, Se), and $MH_2X'O_4$ ($X' = P$, As) undergo a remarkable phase transition at which the proton conductivity jumps by 3−4 orders of magnitude.[3−7] An extraordinary characteristic of these materials is that despite the sharp crystalline diffraction patterns of the so-called superprotonic, high-temperature phases, their conductivities are comparable to those of chemically analogous liquids.[8] Although such behavior is highly unusual, a similar phenomenon is encountered in the classic compound AgI. Silver iodide exhibits a superionic transition at which the silver ionic conductivity rises sharply, again, by several orders of magnitude, and the conductivity subsequently decreases upon melting.[9]

Since the discovery of the superprotonic transition in $CsHSO_4$ in 1982 by Baranov and co-workers,[4] close to 50 papers have appeared detailing the structural, dynamic, and transport properties of this compound alone. Until quite recently, these studies have been primarily of academic interest. However, the solid nature of superprotonic acid salts renders them inherently advantageous for a variety of applications relative to their liquid or even polymeric proton-conducting counterparts. In particular, the authors have demonstrated viable fuel cells incorporating $CsHSO_4$ and CsH_2PO_4 electrolytes,[10,11] raising the prospects of commercially important devices based on these fascinating materials.

The superprotonic transition in $CsHSO_4$ is first order in nature, involving a transformation from a monoclinic, low-temperature phase (phase II) to a tetragonal, high-temperature phase (phase I) at 414 K.[4,12]

$$\text{phase II } (P2_1/c) \xrightarrow{414\ \text{K}} \text{phase I } (I4_1/amd)$$

In the phase II structure,[13] sulfate groups are linked by fully ordered hydrogen bonds so as to form one-dimensional, zigzag chains. In contrast, there is considerable disorder in

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(1) Pauling, L. *J. Am. Chem. Soc.* **1935**, *57*, 2680.

(2) Jirak, Z.; Dlouha, M.; Vratislav, S.; Balagurov, A. M.; Beskrovnyi, A. I.; Gordelii, V. I.; Datt, I. D.; Shuvalov, L. A. *Phys. Status Solidi A* **1987**, *100*, K117−K122.

(3) Baranov, A. I.; Khiznichenko, V. P.; Shuvalov, L. A. *Ferroelectrics* **1989**, *100*, 135.

(4) Baranov, A. I.; Shuvalov, L. A.; Shchagina, N. M. *JETP Lett.* **1982**, *36*, 459.

(5) Pawlowski, A.; Pawlaczyk, Cz.; Hilczer, B. *Solid State Ionics* **1990**, *44*, 17.

(6) Ramasastry, C.; Ramaiah, K. S. *J. Mater. Sci.* **1981**, *16*, 2011.

(7) Kreuer, K. D.; Dippel, Th.; Hainovshy, N. G.; Maier, J. *Ber. Bunsen−Ges. Phys. Chem.* **1992**, *96*, 1736.

(8) Boysen, D.; Haile, S. M.; Liu, H. J.; Secco, R. A. *Chem. Mater.* **2004**, *16*, 693.

(9) Kudo, T.; Fueki, K. *Solid State Ionics*; VCH: New York, 1990; pp 79−84.

(10) Haile, S. M.; Boysen, D. A.; Chisholm, C. R. I.; Merle, R. B. *Nature* **2001**, *410*, 910.

(11) Boysen, D. A.; Uda, T.; Chisholm, C. R. I.; Haile, S. M. *Science* **2004**, *303*, 68.

(12) Komukae, M.; Osaka, T.; Ozaki, T.; Makita, Y.; Itoh, K.; Nakamura, E. *J. Phys. Soc. Jpn.* **1981**, *50*, 3187.

(13) Chisholm, C. R. I.; Haile, S. M. *Mater. Res. Bull.* **2000**, *35*, 999 .

10.1021/cm062070w CCC: \$37.00

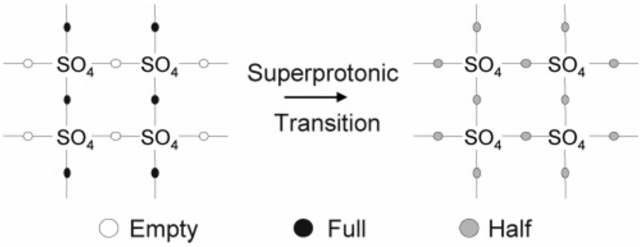

Figure 1. Disordering of protons across the superprotonic transition of $CsHSO_4$ according to the Plakida model. (a) Below T_c, the proton positions in the vertical chains are completely occupied, whereas those of the horizontal, cross-linking chains are unoccupied. (b) Above the transition. the protons are distributed with equal probability over all available sites.

the phase I structure, particularly with respect to librations of the bisulfate (HSO_4) groups.[2] Although there is debate as to the actual number and/or directions of the orientations possible for each tetrahedron, as discussed in detail below, there is general agreement that the librations occur at a frequency of $\sim 1 \times 10^{12}$ Hz,[14] with distinct oxygen positions associated with different tetrahedral group orientations.[15] This rapid reorientation, in combination with a high rate of proton transfer between tetrahedral groups ($\sim 1 \times 10^9$ Hz), is responsible for the dramatic increase in proton conductivity at the superprotonic transition of $CsHSO_4$ and, indeed, all superprotonic solid acids.[7] In the case of $CsHSO_4$, the rise in conductivity is particularly steep, increasing from 1×10^{-6} to 1×10^{-3} or 1×10^{-2} Ω^{-1} cm^{-1} over a temperature window of only ~ 3 °C.[4] The proton-transport process is an example of the Grotthus mechanism, in which proton migration occurs via dipole (in this case, $H_nSO_4^{n-2}$) reorientation, structural relaxation, and proton hopping.[16]

The entropy of the transition to the high-temperature phase of $CsHSO_4$ has been of some discussion. Reported values of this quantity range from 11.0 to 14.3 J mol^{-1} K^{-1}.[12,17−20] To a first approximation, the low-temperature phase can be considered to have zero configurational entropy − the hydrogen bonds are asymmetric with single minima and the positions of oxygen atoms are fixed.[13] Thus, the entropy of the transition, ΔS_{trans}, is simply the entropy of phase I, S_I. In one of the first attempts to quantify S_I (and therefore ΔS_{trans}), Plakida has proposed a model in which protons are taken to be distributed over a two-dimensional lattice of hydrogen-bond positions.[21,22] This idealized structure contains twice as many positions are there are protons to occupy them. At low temperature, the proton positions are fixed, forming the one-dimensional chains known to exist in phase II, Figure 1a. At high temperatures, the protons become randomly distributed, Figure 1b, with each proton position being, on average, 50% occupied.

Although this model correctly represents some aspects of Phase I $CsHSO_4$, such as partially occupied proton sites, it is not entirely adequate. First, the idealized structure is not representative of the experimentally determined structure of $CsHSO_4$, but rather appears to be derived from the close relationship between the room-temperature structures of $CsHSO_4$ and CsH_2PO_4. The latter contains two-dimensional, hydrogen-bonded H_2PO_4 layers,[23,24] which can be constructed from the cross-linking of one-dimensional chains, as found in phase II $CsHSO_4$.[13] In contrast, the high-temperature structure of $CsHSO_4$ (as determined experimentally) has a three-dimensional hydrogen-bond network with oxygen atoms distributed over multiple sites.[2] The differences between the model and experimental structures results in a calculated transition entropy of 9.1 J mol^{-1} K^{-1}, which is lower than even the smallest experimentally measured value (11.0 J mol^{-1} K^{-1}).[12] Second, the Plakida model implies that a compound such as CsH_2PO_4, in which all possible hydrogen-bond positions in the two-dimensional H-bond network are already occupied, should not undergo a superprotonic transition. This is in direct contradiction to the most recent experimental investigations of this material, showing a transition to a high conductivity phase at 230 °C.[25,26]

In an effort to develop a complete picture of the disorder in the high-temperature phase of $CsHSO_4$, we present here new experimental measurements of its thermal behavior, which can be compared to theoretical predictions. More significantly, we present a new methodology for evaluating the entropy of compounds in which orientationally disordered oxyanions are linked by randomly distributed hydrogen bonds. The methodology is based on Pauling's approach for assessing the residual entropy of ice[1] and has important implications for the mechanisms of superprotonic conductivity. The entropy analysis suggests that it is possible to distinguish between various models proposed in the literature for the structure of superprotonic $CsHSO_4$, where those models are differentiated in terms of the details of the sulfate group orientations.

Experimental Procedures and Results

Single crystals of $CsHSO_4$ phase II (space group $P2_1/c$) were grown at room temperature by slow evaporation from an aqueous solution of Cs_2CO_3 and H_2SO_4 with a 1:1 molar ratio of Cs:SO_4. Each crystal used for thermal analysis was individually confirmed to be $CsHSO_4$ by single-crystal X-ray diffraction. Diffraction data were collected on a Syntex 4-circle single-crystal diffractometer using Mo Kα radiation. Differential scanning calorimetry was performed with a Perkin-Elmer DSC 7, calibrated for temperature and heat flow accuracy using In and Zn metal standards (P-E part N519-0762). Data were measured from 14 different samples under flowing argon, using a heating rate of 10 K min^{-1}. Those samples with the highest and lowest, respectively, transition enthalpies were removed from the analysis and the properties were defined as the averages obtained from the remaining 12 datasets.

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(14) Badot, J. C.; Colomban, Ph. *Solid State Ionics* **1989**, *35*, 143.
(15) Colomban, P.; Badot, J. C. *J. Phys. Condens. Matter* **1992**, *4*, 5625.
(16) van Grotthuss, C. J. D. *Ann. Chim.* **1806**, *58*, 54.
(17) Baranowski, B.; Friesel, M.; Lunden, A. *Z. Naturforsch., A: Phys. Sci.* **1986**, *41*, 733.
(18) Lunden, A.; Baranowski, B.; Friesel, M. *Ferroelectrics* **1991**, *124*, 103.
(19) Boysen, D. A.; Chisholm, C. R. I.; Haile, S. M.; Narayanan, S. R. *J. Electrochem. Soc.* **2000**, *147*, 3610.
(20) Ponomareva, V. G.; Lavrova, G. V. *Solid State Ionics* **2001**, *145*, 197.
(21) Plakida, N. M. *JETP Lett.* **1985**, *41*, 114.
(22) Plakida, N. M. *Phys. Status Solidi B* **1986**, *135*, 133.
(23) Nelmes, R. J.; Choudhary, R. N. P. *Solid State Commun.* **1978**, *26*, 823.
(24) Matsunaga, H.; Itoh, K.; Nakamura, E. *J. Phys. Soc. Jpn.* **1980**, *48*, 2011.
(25) Boysen, D.; Haile, S. M.; Liu, H. J.; Secco, R. A. *Chem. Mater.* **2003**, *15*, 727.
(26) Otomo, J.; Minagawa, N.; Wen, C.; Eguchi, K.; Takahashi, H. *Solid State Ionics* **2003**, *156*, 357.

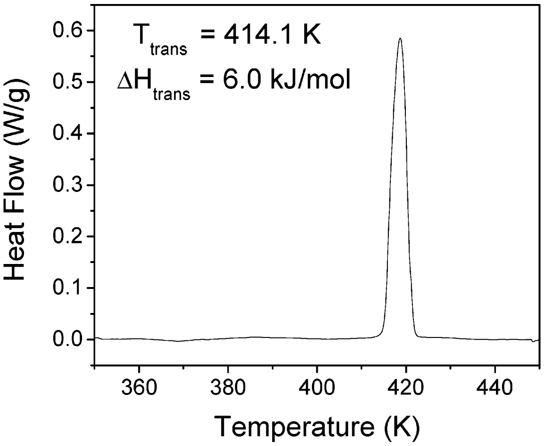

Figure 2. DCS curve obtained from a single crystal of $CsHSO_4$ heated at a rate of 10 K/min under flowing argon.

A typical curve obtained from the calorimetry experiments is shown in Figure 2. There is a clear endothermic transition around 414 K visible in the scan. The enthalpy associated with the transition was calculated from the peak area, after a fitted baseline had been subtracted. The average onset of the II → I transition in $CsHSO_4$ was found to occur at 414.4 ± 1.2 K, very much in agreement with the values reported in the literature, which range from 413 to 419 K, Table 1. The average enthalpy measured here for the II → I transition, 6.11 ± 0.09 kJ mol^{-1}, is higher than that of earlier studies. Consequently, the implied transition entropy of 14.75 ± 0.22 J mol^{-1} K^{-1} is also beyond the upper end of the 11.0−14.3 J mol^{-1} K^{-1} range reported in the literature, Table 1.

There are a number of possible reasons for the wide range of measured values for the superprotonic transition entropy of $CsHSO_4$. A key factor is possible contamination of $CsHSO_4$ with other alkali ions. For example, as described in detail elsewhere,[27] $CsHSO_4$ crystals grown from solutions intentionally contaminated with trace levels of sodium/potassium cations were found to display markedly different thermal properties than crystals obtained from high purity solutions. In particular, although the onset temperature of the II → I transition was unchanged, those samples exhibited a statistically lower transition entropy of 12.5(5) J mol^{-1} K^{-1}. Furthermore, the X-ray powder diffraction patterns of these contaminated samples were indistinguishable from that of high-purity $CsHSO_4$, and thus the presence of alkali impurities at low levels could be easily overlooked. Evaluation of the transition entropy using the Clapeyron relation, $dP/dT = \Delta S/\Delta V$ and published $P-T$ phase diagrams of $CsHSO_4$[28,29] as well as the reported volume change at the transition[30] yields much greater ΔS values than those obtained from any of the thermal methods, Table 1, and provides little insight into the true value of the transition entropy.

Discussion

Structure of Superprotonic $CsHSO_4$. An accurate description of the entropy of any compound requires an understanding of its structure. That superprotonic, phase I $CsHSO_4$ crystallizes in space group $I4_1/amd$ with lattice constants $a \approx 5.75$ Å and $c \approx 14.3$ Å has been confirmed many times over in the literature. Reported high-temperature structures (as determined by both X-ray[31−33] and neutron diffraction experiments[2,34,35]) agree, furthermore, in the placement of heavy atoms. Specifically, the sulfur and cesium ions each fully occupy special positions (a) and (b) with multiplicity 4. The symmetry at these sites is $\bar{4}m2$, which is consistent with the point group symmetry of an ideal tetrahedron. In principle, therefore, sulfate group disorder is not necessary to allow $CsHSO_4$ to crystallize in space group $I4_1/amd$. Orientationally fixed SO_4 groups can be obtained, Figure 3, if the oxygen atoms reside (with full occupancy) on 16(h) sites, which lie on the mirror plane that passes through the central S atom of the tetrahedron. Such an arrangement, however, would result in unreasonably long hydrogen bonds (i.e., minimum O−O distance of 3.22 Å). Thus, as revealed by several experimental studies, the oxygen atoms do not reside on just one 16(h) site with full occupancy, but are instead distributed over multiple sites. Within this framework, two candidate hydrogen-bond positions have been identified, Figure 3b. The first, with protons at 16(f) positions, extend in the <1/2 0 1/8> directions and produce a three-dimensional hydrogen-bond network. The second, with protons at 8(e) positions, extend in the <1 0 0> directions and produce a two-dimensional (layered) hydrogen-bond network.

The many different structural models presented in the literature differ in the details of the oxygen positions and thus the number and type of SO_4 group orientations, as well as the locations of the protons/hydrogen bonds. Difficulty in precisely locating the oxygen atoms (and thus the sulfate group orientations) results from the highly disordered nature of the structure[36] and the tendency of high-quality single crystals to become polycrystalline in phase I.[33] Similarly, oxygen disorder hinders precise structural determinations in certain phases of ice, although in those cases the oxygen disorder is often static.[37,38] What follows is a set of detailed descriptions of the structures corresponding to the various proposed models of $CsHSO_4$−I, descriptions that are necessary for evaluating the entropy associated with the disorder inherent in each of the models.

The reported structural models of superprotonic $CsHSO_4$ can be grouped into four categories, exemplified by those proposed by Jirak,[2] Merinov,[31] Belushkin,[35] and, again, Merinov.[33] All can be considered derivatives of an ideal structure containing no anion disorder, Figure 4. In the Jirak model, the oxygen is displaced from the 16(h) site and resides

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(27) Chisholm, C. R. I. Superprotonic Phase Transitions in Solid Acids: Parameters affecting the presence and stability of superprotonic transitions in the MH_nXO_4 family of compounds (X = S, Se, P, As; M = Li, Na, K, NH_4, Rb, Cs). Ph.D. Thesis, California Institute of Technology, Pasadena, CA, 2003.

(28) Ponyatovskii, E. G.; Rashchupkin, V. I.; Sinitsyn, V. V.; Baranov, A. I.; Schuvalov, L. A.; Shchagina, N. M. *JETP Lett.* **1985**, *41*, 139.

(29) Friesel, M.; Baranowski, B.; Lundén, A. *Solid State Ionics* **1989**, *35*, 85.

(30) Uda, T.; Boysen, D. A.; Haile, S. M. *Solid State Ionics* **2005**, *176*, 127.

(31) Merinov, B. V.; Baranov, A. I.; Shuvalov, L. A.; Maksimov, B. A. *Kristallografiya* **1987**, *32*, 86.

(32) Varma, V.; Rangavittal, N.; Rao, C. N. R. *J. Solid State Chem.* **1993**, *106*, 164.

(33) Merinov, B. V. *Crystallogr. Rep.* **1997**, *42*, 906.

(34) Nozik, Yu. Z.; Lyakhovitskaya, L. I.; Shchagina, N. M.; Sarin, V. A. *Kristallografiya* **1990**, *35*, 658.

(35) Belushkin, A. V.; David, W. I. F.; Ibberson, R. M.; Shuvalov, L. A. *Acta Crystallogr., Sect. B* **1991**, *47*, 161.

(36) Chisholm, C. R. I.; Jang, Y. H.; Yang, L.; Haile, S. M.; Goddard, W. A. **2006**, *Phys. Rev. B* **2005**, *72*, 134103.

(37) Nelmes, R. J.; Loveday, J. S.; Marshall, W. G.; Hamel, G.; Besson, J. M.; Klotz, S. *Phys. Rev. Lett.* **1998**, *81*, 2719.

(38) Kuo, J. L.; Klein, M. L. *J. Phys. Chem. B* **2004**, *108*, 19634.

Table 1. Thermal Properties of the II → I Superprotonic Transition of $CsHSO_4$

source	T_{onset} (K)	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})
this work[a]	414.4 ± 1.2	6.11 ± 0.09	14.75 ± 0.22
Komukae (1981)[12]	413	4.51	11.0
Baranowski (1986)[17]	416	5.3	12.7
Lunden (1991)[18]	415	5.5	13.3
Boysen (2000)[19]	417	5.5	13.2
Ponamareva (2001)[20]	419	6.0	14.3
Clapeyron relation[b]	dT/dP (K/GPa)		$\Delta \boldsymbol{S}$ (J mol^{-1} K^{-1})
Ponyatovskii (1982)[28]	5 ± 3		82 ± 50
Friesel (1989)[29]	12.6 ± 0.5		29.5 ± 1.2

[a] Averaged over 12 measurements (using different single-crystal samples). [b] T and dP/dT values for the transition at 1 atm pressure; ΔV at the transition of 0.54% relative to room-temperature volume.[30]

instead on the 32(i) site with an assigned 50% occupancy, Figure 4b. With this location of oxygen atoms, the sulfate group can exist in one of two possible orientations; the oxygen atoms sites associated with one of those two orientations are indicated in the figure with asterisks. Overall, the sulfate group is quite regular, with all the O−S−O angles within 2° of the ideal tetrahedral value of 109.5°. The two SO_4 group orientations transform into one another by rotation about the $\bar{4}$ axis by 32° (or 58°). Protons in the Jirak model (Figure 4b) sit on a single crystallographic 16(f) site, resulting, as described above, in a three-dimensional hydrogen-bond network and hydrogen bonds that extend in the <1/2 0 1/8> directions. On average, two of the four crystallographically equivalent oxygen atoms of the sulfate anion are involved in hydrogen bond formation at any particular instant, serving as either donor or acceptor in the bond. Unlike the situation with the Belushkin and Merinov models, the orientation of the sulfate group is independent of which hydrogen bonds are formed, i.e., which particular oxygen atoms participate in hydrogen bonding and which particular proton sites are occupied. Thus, for any given hydrogen-bond arrangement about the sulfate group, the tetrahedral unit can reside in either of its two possible orientations.

In the first model proposed by Merinov, the oxygen atoms reside on two different 16(h) sites (identified here as $16(h)_a$ and $16(h)_b$), each with 50% occupancy, Figure 4c. Although there are eight local oxygen positions about each sulfur atom, much as in the Jirak model, there are, in fact, four possible sets of oxygen sites that can be occupied at any time, allowing for four possible SO_4 orientations. One of those orientations is indicated in the figure by the asterisked oxygen atoms. The remaining three can be generated by action of the mirror planes that extend parallel to the $\bar{4}$ axis on this particular orientation, and each oxygen atom can be part of two different "orientations". That is, operation on the asterisked atoms of Figure 4c by one of the mirror plane changes the location of only two of the four oxygen atoms, leaving the remaining two in place. For each orientation, two non-hydrogen-bonded sites, $16(h)_a$, and two mixed donor/acceptor oxygen sites, $16(h)_b$, are occupied. The assignment of oxygen atom types is based on the assumption that protons reside with 50% occupancy in the 8(e) sites discussed above.

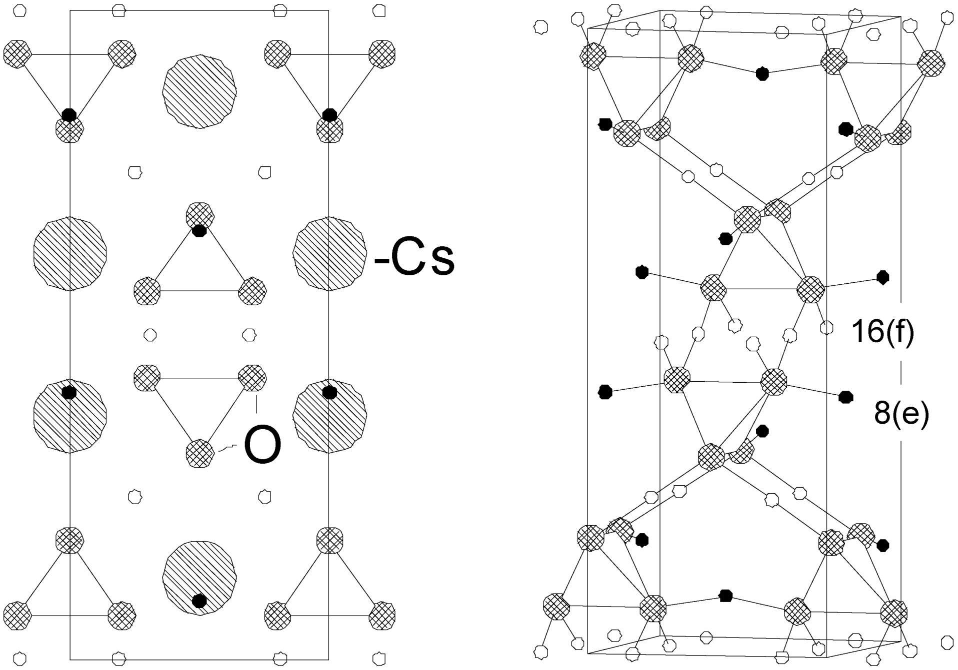

Figure 3. Idealized tetragonal (space group $I4_1/amd$) structure of $CsHSO_4$−I with oxygen atoms residing on fully occupied 16(h) sites, located on mirror planes, and protons residing on either 16(f) or 8(e) positions, open and closed circles, respectively. (a) projection on (100) and (b) clinographic view, with Cs atoms omitted for clarity.

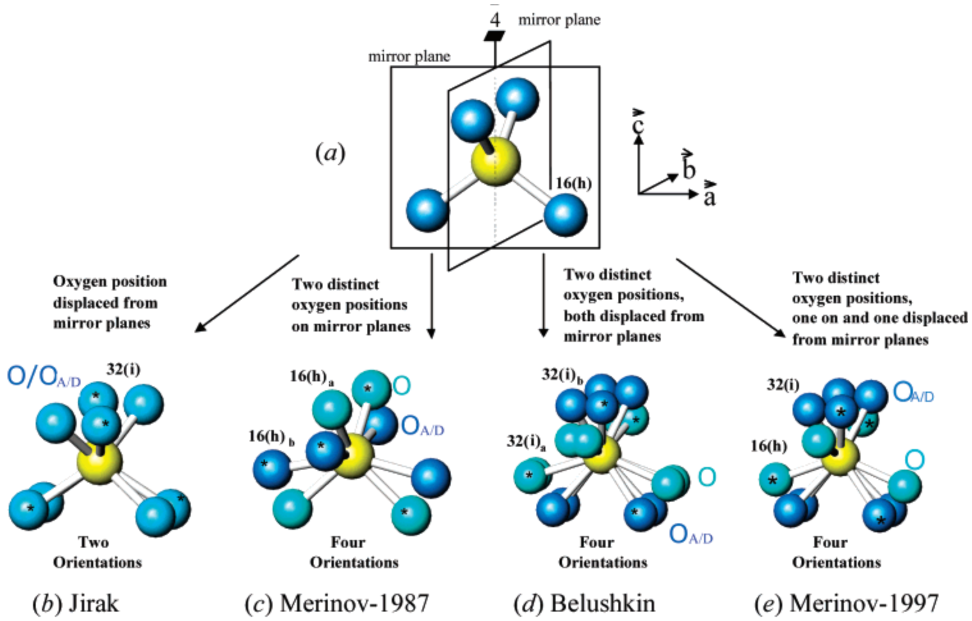

Figure 4. Possible configurations of the sulfate tetrahedra in phase I $CsHSO_4$: (a) idealized configuration containing no disorder, and configurations proposed by (b) Jirak,[2] (c) Merinov,[31] (d) Belushkin,[35] and (e) Merinov.[33] The Jirak model has two distinct orientations of the sulfate group, whereas the Merinov and Belushkin models have four. The * marks in the figures designate one possible arrangement for the oxygen atoms of a tetrahedron.

Unlike the Jirak model, the orientation of the sulfate group fixes the location of the hydrogen bonds (and vice versa) because of the distinction between oxygen atoms that do and do not form hydrogen bonds. Overall, the sulfate group is quite irregular, with three of the O−S−O angles being ∼96° and one being 125°. Only two, with values of 116°, are close to the ideal tetrahedral values. In addition, it is not possible to simply rotate the sulfate group from one orientation to another. Any change in orientation requires readjustment of the O−S−O angles and O−O edge distances.

Belushkin has proposed a model that combines features of the Jirak model and the first Merinov model. Oxygen atoms reside over two distinct oxygen sites, both on 32(i) positions, again labeled a and b, and each with occupancy of 25%. Accordingly, there are 16 local oxygen sites about any sulfur atom, and four distinct sulfate group orientations. The oxygen atoms associated with one particular orientation are asterisked in Figure 4d. The sulfate group indicated is fairly regular, with O−S−O angles ranging from 107.2 to 112.5°. In discussing their structural model, Belushkin et al. state that one SO_4 orientation may be transformed into another by a 30° rotation “around the central sulfur atom.” However, application of a 30° rotation along the −4 axis does not yield such a transformation. Indeed, much like the first Merinov model, any change in orientation appears to require readjustment of the O−S−O angles and O−O edge distances.

Protons in the Belushkin model are placed at both the 16(f) sites of the Jirak model and the 8(e) sites of the Merinov model, with occupancies of 0.246 and 0.094, respectively. The proximity of the protons to the oxygen atoms implies that all oxygen atoms, in principle, serve as mixed donor/acceptor atoms. However, the reported proton site multiplicities and occupancies yield 1.17 protons per formula unit (i.e., $CsHSO_4$), instead of the expected value of 1. If one accepts the 0.246 occupancy value for the 16(e) proton site (presumably more readily resolved in the diffraction data than the largely unoccupied 8(e) site), stoichiometry then demands that the occupancy of the 8(e) site be 0.008. With such a low occupancy, the 8(e) site makes little contribution to the overall configurational entropy. Thus, for simplicity, we take the 16(f) site to be 1/4 occupied and the 8(e) site to be empty, as in the Jirak model. Such a simplification leaves only the oxygen atoms in the $32(i)_b$ sites as mixed donor/acceptors in hydrogen-bond formation, with hydrogen bonds again extending in the <1/2 0 1/8> directions. Furthermore, as in the Merinov model, the identification of any single oxygen as either a hydrogen-bonded or non-hydrogen-bonded oxygen atom fixes the orientation of the sulfate group (and vice versa).

In a later study of the superprotonic structure of $CsHSO_4$, Merinov proposed a revised model that, in turn, combines features of the Belushkin model and his earlier one. Again, oxygen atoms are placed in two distinct sites, but in this case only one is displaced from the mirror plane to a 32(i) position, whereas the other resides on the mirror plane in a 16(h) position. Essentially, the $32(i)_a$ site from the Belushkin model, which is only slightly displaced from the mirror plane, is forced onto the higher symmetry location. Thus, the number of local oxygen positions about each sulfur atom is reduced from 16 of the Belushkin model to 12. In further analogy to Belushkin’s result (and also analogous to Merinov’s first result) there are four distinct sulfate group orientations, with one of these indicated in Figure 4e as the asterisked oxygen atoms. Four rather than three orientations (which might be expected simply from dividing 12 sites by 4 oxygen atoms) are possible because each of the 16(h) positions contribute to two different orientations. This can be understood by noting that action of either of the mirror planes (which places the sulfate group in a new orientation) changes the location of both of the 32(i) oxygen atoms but only one of the two 16(h) oxygen atoms. This is consistent

Table 2. Comparative Summary of the Crystal−Chemical Features of the Four Main Structural Models Proposed for $CsHSO_4$ in Phase I

structure type	Jirak (1987)[2]	Merinov (1987)[31]		Belushkin (1991)[35]		Merinov (1997)[33]	
similar structures	Varma(1993)[32]	Nozik (1990)[34]					
no. of orientations	2	4		4		4	
oxygen	O(1)	O(1)	O(2)	O(1)	O(2)	O(1)	O(2)
site	16(h)	16(h)	16(h)	32(i)	32(i)	32(i)	16(h)
chemistry[a]	A/D/N	N	A/D	A/D	N[b]	A/D	N[b]
occupancy	1/2	1/2	1/2	1/4	1/4	0.25(1)	0.51(3)
proton	H(1)	H(1)		H(1)	H(2)	H(1)	H(2)
site	16f	8e		16f	8(e)	16(f)	8(e)
occupancy[b]	1/4	1/2		0.246(7) → 1/4	0.094(7) → 0	0.21 → 1/4	0.09 → 0
d(S−O) (Å)	4 × 1.48(2)	2 × 1.48(7)	to $O(2)_{A/D}$	2 × 1.504(10)	to $O(1)_{A/D}$	2 × 1.492	to $O(1)_{A/D}$
		2 × 1.46(5)	to $O(1)_N$	2 × 1.570(5)	to $O(2)_N$	2 × 1.479	to $O(2)_N$
∠O−S−O (deg)	2 × 111.9(8)	95.5(8)	2 × 116.8(8)	112.5(3)	112.5(3)	97.7	2 × 108.8
	4 × 108.3(9)	125.5(9)	2 × 98.2(10)	108.9(3)	108.9(2)	104.7	2 × 118.9
				107.2(2)	107.1(4)		
d(O···O) (H-bond) (Å)	2.79(4)	2.84(6)		2.59(1)	[2.806(18)][b]	2.56	[2.98][b]
species	O(1), H(1)	O(2), H(1)		O(1), H(1)	[O(2), H(2)]	O(1), H(1)	[O(2), H(2)]

[a] A/D = donor/acceptor; *N* = non-hydrogen-bonded. [b] Proton occupancies simplified from as-published results in manner indicated, resulting in the redefinition of selected oxygen atoms as non-hydrogen-bonded.

with the 25% occupancy on the 32(i) site and the 50% occupancy on the 16(h) site.

The sulfate group of the second Merinov model is somewhat distorted, with O−S−O angles ranging from 97.7 to 118.9°. Moreover, as in all but the Jirak model, the SO_4 group cannot be transformed from one orientation to another by a simple rotation operation. The proton positions and site occupancies are essentially taken from the Belushkin model, and again, for simplicity, the 16(f) proton site is assumed, for the present analysis, to be 25% occupied (as opposed to 21%, as reported) and the 8(e) site taken to be unoccupied (as opposed to 9% occupied, as reported). With this simplification, only the oxygen atoms of the 32(i) sites participate in hydrogen-bond formation as mixed proton acceptor/donors, and once again, identification of any single 32(i) oxygen atom as the site of a hydrogen bond fixes the positions of all the other oxygen atoms.

In summary, see Table 2, it is evident that the four models disagree in terms of (1) the number of orientations of the sulfate group, (2) the directions of those orientations (and thus the directions of the hydrogen bonds formed between sulfate groups), (3) the existence (or not) of crystallographically inequivalent oxygen atoms, (4) the local geometry of the sulfate group and of the hydrogen bond, and (5) the extent of correlation between hydrogen bond formation and sulfate group orientation. In particular, with respect to the fifth point, the Jirak model is unique in that the sulfate group orientation is independent of the location of the hydrogen bonds. Despite the differences between the models, in all cases, the sulfate group is expected to participate, on average, in the formation of two hydrogen bonds, with, on average, one donor and one acceptor oxygen atom existing per oxyanion group at all times.

Preliminary Entropy Evaluations. For those structural models in which the location of the hydrogen bonds is explicitly determined by the orientation of the sulfate group, the number of possible configuration is simply given by the number of sulfate group orientations. Somewhat coincidentally, all three of the "correlated" models incorporate four sulfate group orientations, implying a molar configurational entropy of $R \ln(4) = 11.5$ J mol^{-1} K^{-1},[35] where R is the universal gas constant (8.314 J mol^{-1} K^{-1}). Moreover, because the entropy of $CsHSO_4$ phase II is zero (as also noted above), this entropy corresponds to the II → I transition entropy. The value from this simple approach was in good agreement with contemporaneous reports for the experimentally measured entropy, 10.9−13.3 J mol^{-1} K^{-1}, Table 1. Accordingly, the entirety of the entropy of $CsHSO_4$ phase I was thought to be adequately accounted for by simply considering the four orientations of the sulfate group without accounting for additional entropy due to hydrogen-bond disorder.[35]

The present work, as well as the more recent experimental studies,[20] indicate that the II → I transition entropy of $CsHSO_4$ is substantially greater than previously thought, ∼14.8 rather than ∼ 12 J mol^{-1} K^{-1}, Table 1. This value is greater than can be accounted for by the Merinov or Belushkin structural models of $CsHSO_4$−I. In what follows, we show that the Jirak structure, in which sulfate-group orientation and hydrogen-bond location are independent of one another, does imply an entropy that coincides with the experimental value measured here. To provide an adequate description of the entropy, we develop a formalism that is applicable not only to $CsHSO_4$ phase I but to superprotonic phases in general in which anion-group disorder and hydrogen-bond disorder must be accounted for simultaneously. The approach is based on Pauling's analysis of the residual entropy of ice, in which OH dipole orientational disorder and local hydrogen-bond disorder (O_A vs O_D) are simultaneously described.[1]

Ice Reviewed. Hexagonal ice (ice I_h) is composed of oxygen ions and protons, with each oxygen atom coordinated by four nearest neighbor oxygen atoms, at distances of 2.76 Å, residing on the corners of a regular tetrahedron, Figure 5.[39] Hydrogen bonds, with O−H distances of 1.0 Å, connect the oxygen atoms to one another and thus each oxygen atom is surrounded by four possible proton sites. Between each pair of oxygen atoms, there are two such proton sites that are separated by 0.76 Å. In the absence of defects, the oxygen ion serves as a donor in two hydrogen bonds and as an acceptor in two additional bonds. Thus, all possible hydrogen bonds are formed, with one-half of the proton sites occupied.

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(39) Bernal, J. D.; Fowler, R. H. *J. Chem. Phys.* **1933**, *1*, 515.

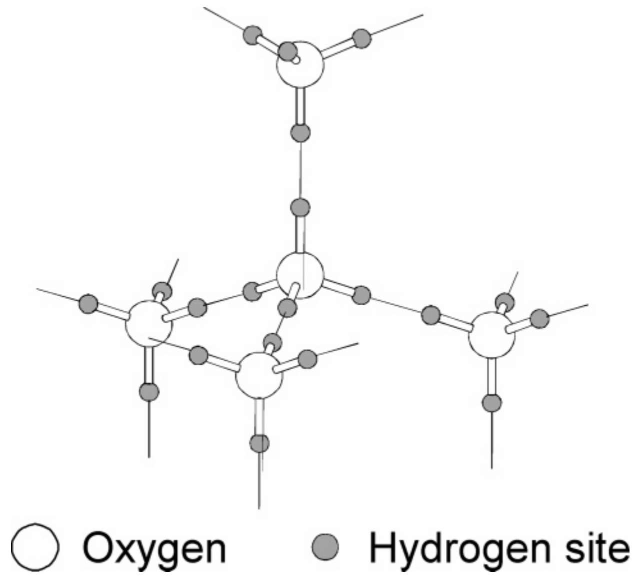

Figure 5. Structure of hexagonal ice: each oxygen atom is tetrahedrally surrounded by four oxygens and four possible proton sites.[39]

Upon cooling, the entropy of hexagonal ice as measured experimentally does not approach zero, but rather retains a residual value due to the random manner in which protons occupy the available proton positions.[40] Pauling quantitatively explained the magnitude of this residual entropy by first restricting the possible configurations according to the so-called ice rules[1]:

(i) two and only two protons are bonded to each oxygen atom;

(ii) one and only one proton occupies each hydrogen bond;

(iii) the hydrogen bonds are directed approximately toward two of the four neighboring oxygen atoms;

(iv) interaction between non-neighboring water molecules does not energetically favor one possible configuration of protons with respect to other possible configurations, so long as those configurations satisfy (i)−(iii).

The first two of these rules, originally proposed by Bernal and Fowler,[39] imply that defects such as hydroxyl groups, hydronium ion groups, and D- and L-defects (doubly occupied bonds and unoccupied bonds, respectively) do not substantially add to the total number of accessible configurations and, accordingly, their contribution to the residual entropy is inconsequential.

A single, isolated H_2O molecule obeying the “ice rules” has, in principle, several configurations available to it. The first proton can be situated in one of four possible locations and the second in any one of the three remaining locations. Of these twelve configurations, only one-half are distinct, and the number of possible configurations becomes six. Stated for the general case, the molecule has $\binom{n}{m}$ configurations available to it, where n is the number of proton positions neighboring each oxygen atom and m is the number of protons that are present to fill them. Within the three-dimensional structure of ice, on average, one-half of the proton sites are occupied, and thus the probability that any particular proton could, in fact, be placed at any particular site is only 50% if doubly occupied hydrogen bonds are to be avoided. Consequently, the number of accessible configurations must be modified by a factor of (1/2) for each proton. The number of configurations for each H_2O molecule is then

$$\Omega = \begin{pmatrix} \#\ of\ proton \\ configurations \end{pmatrix} * \begin{pmatrix} probability\ a\ proton \\ site\ is\ open \end{pmatrix}^{\begin{pmatrix} \#\ of \\ protons \end{pmatrix}} \\ = \binom{4}{2} * \left(\frac{1}{2}\right)^2 = 6 * \left(1/4\right) = 3/2 \tag{1}$$

This calculated value for the residual molar entropy, R ln(3/2) = 3.37 J mol^{-1} K^{-1}, is in extremely good agreement with the experimental data, 3.65 J mol^{-1} K^{-1}.[40]

Ice Rules Adjusted for Phase I $CsHSO_4$. The modifications we make to the above ice rules in applying them to superprotonic phases such as that of $CsHSO_4$ are very similar to those given by Slater in describing the ferroelectric transition of KH_2PO_4,[41] which, in turn, remain relatively unchanged from those used by Pauling. To apply the Pauling approach to superprotonic $CsHSO_4$, three key structural differences between $CsHSO_4$ and ice must be accounted for. First, the structural unit of interest in the former is the sulfate group rather than the oxygen ion. Second, the $H:SO_4$ ratio is 1:1, as compared to the H:O ratio of 2:1 in ice. Third, in addition to the random distribution of hydrogen bonds, which will be described in analogy to ice, the sulfate group can be oriented in one of multiple directions for any given location of the hydrogen bond, introducing additional possible configurations and therefore, configurational entropy. The $H:SO_4$ ratio in $CsHSO_4$ of 1:1 changes the first ice rule to

(i) one and only one proton is associated
with each tetrahedron (2a)

The second rule remains essentially unchanged from its previous formulation:

(ii) one and only one proton occupies each hydrogen bond
(2b)

This rule applies only to hydrogen bond sites where bonds are actually formed, not to all possible hydrogen bond sites (1/2 of which remain unoccupied). The third and fourth rules are modified only to reflect the fact that hydrogen bonds are formed between the oxygen atoms of neighboring sulfate groups (rather than just between oxygen atoms):

(iii) hydrogen bonds are directed toward oxygen
atoms of neighboring tetrahedra (2c)

(iv) interaction between non-neighboring
tetrahedra does not energetically favor one possible
configuration of a tetrahedron and its proton
with respect to other possible configurations,
so long as those configurations satisfy (i)−(iii) (2d)

Although not explicitly stated, the fourth rule reflects the independence of the tetrahedral group orientation and

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(40) Giauque, W. E.; Ashley, J. W. *Phys. Rev.* **1933**, *43*, 81.

(41) Slater, J. C. *J. Chem. Phys.* **1941**, *9*, 16.

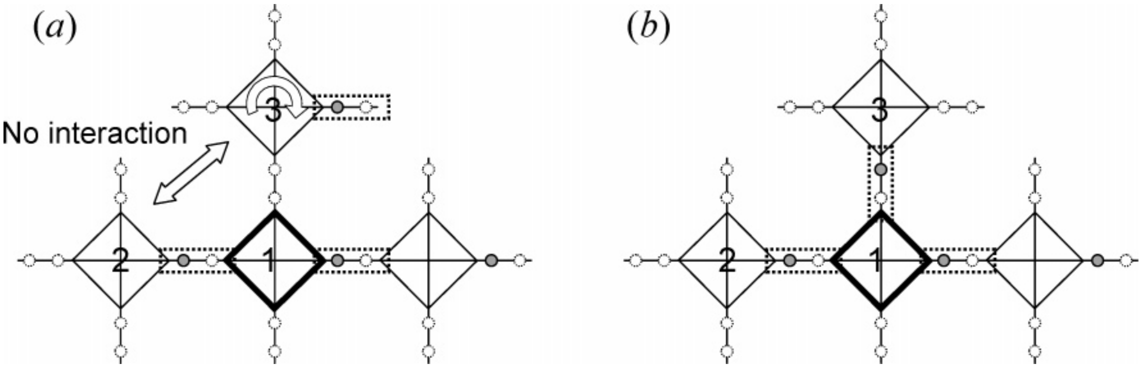

Figure 6. Illustration of the independence of hydrogen bond direction between second nearest neighbor tetrahedra: (a) two bisulfate tetrahedra, directly neighboring a common sulfate group, do not interact with respect to the direction of their hydrogen bonds, so that one tetrahedron may reorient; (b) the reorientation changes the number of hydrogen bonds associated with the central group from two to three. Locations of hydrogen bonds emphasized by dotted rectangles.

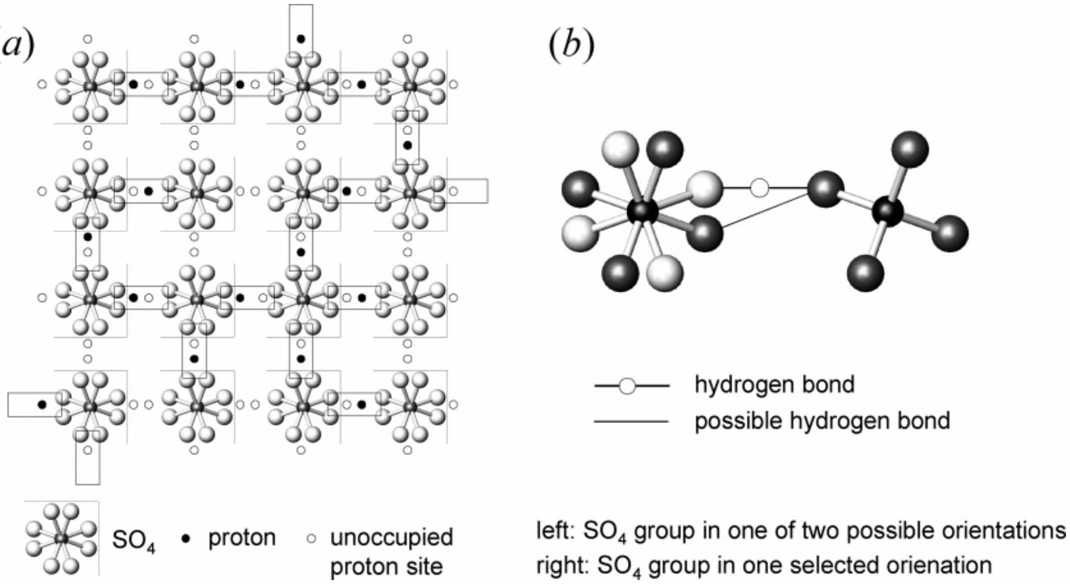

Figure 7. Schematic descriptions of the disorder accounted for by adjusted ice rules: (a) random distribution of protons (and hence, hydrogen bonds) over all available positions while maintaining a $H:SO_4$ ratio of 1:1 in the superprotonic phase of $CsHSO_4$; and (b) local disorder of sulfate group in a manner independent of the overall position of the hydrogen bond. Locations of hydrogen bonds emphasized by rectangles in (a).

hydrogen bond direction. Furthermore, implicit in these rules is the assumption that (as in the case of ice) double-minima hydrogen-bonds exist between oxygen atoms such that, at any given instance, a proton is associated with only one particular sulfate tetrahedron.

The fourth rule has the important implication of allowing any number of the non-donor oxygen atoms of the bisulfate group to serve as acceptors in a hydrogen bond. This is equivalent to stating that, for any given orientation, the tetrahedral group forms a minimum of one to a maximum of four hydrogen bonds. The reasoning is as follows. Consider the bisulfate group generically identified as group 1 in Figure 6, with neighbors group 2 and group 3. Group 1 forms a hydrogen bond with group 2 as a consequence of the donor oxygen atom in group 2 being directed toward group 1. The orientation of group 3, which is not a direct neighbor of group 2, is not influenced by the latter, so long as rules (i)−(iii) are obeyed. Thus, group 3 may be oriented as shown in Figure 7a, so as not to form a hydrogen bond with group 1, or may reorient (Figure 7b) to generate the configuration shown in Figure 7c, in which groups 3 and 1 share a hydrogen bond. Thus, the absence of direct interaction between groups 2 and 3 renders possible both two different configurations, which generate differing numbers of hydrogen bonds on group 1.

Physical justification for this interpretation of the structure of superprotonic $CsHSO_4$ derives from the observation, as noted above, that the sulfate group reorientation rate is orders of magnitude greater than the proton-transfer rate and from the absence of any experimental evidence of correlated sulfate group dynamics. It is noteworthy that this feature of $CsHSO_4$ (a variable number of hydrogen bonds per anion unit) differs from the situation in ice because one-half of the possible hydrogen bonds are unoccupied, whereas in ice all are occupied. A further consequence is that so-called L-defects ("leer" or empty hydrogen bonds) have no meaning as defects in $CsHSO_4$ because they are an inherent part of the structure.

The modified rules allow us to evaluate the number of configurations associated with the random distribution of hydrogen bonds in the structure, Ω_H, in a manner entirely analogous to ice. To account for the multiple sulfate orientations, we introduce a second term, Ω_O, which is simply the number of oxygen positions possible for any particular hydrogen bond. Together, these imply a total number of configurations for $CsHSO_4$ of

$$\Omega = \underbrace{\begin{pmatrix}\#\text{ of}\\ \text{proton}\\ \text{configurations}\end{pmatrix} * \begin{pmatrix}\text{probability}\\ \text{a proton}\\ \text{site is open}\end{pmatrix}^{\begin{pmatrix}\#\text{ of}\\ \text{protons}\end{pmatrix}}}_{\Omega_H} * \underbrace{\begin{pmatrix}\#\text{ of}\\ \text{oxygen}\\ \text{positions}\end{pmatrix}}_{\Omega_O} \qquad (3)$$

The types of configurational disorder described by these two terms are shown schematically in Figure 7.

Numerical evaluation of eq 3 on the basis of the Jirak model for superprotonic $CsHSO_4$ is straightforward. There is one proton per sulfate group ($m = 1$), which can reside in one of four hydrogen bond sites ($n = 4$). Furthermore, on average, $^1/_4$ of the proton sites are occupied, such that the probability that a particular proton site is open is 3/4. Finally, as described above, there are two possible orientations of the sulfate group for any given hydrogen-bond arrangement, which is equivalent to the existence of two oxygen positions, again, for any particular hydrogen bond. These data imply a molar number of configurations of $\Omega = \binom{4}{1}(^3/_4)^1{\cdot}2 = 6$ and a molar configurational entropy of

$$S_{\text{config}} = R\ln(\Omega) = 14.90\ \text{J mol}^{-1}\ \text{K}^{-1}$$

The calculated value is in remarkably good agreement with that measured here experimentally, 14.75(22) J mol^{-1} K^{-1}. On this basis, we propose both that (1) the formalism developed here is appropriate to describe the entropy of superprotonic $CsHSO_4$, and (2) the structure proposed by Jirak, which provides a chemically satisfactory picture of regular sulfate tetrahedra undergoing simple reorientations, correctly describes the physical reality. A third important conclusion is that essentially all of the entropy of the superprotonic transition is configurational in nature. This implies that vibrational and other types of entropy are unchanged between the low- and high-temperature phases of $CsHSO_4$, consistent with observations that the internal vibrational modes of the sulfate group do not change appreciably across the transition (and hence do not greatly impact proton transport mechanisms).[42−44]

It must be emphasized that the formalism presented here for the evaluation of the Jirak model of superprotonic $CsHSO_4$ is inappropriate for the evaluation of the Merinov and Belushkin models. For these structures, as noted previously, the number of orientations accounts for the full entropy of both models, and hence the application of this formalism is unnecessary. In principle, one could argue that some vibrational contribution to the transition entropy is expected in the Merinov and Belushkin structures because of the distortion that the sulfate groups undergo at high temperature according to these models, Table 2. Accounting for the vibrational contribution might, in turn, bring the calculated entropy of the Merinov and Belushkin models in line with the experimental value measured in this work. However, the internal vibrational modes of the sulfate groups are rather similar to those at lower temperatures (exhibiting a gradual transition to T_d symmetry upon heating),[42] inconsistent with a large change in vibrational entropy and with the presence of highly distorted tetrahedra.

Adjusted Ice Rules and Superprotonic Conductivity. A key assumption in the entropy formalism developed here is that the concentration of defects in the hydrogen bond system of $CsHSO_4$ is negligible. At first glance, this assumption would seem to be odds with the observation of high conductivity of phase I $CsHSO_4$, which certainly relies on the presence of defects. In analogy to ice, defects in the hydrogen-bond system must be either ionic (i.e., $2HSO_4^- \rightarrow H_2SO_4^0 + SO_4^{-2}$) or comprise D- and L-hydrogen-bond defects (doubly occupied or empty hydrogen bonds, respectively). However, as already discussed, L-defects have no meaning for this structure because one-half of the possible hydrogen bonds are already unoccupied and these unoccupied sites are completely randomly arranged. D-Defects, on the other hand, are ruled out because they are typically of very high energies (60 kcal mol^{-1} in the case of ice),[45] leaving ionic defects as the mostly likely defect species in superprotonic $CsHSO_4$.[46,47]

The concentrations of $H_2SO_4^0$ and SO_4^{-2} defects in phase I have not been experimentally measured; however, their values can be approximated by comparison to molten sulfuric acid. At 25 °C, the autoprotolysis of H_2SO_4 results in concentrations of $H_3SO_4^+$ and HSO_4^- of only 0.15 and 0.11 mol %, respectively.[48] Nevertheless, anhydrous sulfuric acid exhibits a high electrical conductivity ($\sigma(25\ °\text{C}) = 1.04 \times 10^{-2}\ \Omega^{-1}\ \text{cm}^{-1}$). The mechanism of proton conduction in sulfuric acid is nearly identical to that in phase I $CsHSO_4$, with reorientations of the ionic defects and surrounding H_2SO_4 molecules leading to breaking and re-forming of hydrogen bonds through which protons are transferred.[49] With increasing temperature, the concentration of these ionic defects in sulfuric acid increases, but only to ∼1 mol % at 414 K,[50] the temperature of the superprotonic transition of $CsHSO_4$.

Given the similar mechanisms of proton conduction and comparable magnitudes of conductivity in liquid sulfuric acid and superprotonic $CsHSO_4$, it is reasonable to assume that the concentration of ionic defects in phase I $CsHSO_4$ is approximately 1 mol % or less. Therefore, we propose that the conductivity jump at the transition is due to a dramatic increase in the *mobility* of the protons (due to the reorientations of the sulfate tetrahedra), rather than an increase in the *concentration* of protonic defects. This interpretation has

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(42) Baran, J.; Marchewka, M. K. *J. Mol. Struct.* **2002**, *614*, 133.

(43) Dmitriev, V. P.; Loshkarev, V. V.; Rabkin, L. M.; Shuvalov, L. A.; Yuzyuk, Yu. I. *Sov. Phys. Crystallogr.* **1986**, *31*, 673.

(44) Pham-Thi, M.; Colomban, Ph.; Novak, A.; Blinc, R. *J. Raman Spectrosc.* **1987**, *18*, 185.

(45) Dunitz, J. D. *Nature* **1963**, *197*, 860.

(46) Baranov, A. I. *Bull. Acad. Sci. USSR, Phys. Ser.* **1987**, *51*, 60.

(47) Sharon, M.; Kalia, K. *J. Solid State Chem.* **1977**, *21*, 171.

(48) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon Press: New York, 1985.

(49) Flowers, R. H.; Gillespie, R. J.; Robinson, E. A.; Solomons, C. *J. Chem. Soc.* **1960**, 4327.

(50) Gillespie, R. J.; Robinson, E. A.; Solomons, C. *J. Chem. Soc.* **1960**, 4320.

also been suggested by recent ^{1}H NMR measurements.[51] That the concentration of defects is largely unchanged at the transition is furthermore consistent with the similarity of the overall structural features of the phases of $CsHSO_4$ below and above the superprotonic transition. That is, the energetics of ionic defect formation are surely dominated by coulombic interactions, in turn governed by interatomic distances, which do not change significantly at the transition. Thus, even the 0.61 J mol^{-1} K^{-1} in configurational entropy that can be contributed by an estimated total defect concentration of 1 mol % (assuming 0.5% concentrations for both $H_2SO_4{}^0$ and $SO_4{}^{-2}$ defects) does not add to the entropy of the transition, if the concentration of such defects is unchanged as a result of the structural transformation. A slightly alternative but nevertheless consistent interpretation is that the mobility increases to such a level that, in effect, all protons participate in the charge-transport process and that there is no clear distinction between defects and normal protons or normal proton sites. This type of perspective is taken by Beluskin, who has proposed, on the basis of a preliminary reverse Monte Carlo (RMC) analysis of total neutral diffraction data, that constant density isosurfaces for deuterium ions in $CsDSO_4$ form a continuous, percolative network throughout the structure.[52]

Summary and Conclusions

The entropy of the superprotonic phase transition in $CsHSO_4$ has been experimentally re-evaluated and theoretically analyzed. The value, 14.75 ± 0.22 J mol^{-1} K^{-1}, cannot be explained in terms of the configurational entropy of structural models of superprotonic $CsHSO_4$ in which hydrogen-bond location and sulfate group orientation are correlated. Such correlation is implicit in the structures proposed by Belushkin[35] and by Merinov.[31,33] In contrast, these features are uncorrelated in the model proposed by Jirak,[2] giving rise to additional contributions to the configurational entropy. To describe the entropy of structures simultaenously displaying dynamically disordered hydrogen-bond networks and orientationally disordered polyhedra, we have extended in this work the approach developed by Pauling to evaluate the residual entropy of ice at 0 K.[1] The disordered phase is assumed to obey a set of structural rules, analogous to the so-called ice rules. The formalism developed correctly predicts the entropy of the superprotonic transition of $CsHSO_4$. Thus, the analysis provides strong evidence that the Jirak model of phase I $CsHSO_4$, in which sulfate tetrahedra have regular geometries and exhibit no crystallographic distinction between oxygen atoms that participate in hydrogen bonds and those that do not, is the most probable. The likely applicability of this approach to superprotonic phases with distinct structures (e.g., $Rb_3H(SeO_4)_2$, CsH_2PO_4) but with similarly disordered hydrogen-bond networks and rotationally disordered oxyanion groups[53,54] is discussed in detail elsewhere.[27,55]

The entropy formalism developed here, in principle, forbids the presence of ionic defects. At first glance, this contradicts the observation of high conductivity in phase I $CsHSO_4$. A comparison to anhydrous sulfuric acid suggests, however, that only small concentrations of defects are necessary to accommodate high proton-transport rates, and thus, that the jump in conductivity across the superprotonic transition is due to a sharp increase in proton mobility rather than a sharp increase in the concentration of ionic defects. The extremely high mobility can alternatively be interpreted to imply that all protons participate in charge transport, without distinction between defects and normal protons/proton sites.

Acknowledgment. The authors thank Dr. Jeff Snyder and Dr. Dane Boysen for insightful discussions. This work has been supported by the National Science Foundation, DMR-0435221, and by the Donors of the American Chemical Society Petroleum Research Fund.

CM062070W

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(51) Yoshida, Y.; Matsuo, Y.; Ikehata, S. *J. Phys. Soc. Jpn.* **2003**, *72*, 1590.

(52) Belushkin, A. V.; McGreevy, R. L.; Zetterstrom, P.; Shuvalov, L. A. *Physica B* **1998**, *241−243*, 323.

(53) Bohn, A.; Melzer, R.; Sonntag, R.; Lechner, R. E.; Schuck, G.; Langer, K. *Solid State Ionics* **1995**, *77*, 111.

(54) Preisinger, A.; Mereiter, K.; Bronowska, W. *Mater. Sci. Forum* **1994**, *166−169*, 511.

(55) Haile, S. M.; Chisholm, C. R. I.; Sasaki, K.; Boysen, D. A.; Uda, T. *Faraday Discuss.* **2007**, *134*, 17.