

An Explanation of the Removal of Metastability in Some Hydroacid Salts by Water Adsorption

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Z. Naturforsch. **56a**, 869–872 (2001); received October 31, 2001

The metastability of some phases of CsHSO_4 and RbH_2PO_4 is due to the volume decrease at an endothermic phase transition which “locks in” the metastability in question. Water adsorption, which removes these metastabilities, probably exerts a “wedge-like” force which expands the lattice spacing in the surface layer, thus facilitating the start of the phase transition. The induction time and the zeroth order kinetics of the transition in RbH_2PO_4 are exponential functions of the water activity applied.

Key words: Phase Metastability; Adsorption of Water.

Metastable solid phases have been found in some hydroacid salts of cesium and rubidium [1, 2]. Differential scanning calorimetry (DSC) is a convenient technique for detecting such metastabilities during thermal cycling. Thus a transition peak which appears when the sample is heated might not be detectable when the temperature is lowered. The existence of such metastabilities explains why it has been very difficult to detect some phases.

In order to clear up the existence of such metastabilities and their removal, we have previously focussed our attention on two cases. (We are using Roman numerals to denote the phases of the two salts, starting with I for the high-temperature phase for CsHSO_4 [3] as well as for RbH_2PO_4 [4]. We have used the same notations since 1993. The numbering is different in our first paper [1] as well as in many papers in the literature):

Case A: The transition on heating of RbH_2PO_4 from tetragonal to monoclinic structure at 352 K with the following thermal and volumetric characteristics [2, 5]:

RbH_2PO_4 (tetragonal; phase III) \rightarrow RbH_2PO_4 (monoclinic; phase II). $\Delta H = (4.17 \pm 0.1)$ kJ/mole; $\Delta V = 0.6$ cm³/mol.

Case B: The transition of CsHSO_4 at 333 K between two monoclinic phases with the following thermal and volumetric characteristics [1, 6]:

CsHSO_4 (phase III) \rightarrow CsHSO_4 (phase II). $\Delta H = (0.55 \pm 0.03)$ kJ/mole; $\Delta V = -0.66$ cm³/mole.

As mentioned above, the transition temperatures and enthalpies were determined by DSC [1, 2], and the ac-

companying volume changes by X-ray technique as well as by the pressure dependence of the transition temperatures [3, 7, 8].

The metastabilities of cases A and B [1, 2, 5], as well as of other examples not to be discussed here [2], can be removed by exposing the metastable crystals for a certain time to air with a suitable water activity a_w , which is the ratio of the given water vapour pressure to the saturated vapour pressure at the temperature in question. Thus, a_w varies between 0 and 1. As no solid hydrates are known for the salts considered, the only possibility for removing the metastability is the adsorption of water molecules on the surface of the salts. Among the different cases reported in the past, we limit ourselves here to the cases A and B mentioned above. They are the only cases that have been studied in some detail [5]. We think that other cases can be explained in a similar way.

The purpose of this communication is twofold: 1) We propose an explanation why water adsorption removes phase metastability in cases like A and B. 2) We take advantage of our previous investigation of cases A and B [5] to express a more detailed characteristic of the discussed removal of metastability.

Adsorption of Water Triggers Phase Transitions

It is characteristic for the cases A and B that the volume *decreases* during the endothermic phase transition from III to II. This means that one can expect steric hindrances for a reverse exothermic II–III transition, and it

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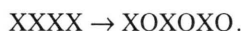
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was not possible to find any evidence for the latter transition by means of DSC during thermal cycles which started with $\text{CsHSO}_4(\text{III})$ near room temperature. In most of our experiments we went up to some 420 to 440 K, i.e. even beyond the II–I phase transition (416 K). After annealing, the waterless sample was cooled down to room temperature, and it was only the exothermal I–II transition that occurred. The metastable phase II was converted to $\text{CsHSO}_4(\text{III})$ at room temperature by isothermal exposure to water vapour, see above [1]. We also made experiments where the temperature span of the cycle was much smaller [9].

We have thus found that adsorbed water can weaken the steric hindrance for a II–III transition sufficiently to allow a very sluggish transition. Our x-ray studies of single crystals gave no indication that water molecules had penetrated into the bulk of solid CsHSO_4 [3]. Let us assume that adsorbed water molecules, represented by O, place themselves between the elements (X) of the initial (waterless) surface according to the simple scheme



Thus, the adsorption of water causes a local expansion of the surface, and consequently also of the subsurface lattice due to elastic interaction. Such a local expansion can initiate the II–III transition, which requires an expansion of the bulk. The adsorbed water molecules would act as “wedges” that facilitate the II–III transition. Our explanation is based on a simple “mechanical” aspect, which requires a surface reconstruction caused by the adsorbed water molecules. The action of water is clearly of a catalytic character. In other words, the water molecules initiate a reconstruction of the surface without being involved in the formation of three-dimensional hydrates or of saturated solutions. The water activity responsible for the II–III transition may be lower than the activity corresponding to a saturated salt solution at the same temperature. A simplified statement would be to claim that the formation of “surface hydrates” facilitates the removal of the bulk metastability of the considered salts.

A More Detailed Characteristic of the Removal of Metastability

Figure 1 of [5] concerns the kinetics of the exothermic II–III transition from monoclinic to tetragonal RbH_2PO_4 (i.e. the reverse reaction of case A) for three different activities at 293 K. The fraction of phase III present in a

sample was determined for several exposure times. First of all, the rate with which phase III is recovered is of zeroth order, at least up to when 80% of phase II has been transformed. This means that the transition front of the metastable \rightarrow stable phase proceeds linearly with time. Thus neither a retardation nor an acceleration can be detected. Such a kinetics proves that the direct neighbour of a transformed lattice layer is continuing the process with the same rate. Furthermore, an evident induction time (or inhibition time, both names are used frequently) is noticed for all three chosen water activities. This proves that a certain critical water activity is required at the surface in order to start the removal of metastability. The dependence of the induction time on the water activity is an interesting question. We have only used three different vapour pressures (9.95, 7.80 and 6.65 mmHg), corresponding to the water activities 0.57, 0.44 and 0.38 at 293 K. One can ask which quantitative dependencies between the two quantities are most adequate. It is shown in the above-mentioned Fig. 1 of [5] that an exponential dependence on the water activity is reasonable for the induction times as well as for the rate constants of the metastability removal:

$$\ln A = \alpha a_w + \ln A_0,$$

where A denotes either the induction time (t_{ind}) or the rate constant of the zeroth order kinetics of the metastability removal (rate $d\Delta H/dt$, a_w = water activity, $\alpha = a$ constant). The induction time decreases exponentially with the water activity. Contrary to this, the rate constant of metastability removal increases exponentially with the water activity. Such dependencies suggest a self-accelerating mechanism for both processes in the considered range of water activities. This is contrary to a probable cut-off region for much smaller water activities than those presented in our Fig. 1 and to an expected saturation effect for higher water activities.

A more detailed analysis would require an extension to both smaller and higher water activities than considered in the present investigation. It should be important to have a quantitative knowledge of what is characteristic for the adsorption of water on the crystal surface, as well as information whether the desorption of water after the induction period changes the kinetics of the process of metastability removal. The observed induction period suggests that a critical “adsorption complex” has to be formed before an effective removal of the metastability can start. This concept is in accordance with the existence of a cut-off region of the water activity at lower values, as expressed above.

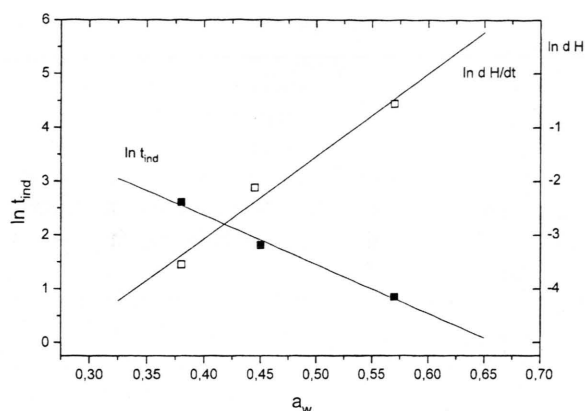


Fig. 1. Conversion of metastable monoclinic RbH_2PO_4 (phase II) to the tetragonal phase III under the influence of water vapour at 293 K [5]: t_{ind} = induction time, dH/dt = rate constant, a_w = water vapour activity, i.e. ratio of the actual water vapour pressure to the saturated water vapour pressure at the temperature in question.

Adsorption of water on the surface of the metastable phase II creates two-dimensional regions of the stable phase III. When this two-dimensional phase has reached a critical size and number density, phase III will start to expand into the three-dimensional bulk crystals. The process is like the initiation and propagation of an avalanche which proceeds into the previously metastable region with a constant velocity.

Our above discussion of the kinetics of an exothermic II–III phase transition has concerned case A where there is a change in phase symmetry of RbH_2PO_4 . Interesting conclusions can also be drawn from studies regarding case B, where there is only a slight difference between the structures of the two involved monoclinic CsHSO_4 lattices [9]. This fits well with the fact that the transition enthalpy is some seven or eight times higher in case A than in case B, while the volume decrease is about the same in the two cases.

CsHSO_4 should be suitable for studies whether the temperature of the endothermic III–II transition can be affected by various parameters. Figure 3 of [5] shows that there is a correlation between the transition temperature and the water vapour pressure at which the polycrystalline samples of CsHSO_4 (III) had been stored for a long time at 293 K. When we reduced the water vapour pressure from 13 to 6 mmHg (which means that the water activity decreased from 0.74 to 0.34), the transition temperature increased from 334 to 342 K. Thus, this study shows that the temperature of an endothermic phase transition can depend on the sample history;

which in our case means the conditions under which the metastable phase II had been stored. This observation is of great importance since it explains the divergency of transition temperatures reported in the literature for CsHSO_4 and other hydroacid salts [10–15].

The observed correlation between the transition temperature and the water vapour pressure can be approximated by three straight lines, see Fig. 3 of [5]. There is a plateau which means that the transition temperature remains constant (337 K) for water activities between 0.75 and 0.49. Furthermore, the slope of the straight line, dT/da_w , is the same on both sides of the plateau, being numerically equal to about 24 degree/ a_w . A low water activity at the surface of a metastable phase would mean that the “wedge effect” on the surface elements is small, while a higher water activity at the surface should mean a stronger “wedge effect”. One can expect that the temperature of the endothermic phase transition is slightly lower in the latter case, cf. our discussion above of the interaction between adsorbed water and the surface. The estimated gradient of about 24 degree/ a_w for the two sloping lines indicates a very high upper limit for how the transition temperature would change if the water activity is varied between 0 and 1. On the other hand, the existence of a plateau speaks against a large difference. The plateau indicates that at least two different phases of water molecules can be present on the surface of CsHSO_4 . It should not be overlooked that the reproducibility of experiments with CsHSO_4 is much lower than what is the case for studies of RbH_2PO_4 . The induction times are of the order of hours in the first case, thus much larger than for RbH_2PO_4 .

A network of hydrogen bonds is surely fundamental for the detailed mechanism of the phase transitions. Different configurations of these bonds are probably causing the observed variation of the transition temperatures. One can thus state that the transition between two monoclinic phases of CsHSO_4 does not occur at a well-defined temperature but in a temperature range, as shown in Fig. 3 of [5]. It would be an achievement to ascribe each transition temperature to a well-defined configuration of the involved hydrogen bonds. Are we already prepared to take up such a task? It would surely be of great importance to have a technique which could make it possible to characterize the structure of the surface layer of the phase II before and during the removal of metastability.

Could the adsorption of other compounds than water remove the discussed metastability in a similar effective way? One should look for acid or alkaline compounds which could have a strong influence on the hydrogen bond.

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