

BRIEF COMMUNICATION

Thermally Induced Phase Transitions of CsHSO₄: A Reexamination

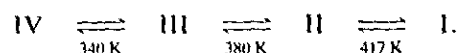
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A reexamination of the thermally induced phase transitions of CsHSO₄ shows that the room-temperature phase IV transforms to II around 373 K. Phase III is, however, not obtained by heating IV to 340 K. Phases IV and III can coexist at room temperature under certain conditions; and phase III appears to transform to II at 340 K. © 1995 Academic Press, Inc.

Based on vibrational spectroscopic studies, Varma *et al.* (1) suggested that CsHSO₄ undergoes three transitions in the solid state:



The room-temperature phase IV has a monoclinic structure while the high-temperature superionic phase has a tetragonal structure involving the free rotation of the HSO₄⁻ ions. The transition from IV to III at 340 K is subject to considerable doubt. Varma *et al.* (1) found some changes in the vibrational spectrum at this temperature and therefore reported it as due to the IV-III transition. It has been pointed out by Lunden *et al.* (2) that the monoclinic phase III can only be produced from IV by exposure to water vapor or by the application of pressure. Phase III apparently undergoes a phase transition around 340 K to another monoclinic phase, II. Accordingly, Varma *et al.* did not find any change in the X-ray powder diffraction pattern on heating phase IV to 340 K. It seems possible that the changes in the spectra found by Varma *et al.* at 340 K arise from the coexistence of phases III and IV in their sample. They indeed reported some evidence for the coexistence of phases in the spectra. There is little doubt, however, that phase II is formed on heating IV to around 380 K.

In order to understand the thermal phase transitions of CsHSO₄, a detailed single crystal X-ray diffraction study

has been carried out. The study shows no thermally induced transition at 340 K. The unit cell parameters of CsHSO₄ at 338 K are found to be $a = 5.5075(17)$, $b = 5.8280(33)$, $c = 7.3238(27)$ Å, $\beta = 101.373(27)^\circ$, ($Z = 2$), and $V = 230.46$ Å³, close to those of the room-temperature phase IV. The space group of IV is not altered at this temperature ($P2_1/m$ or $P2_1/c$). The structure at 338 K has a Cs and a SO₄ group positioned on the mirror plane at $y = 1/4$ and $3/4$ with infinitely hydrogen bonded chains of SO₄ tetrahedra running along the b axis, just as the structure of phase IV did. There are three different S-O distances in the SO₄ unit. Two of the S-O bonds are long (1.517(20) Å) and the other two S-O distances are 1.420(25) and 1.423(22) Å. Around 373 K, however, there is a phase transition associated with a change in the space group to $P2_1/a$ (phase II). The unit cell parameters at 373 K are found to be $a = 7.7094(54)$, $b = 8.1542(105)$, $c = 7.8032(34)$ Å, $\beta = 110.959(47)^\circ$, ($Z = 4$), and $V = 458.09$ Å³. The transition from IV to II at 373 K involves a shift of the atoms away from the mirror plane leading to the reorientation of the SO₄ tetrahedra. The structure of phase II thus has SO₄ tetrahedra connected by hydrogen bonds into zigzag chains running parallel to the c -axis. All the oxygen atoms in the coordination polyhedra of Cs simultaneously take part in the formation of SO₄ tetrahedra. The structural projection along the ab plane of phase IV (with the SO₄ tetrahedra oriented along the b axis) is compared with the projection along the bc plane of phase II (with the SO₄ tetrahedra oriented along the c -axis) in Fig. 1. There are four unique S-O distances in phase II compared to three in phase IV. Two of the S-O distances in phase II are long (1.652(44) and 1.534(44) Å), with the shorter S-O distances being 1.476(39) and 1.497(38) Å. The O-H-O bond is linear in phase IV with a O...O distance of 2.54 Å while it is bent in phase II (with a O...O distance of ~2.5 Å).

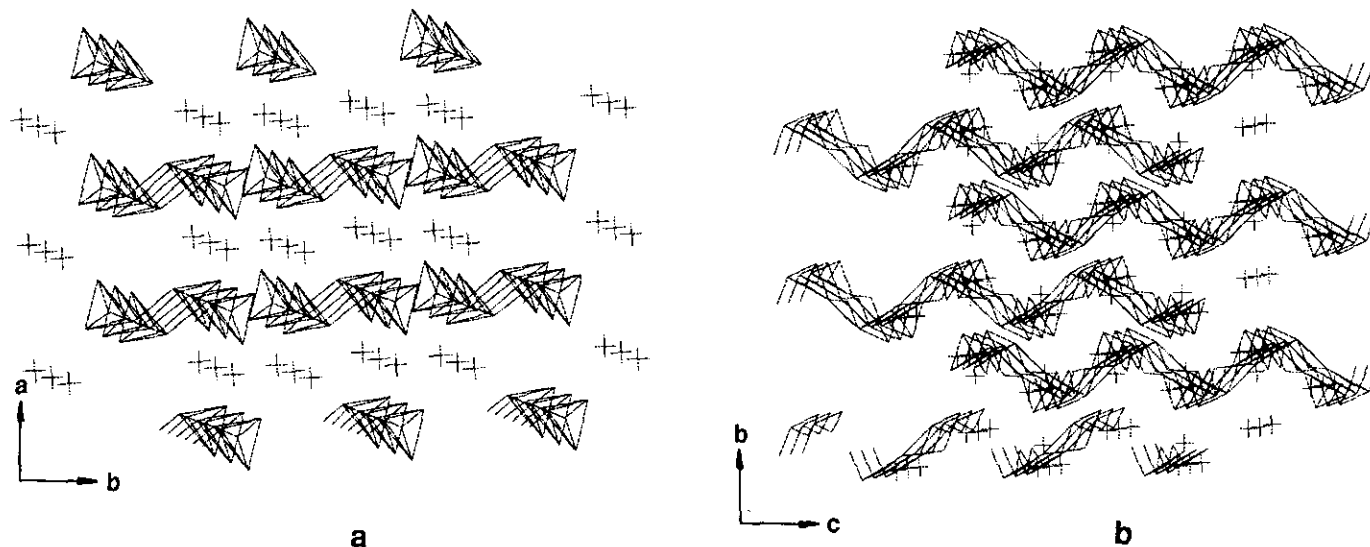
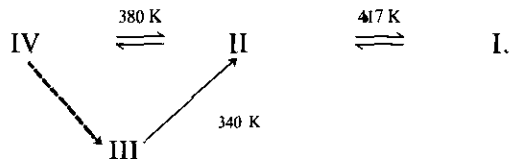


FIG. 1. Structural projections along the ab plane of phase IV (a) and the bc plane of phase II (b) of CsHSO_4 .

Based on the above observations and those of Lunden *et al.* (2), we represent the thermal transitions of CsHSO_4 as



The IV–III transition is not driven thermally. There is

reason to believe that phase II reverts to IV on standing. In contrast to phase II, there is only one S–O distance (1.401 Å) in the high-temperature superionic phase I, because of the free rotation of the anion [1].

REFERENCES

1. V. Varma, N. Rangavittal, and C. N. R. Rao, *J. Solid State Chem.* **106**, 164 (1993).
2. A. Lunden, B. Baranowski, and M. Friesel, *Ferroelectrics* **124**, 103 (1991).