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On the Phase Transitions of Cesium Hydrogen Sulfate ($CsHSO_4$)

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V. Varma, N. Rangavittal, and C. N. R. Rao (*J. Solid State Chem.* 106, 164 (1993)) have concluded from infrared and Raman spectroscopic studies of $CsHSO_4$ that reversible phase transitions occur near both 340 and 380 K. However, both transitions are "irreversible"; i.e., they do not occur spontaneously when the temperature is decreased. Actually, three different monoclinic phases can exist "indefinitely" at room temperature. The decisive factor is the water vapor pressure above the salt, and changes in water vapor pressure can trigger phase transitions in the bulk of the salt. Similar triggering can be caused by grinding, pellet pressing, etc. An analysis of the results reported by Varma *et al.* leads to the conclusion that their phases "IV" and "III" were not pure, but instead were mixtures of two or three monoclinic phases. © 1995 Academic Press, Inc.

Varma *et al.* have recently studied $CsHSO_4$ and $Cs_{1-x}Li_xHSO_4$ by means of vibrational spectroscopy and X-ray diffraction (1). Their paper appeared at about the same time that we published a study of the interaction between $CsHSO_4$ and water vapor (2), as well as one on the structure of two monoclinic phases (3).

A large number of papers on acid sulphates and selenates of cesium, rubidium, ammonium, etc., have been published during the 1980s and 1990s. Much work has also been done on acid phosphates and arsenates. We shall limit the discussion here to cesium hydrogen sulfate. There is consensus in the literature concerning the transition near 416 K between a monoclinic and a tetragonal phase, but there are many discrepancies regarding lower temperatures. Thus, Komukae *et al.* found a phase transition at about 373 K (4), while, starting with Baranov *et al.* (5), nearly all later studies showed a transition near 330 K but nothing at 373 K. However, Colomban *et al.* have produced a diagram showing 10 transitions between 12 solid phases (6). There are also discrepancies concerning the structure of the phases; this will be discussed below.

When we became aware of the above-mentioned discrepancies concerning phase transitions (4, 5), we decided to make a systematic investigation. A characteristic of our work is that we use differential scanning calorimetry (DSC) not only to detect phase transitions and to determine transition enthalpies, but also to estimate the composition of a mixture of two or more phases (7–9). While most other investigators speak of only two monoclinic phases, we have demonstrated that three such phases can exist "indefinitely" at room temperature. The decisive factor for phase stability is actually the water vapor pressure above the salt sample. Phase transitions in the bulk can thus be triggered by interaction with water vapor at the surface, and transitions can go on gradually while a sample is stored. Transitions can also occur during grinding, pellet pressing, etc. Mixtures of any desired composition can be prepared by a combination of treatments.

Our results are summarized in Fig. 1, which includes both thermal transitions and processes at room temperature. (The labels I and II are used in the same way by Varma *et al.* and by us; there are discrepancies when it comes to III and IV.) We have shown that the actual temperatures of the III → II and IV → II transitions are influenced by the sample history.

The transition enthalpy is 0.55 kJ/mole at 333 K, 1.1 kJ/mole at 375 K, and 5.3 kJ/mole at 416 K (7), while the enthalpy of melting is 13.2 kJ/mole at 484 K (10).

Phase III is obtained when a solution of equimolar amounts of Cs_2SO_4 and H_2SO_4 is crystallized at room temperature. If the samples are stored for a long time in a desiccator with sulfuric acid as drying agent, a complete transformation to phase IV should occur, which we have suggested as the cause of seemingly conflicting transition

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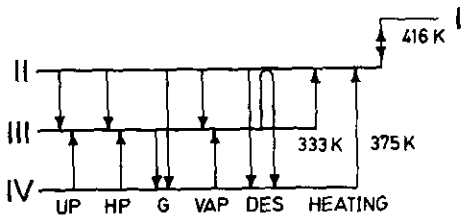

FIG. 1. Schematic representation of phases and phase transitions in cesium hydrogen sulphate. The transitions at room temperature are caused by uniaxial pressure (UP), hydrostatic pressure (HP), contact with water vapour (VAP), storage in a desiccator (DES), or grinding (G). Crystallization from an aqueous solution gives III.

temperatures as well as of disagreements concerning the structure of the "room temperature" phase (9, 11, 12).

Varma *et al.* summarize their results by presenting a transition scheme with a sequence of reversible solid–solid transitions occurring near 340, 380, and 417 K, respectively (1). They make no attempts to compare their transition scheme with the work of previous investigators, and they do not say what evidence they have that the transitions near 340 and 380 K also occur when a sample is cooled. Their transition scheme is based on their spectroscopic studies (see below), but it is in conflict with their DSC scan shown in Fig. 1 of Ref. (1). They give no numbers for any of their measured transition enthalpies, but they say that they obtained only "a somewhat vague suggestion" of a transition around 380 K. However, there is not much to be seen in their Fig. 1 at 340 K either, and the only distinct peaks are at 417 K and the melting point. From a comparison with our enthalpies quoted above, it seems as if the DSC scan had been made on a sample that was nearly pure phase II at room temperature with minor amounts of phases III and IV present.

Varma *et al.* discuss the results of their spectroscopic study in much more detail, and they conclude that transitions occurred around both 340 and 380 K. This suggests that considerable amounts of both phase III and phase IV were present at room temperature, i.e., that the composition was different from the above-mentioned DSC sample. It is said that a powdered sample was used for the infrared measurements, but "powdering" can mean anything from gentle crushing to intense grinding, and one does not know to what extent phases II and III had been converted to IV (see our Fig. 1). It is not said whether the samples used for the Raman and X-ray work were "powdered," or if they were treated in some other way. In any case, it is very likely that the samples studied by means of IR or Raman spectroscopy contained a large fraction of phase III at room temperature.

Varma *et al.* have performed X-ray powder diffraction studies at 300, 340, 413, and 418 K. They say that they have confirmed that the space group is $P2_1/m$ for the "room temperature phase," as reported in 1981 by Itoh *et al.* (13). However, a redetermination by Itoh *et al.* gave $P2_1/c$ (14), which is in excellent accordance with our study (3). We have, however, chosen another option for the unit cell axes, corresponding to the space group $P2_1/n$. The results found by Varma *et al.* for phase II (413 K) are difficult both to understand and to accept. The volume of their unit cell is 818 $Å^3$, which is 1.8 times the unit cell that we found for phase II, or 3.6 times the unit cell that they found at 300 K.

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