

Adsorption of Water as a Means to Remove Bulk Metastability of CsHSO₄ and RbH₂PO₄

Bogdan Baranowski*, Milan Friesel, and Arnold Lundén

Department of Physics, Chalmers University of Technology, Göteborg, Sweden

Z. Naturforsch. **42 a**, 565–571 (1987); received March 5, 1987

Differential scanning calorimetry (DSC) and thermogravimetry (TG) are applied to study the conditions required for CsHSO₄ and RbH₂PO₄ to undergo phase transitions at 333 ± 1 K and 352 ± 3 K, respectively. It is demonstrated that water adsorption on the surface of metastable polycrystalline samples triggers their transition to the stable state. It is further shown that the transition of CsHSO₄ only occurs if the water vapour pressure is sufficiently high. If the sample is prepared at 293 K this threshold is 6.3 ± 0.7 mm Hg. A correlation is found between the transition temperature and the water vapour pressure. While it has been reported recently that adsorbed molecules can cause phase transitions in the surface layer of a solid matrix, our results are the first well-established examples of a direct correlation between surface adsorption and bulk phenomena. There is a relation to an early idea of Schwab.

Introduction

Some phase transitions, most of them with rather small transition enthalpies, have been discovered recently in alkali metal (cesium or rubidium) hydrogen salts (sulphates, selenates, and phosphates) [1] in addition to previously known similar transitions in cesium hydrogen sulphate [2], rubidium hydrogen selenate [3, 4] and rubidium hydrogen phosphate [5, 6]. The impulse for our further searching into these new transitions came from the discovery of a surprisingly strong influence of the sample preparation technique on the phase transitions in cesium hydrogen sulphate [7], which cleared up a controversy in the literature concerning the latter salt [2, 8, 9].

Three main methods for the sample preparation have been investigated by us: 1) grinding, 2) applying one-dimensional (uniaxial) pressure, and 3) contact with water vapour of suitable pressure. The last treatment proved to be the most influential one. Similar observations are, to our knowledge, only found in one recent paper [10], while two other

recent papers [11, 12] give no reference to the importance of water activity. All of these papers [10–12] are dealing with phase transitions in CsHSO₄. In paper [10] the influence of water on the phase transition at about 333 K was reported in rather unclear and general terms. The authors are speaking of “moisture” on the samples, of “wet” samples, and of their “saturation” with water. They even claimed that solid CsHSO₄ “absorbs” water. In fact, they are using terms that do not have any well-defined physical meaning and which can be misleading. Thus, no solid hydrates of CsHSO₄ are known, and an attempt to “saturate” with water at ambient temperature would finally result in an aqueous solution. Hence, the only realistic process to be considered is the adsorption of water molecules on the surface of the investigated salt.

A quantitative way to investigate the influence of adsorbed water molecules is to maintain a known constant water vapour pressure above the solid samples at a chosen temperature. This procedure was used in our experiments.

There is a controversy between the papers [2] and [10]. The parameters given in the two papers coincide for the monoclinic phase of CsHSO₄ at room temperature (called phase III in [10]). But according to paper [2], no phase transition was observed during a determination of the heat capacity with an adiabatic calorimeter, which should have been the case according to results described in paper [10]. It

* Permanent address: Institute of Physical Chemistry, Polish Academy of Sciences, ul. Kasprzaka 44/52, PL-01-224 Warszawa, Poland.

Reprint requests to Prof. Dr. A. Lundén, Department of Physics, Chalmers University of Technology, S-412 96 Göteborg/Sweden.

0932-0784 / 87 / 0600-0565 \$ 01.30/0. – Please order a reprint rather than making your own copy.



Dieses Werk wurde im Jahr 2013 vom Verlag Zeitschrift für Naturforschung in Zusammenarbeit mit der Max-Planck-Gesellschaft zur Förderung der Wissenschaften e.V. digitalisiert und unter folgender Lizenz veröffentlicht: Creative Commons Namensnennung-Keine Bearbeitung 3.0 Deutschland Lizenz.

Zum 01.01.2015 ist eine Anpassung der Lizenzbedingungen (Entfall der Creative Commons Lizenzbedingung „Keine Bearbeitung“) beabsichtigt, um eine Nachnutzung auch im Rahmen zukünftiger wissenschaftlicher Nutzungsformen zu ermöglichen.

This work has been digitalized and published in 2013 by Verlag Zeitschrift für Naturforschung in cooperation with the Max Planck Society for the Advancement of Science under a Creative Commons Attribution-NoDerivs 3.0 Germany License.

On 01.01.2015 it is planned to change the License Conditions (the removal of the Creative Commons License condition “no derivative works”). This is to allow reuse in the area of future scientific usage.

is difficult to understand how the enthalpy change accompanying the transition around 333 K (III → II in terms of paper [10]) could be lost during a heat capacity measurement in an adiabatic calorimeter.

In the most recent paper [12] the thermal history of the CsHSO₄ material was taken to be responsible for the observed differences between differential scanning calorimetry (DSC) peaks. According to our opinion a considerable part of these differences was due to the uncontrolled amount of adsorbed water on the investigated samples.

The common feature of all of the transitions studied by us [1, 7] is that their characteristic DSC peaks are obtained only when a properly prepared sample is heated, while, during the subsequent cooling of the sample, the reverse transition cannot be recorded by DSC.

Based on these facts, the present investigation was undertaken in order to clear up two main points:

1) Either the recorded enthalpy change is due to the formation and decomposition of a surface hydrate, or the presence of adsorbed water triggers the phase transition in the bulk phase. In the latter case there should be no correlation between the measured enthalpy change and any simultaneous transition of water between the gas phase and the salt. This problem will be cleared up by studying one of the phase transitions of RbH₂PO₄.

2) We wanted to see if a sample that has been in contact with water vapour for a sufficient time undergoes a phase transition only if the water vapour pressure has been above a certain value. The existence of such a threshold could be expected from our observation concerning the 333 K phase transition of CsHSO₄ [7].

It has recently been demonstrated for metals that adsorbed foreign molecules can cause rearrangement of the surface molecules, i.e. two-dimensional first-order phase transitions are forced to occur [13–16]. Adsorption of hydrogen on single crystals of tungsten and nickel were found to be good examples. In our case the adsorption of water molecules could instead induce a three dimensional transition from the metastable to the stable state of a matrix with ionic (hydrogen) bonds. This could be treated as an example of a direct interaction between surface and bulk phenomena, similar to the assumption by Schwab and Schwab-Agallidis [17] that a heterogeneously catalysed gas reaction can in-

fluence the rate of a transition occurring in the solid catalyser; they were not able to find any evidence for this in their own experiments.

Experimental

As described previously [1, 7], polycrystalline CsHSO₄ and RbH₂PO₄ were prepared by crystallization from aqueous solutions. The crystals were crushed (without grinding), and the samples consisted of a loose rather coarse powder that was pre-treated thermally as described below.

RbH₂PO₄

The rôle of adsorbed water in the discussed phase transitions was tested for RbH₂PO₄ by following the changes of enthalpy and weight that accompany the phase transitions. The transition temperatures and enthalpies were determined with a commercial Rigaku (Japan) DSC device. The weight changes were recorded in separate runs with a Perkin-Elmer TG-2 analyzer. Since it was not possible to carry out the DSC and thermogravimetry (TG) simultaneously, each sample was divided into two parts, one for the DSC and the other for the TG.

A conventional x-ray powder diffractometer (Philips) was used to check the nature of the 352 K phase transition in RbH₂PO₄. Thus, x-ray patterns taken at ambient temperature confirmed that the structure of a fresh sample was tetragonal, while it was monoclinic for a sample that had been subject to a thermal treatment (373 K for 5 minutes); the first x-ray pattern was taken at atmospheric pressure, but the second one at 10⁻² torr to avoid any uptake of moisture. The sample was then kept at ambient temperature in contact for 30 minutes with water vapour of a pressure of 13.65 mm Hg, and the result was that the x-ray pattern (taken at atmospheric pressure) had been transferred back to the original one. Thus, the salt was obtained in the tetragonal phase after preparation by crystallization from aqueous solutions as well as after contact for some time with water vapour of sufficiently high pressure, while cooling of an annealed sample leaves the salt in the monoclinic phase which is metastable at ambient temperature.

CsHSO₄

The search for a threshold water vapour pressure was performed in the following way. Crushed crystals of CsHSO₄ were placed in open aluminium capsules of the type used for the DSC runs, and they were heated for 1 to 4 hours in air at about 420 K. When cycled thermally, these samples showed neither the 375 K nor the 333 K transition [7]. Such "transition empty" samples were kept in open glass containers surrounded by the free surface of an aqueous sulphuric acid solution within a closed, thermostated volume (a small desiccator). We chose 293 K as constant temperature in a well-stirred liquid thermoset with a constancy better than 0.1 K. For a chosen concentration of sulphuric acid a well-defined activity of water vapour could be maintained for an arbitrary time above the investigated samples. The volume of the gas phase above the sulphuric acid was sufficiently small to ensure a rapid establishment of equilibrium between the liquid and gas phases, and also a negligible change of the concentration of the sulphuric acid due to repeated exchange of the samples. The time of contact with the constant water activity varied between 1 hour and 1 month. Long durations were necessary especially when the activity threshold was approached, because very often the DSC gave no transition peak if the exposure time had been too short. This behaviour suggests the existence of a long induction period, probably because the creation of the nuclei of the new phase is sluggish when the water activity is close to the lower limit of what is required for the nucleation. After each DSC heating run the sample was annealed again for some hours at 420 K in air.

In order to determine the threshold water activity as accurately as possible 6 different samples were treated under similar conditions, applying sequences of either increasing or decreasing water activities in approaching the threshold. Especially in the vicinity of the threshold the reproducibility of the experiments was strongly dependent on details of the experimental procedure. Thus, much larger deviations (concerning the appearance of the 333 K transition) between adjacent experiments were obtained if we contented ourselves with bringing the sample in contact again with water vapour directly after a DSC run instead of performing the annealing at 420 K.

Results and discussion

RbH₂PO₄

Figure 1 shows how the pretreatment with water at ambient temperature affects the possibility of a sample of RbH₂PO₄ to undergo a structural (tetragonal → monoclinic) phase transition at about 352 K. The measured enthalpy of the incomplete transition of the sample depends both on the pressure of the water vapour and the duration of the contact with this water vapour. The ratio of the measured enthalpy change to its maximal value (4.17 ± 0.10 kJ/mol) can be assumed to be equal to the monoclinic phase that, due to the pretreatment, was transformed to the tetragonal phase. For the two low water vapour pressures (6.65 and 7.80 mm Hg) there is evidently an induction period, that is, a transition can only be noticed if the sample had been exposed for a certain time to the water vapour. This induction period is clearly shortened when going over to higher water activities. Such induction periods are well-known for certain solid-solid transitions. All the experimental points presented in Fig. 1 were measured for the same polycrystalline sample, i.e. the grain size distribution and the total surface area were approximately the same during the whole series of measurements. The DSC measurement was always done as quickly as possible after the exposure to water vapour, which means that only phase transitions occurring during the exposure time are registered in the experiment. After each DSC measurement of the enthalpy change of the 352 K transition, the sample was heated a second time to about 368 K, and it was checked that it had become "transition empty" again.

The main uncertainty concerning the observed phase transitions [1, 7] was whether they were due to the formation and decomposition of surface hydrates, i.e. if there is a correlation between the uptake of water during the pretreatment and the recorded enthalpy changes, or not. The two possibilities are:

A) The adsorbed water molecules are very strongly bound to the surface, and they are released during the phase transition, thus being entirely or partly responsible for the recorded endothermic enthalpy change. In the extreme case the total transition enthalpy would be caused by the decomposition of a surface hydrate.

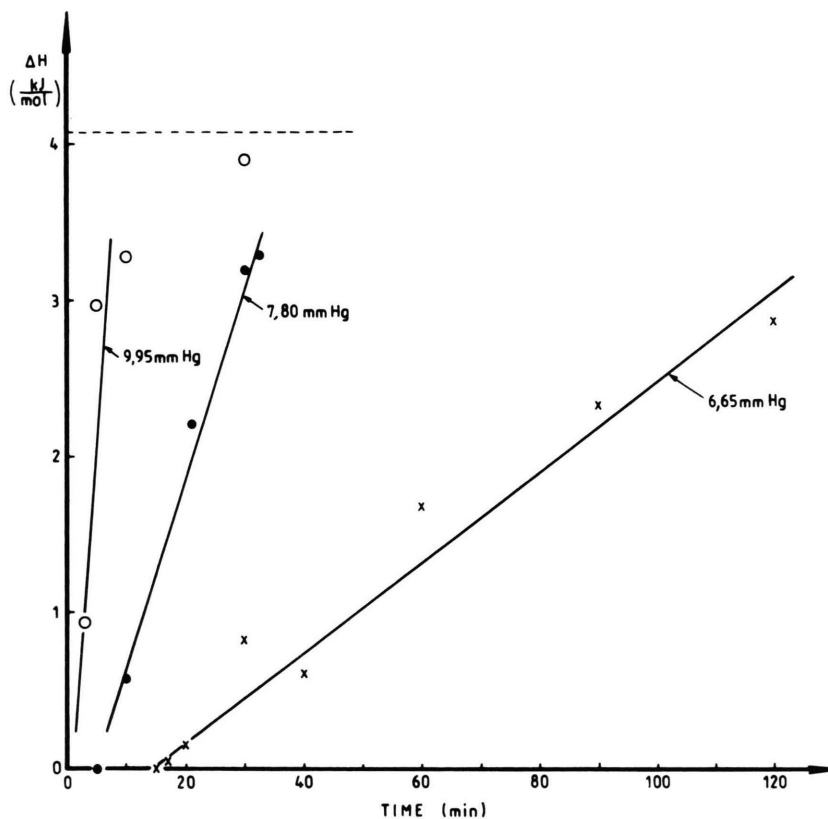
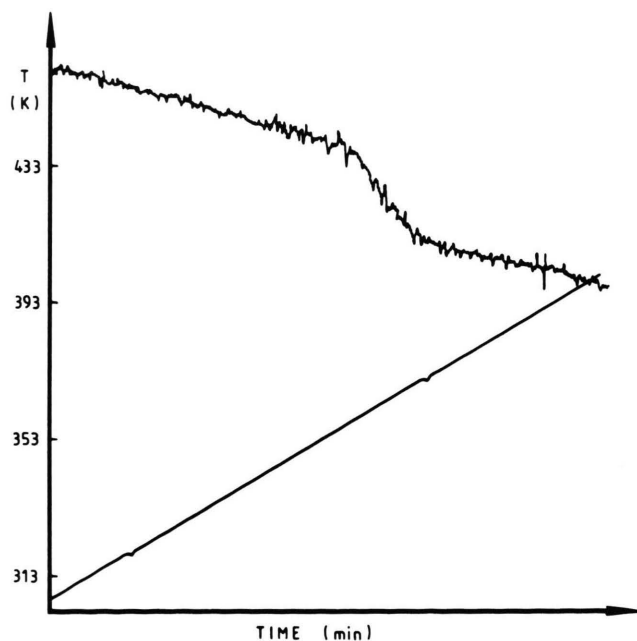


Fig. 1. Correlation for the 352 K phase transition of RbH_2PO_4 between the measured transition enthalpies and the time for which the (previously annealed) sample had been in contact at 293 K with water vapour of a pressure of 6.65 (x), 7.80 (●) or 9.95 (○) mm Hg, respectively.



B) The adsorbed water acts only as a catalyst, i.e. it triggers the phase transition in the bulk but does not contribute to the observed enthalpy change.

In order to distinguish between these two alternatives a parallel study of the weight changes during the phase transition was performed by means of TG. An example of such an analysis is shown in Figure 2. The weight of the sample of RbH_2PO_4 , 34.1 mg, remained constant up to about 359 K, i.e. well above the accepted transition temperature

Fig. 2. Thermogravimetric (TG) diagram for a RbH_2PO_4 sample that had been exposed for 5 minutes to a water vapour pressure of 13.65 mm Hg at 293 K. The time course of the sample weight is shown by the scattered line, and that of the temperature by the smooth straight line. (The bumps in the latter line are instrumental.) The sample weight remains constant up to 359 K, which is the starting point of a weight loss of 0.007%, while the transition temperature obtained by DSC is 348 K (Transition enthalpy: 4.24 kJ/mole.) The initial and final slopes of the weight curve are thus due to instrumental drift.

352 K and the transition temperature of 348 K that had been recorded by DSC for another part of this sample. Over a range of some 11 K a weight decrease of 0.0023 mg was detected, corresponding to a change of about 0.007% for this particular sample. Some 16 samples were studied by TG, and no weight change at all could be detected for a few of them, while the largest observed change was of the order of 0.02%.

There are two reasons why the results of the TG experiment eliminate our alternative A. 1) If detectable at all, the weight decrease, which hardly can have any other cause than the release of water, does not occur until about 10 degrees above the temperature of the recorded DSC peak. Thus, water molecules are not released until after the phase transition is completed. 2) Let us assume that the released water is directly responsible for the observed enthalpy change. Since the mole fraction of water in the sample is of the order of 0.0007 (for the sample considered in Fig. 2) the transition enthalpy of 4.24 kJ/mol found for this particular sample, would correspond to 6060 kJ per mole of water, which is about 130 times the molar enthalpy of sublimation of pure water, and it is not realistic to expect such a strong binding of the water to the salt.

To our opinion reasons 1) and 2) exclude even a partial involvement of water in the recorded enthalpy changes. Thus, we have here a case where a surface phase of adsorbed foreign molecules triggers a transition from a metastable to a stable phase of the crystal. In contrary to this, the recently observed changes of a metallic matrix by adsorbed hydrogen or carbon monoxide [14–16] are limited to the surface and (at least to some extent also) to the sub-surface layer. Thus, in our case we deal with a kinetic effect, but it obviously requires a reconstruction of the surface layer of the salt before the propagation into the bulk phase can take place. In this aspect our results are directly related to the phenomena found for metal-gas systems [14–16].

The fact that no weight loss could be detected by TG for some of our samples does not exclude that minute amounts of adsorbed water were given off also from these samples. If the salt surface becomes “completely waterfree” (or the water content is reduced below some critical limit) this might explain why the reverse transition neither is detected during a subsequent cooling of the sample nor occurs when the sample is reheated. In a certain sense our results

confirm the above-mentioned early idea of Schwab and Schwab-Agallidis [17], which they, however, were unable to find in their own experiments.

An influence of adsorbed lecithin molecules on phase transitions in liquid crystals has been observed previously [18], and it may be treated as a phenomenon related to our results.

CsHSO₄

The question whether the water vapour pressure must exceed a threshold to become active was carefully investigated for the case of the 333 K phase transition of CsHSO₄. When the samples, pretreated as described, were heated they showed the 333 K transition only if the sulphuric acid had contained at most 51 ± 2 weight percent of H₂SO₄, which corresponds to an absolute threshold water pressure of 6.3 ± 0.7 mm Hg at 293 K. The transition peak could be observed if the water vapour pressure had exceeded the threshold by 0.5, or sometimes even by 0.3 mm Hg. It is quite probable that the range could be made still narrower by applying a more careful procedure, but one has on the other hand to remember that the numerical values given above for the upper and lower threshold limits are strongly sample dependent, and furthermore, for a certain sample they might even depend on its history. Thus, one should not consider the determined values as real material constants. As the saturation pressure of water vapour is 17.4 mm Hg at 293 K, the threshold corresponds to a relative humidity of about 36%.

As already stated, the determination of the threshold was a tedious and time consuming procedure, and as an unexpected result it is found that there exists a correlation between the transition temperature obtained by DSC and the water vapour pressure under which the sample had been stored, see Figure 3. Since six different samples were used in the determination of the threshold, the scatter in Fig. 3 is at least partly due to differences in the history of these six samples; the most important factor being the sequences of increasing or decreasing water activities chosen in the tests.

The remarkable feature of the curve shown in Fig. 3 is a quasi-plateau. The transition takes place at about 337 K for samples that have been treated with water vapour activities between 8.5 and 11.5 mm Hg. On both sides of this range the transition temperature increases with decreasing water

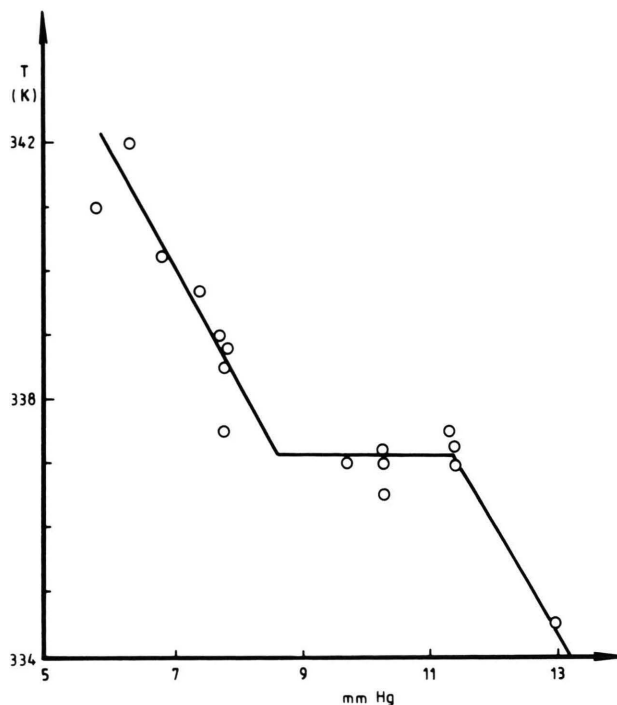


Fig. 3. Transition temperature recorded by DSC as a function of the water vapour pressure at which the polycrystalline samples of CsHSO_4 were kept for a long time (hours to weeks) at 293 K. Six different samples were used when obtaining this curve.

activity. The shape of Fig. 3 suggests that there exist two different types of phase transitions, and that their occurrence depends on the activity of the water vapour.

Conclusion

Both from the thermogravimetric investigation of RbH_2PO_4 and the threshold study of CsHSO_4 the conclusion is clear that water molecules that are adsorbed on the surface of hydrogen salts can trigger phase transitions in a catalytic way. This initiation of a phase transition requires that the concentration of water molecules on the surface exceeds a lower limit, as was clearly manifested by the existence of a threshold value for the water vapour activity. Furthermore, the concentration of adsorbed water affects the transition temperature. This might be due to the existence of different states for the adsorbed water molecules, corresponding to either continuous or discontinuous phase transitions in the

surface layer, also including order-disorder transitions [19, 20]. If such different states occur in the two-dimensional layers of water adsorbed on the salt surface, it is quite likely that there will be a direct influence on the kind of metastability removal that will occur. This means that the structure of the surface phase can directly determine the temperature at which the bulk undergoes a phase transition. This is probably due to the possibility that the two-dimensional phase can induce different types of ordered states in the three-dimensional phase.

The involvement of hydrogen bonds seems obvious for the investigated phase transitions. In all of the considered hydrogen salts a disordered hydrogen bond has been found to be located in one-dimensional chains [21–23]. This disordered hydrogen bond can probably be partly ordered at the surface under the influence of adjacent layers of adsorbed water molecules. This ordering process can later propagate into the bulk phase, thus removing the metastable state of a “transition empty” sample. The partial change of order in the hydrogen bond may in consequence influence the orientation of the XO_4 ($\text{X} = \text{S}, \text{Se}, \text{P}$) groups. In this way the discussed phase transitions might be considered as combined order-disorder processes of coupled hydrogen bonds and anion groups, triggered by the adsorbed water molecules in the direction of restoring the ordered states. In other words – the process of disordering (which probably is of orientational character) proceeds rapidly enough to be easily detectable by the DSC technique, while the reverse process either is so sluggish that it never is observed by DSC, or it might in fact need a catalytic intervention in order to occur at all.

The conclusions from the present study might have some importance also for other types of materials with hydrogen bonds, and effects of surface layers of water might also exist e.g. in biological systems.

Acknowledgements

This investigation is supported financially by the Swedish Natural Science Research Council and by Anna Ahrenbergs Fond. We are indebted to the Polymer Group of this university for placing the instrument for thermogravimetry at our disposal, and to Ingvar Albinsson and Per-Arne Svantesson for performing the x-ray powder diffraction study.

- [1] B. Baranowski, M. Friesel, and A. Lundén, *Z. Naturforsch.* **41 a**, 981 (1986).
- [2] M. Komukae, T. Osaka, Y. Makita, T. Ozaki, K. Itoh, and E. Nakamura: *J. Phys. Soc. Japan* **50**, 3187 (1981).
- [3] R. Poprawski, J. Mróz, Z. Czapla, and L. Sobczyk, *Acta Phys. Polon.* **A55**, 641 (1979).
- [4] Z. Czapla, T. Lis, L. Sobczyk, A. Waškowska, J. Mróz, and R. Poprawski, *Ferroelectrics* **26**, 771 (1980).
- [5] R. Blinc, D. E. O'Reilly, E. M. Peterson, and J. M. Williams, *J. Chem. Phys.* **50**, 5408 (1969).
- [6] J. Grünberg, S. Lewin, I. Pelah, and D. Gerlich, *phys. stat. sol. (b)* **49**, 857 (1972).
- [7] B. Baranowski, M. Friesel, and A. Lundén, *Z. Naturforsch.* **41 a**, 733 (1986).
- [8] E. G. Ponyatovskii, V. I. Rashchupkin, V. V. Sinitsyn, A. I. Baranov, L. A. Shuvalov, and N. M. Shchagina, *Pis'ma Zh. Eksp. Teor. Fiz.* **41**, 114 (1985).
- [9] A. I. Baranov, L. A. Shuvalov, and N. M. Shchagina, *Pis'ma Zh. Eksp. Teor. Fiz.* **36**, 381 (1982).
- [10] A. M. Balagurov, A. V. Belushkin, I. D. Dutt, I. Natkaniec, N. M. Plakida, B. N. Savenko, L. A. Shuvalov, and J. Wasicki, *Ferroelectrics* **63**, 59 (1985).
- [11] M. Pham-Thi, Ph. Colomban, A. Novak, and R. Blinc, *Solid State Comm.* **55**, 265 (1985).
- [12] Ph. Colomban, M. Pham-Thi, and A. Novak, *Solid State Ionics* **20**, 125 (1986).
- [13] K. H. Lou and S. C. Ying, *Phys. Rev. Lett.* **44**, 1222 (1980).
- [14] K. Müller, *Ber. Bunsenges. Phys. Chem.* **90**, 184 (1986).
- [15] G. Ertl, *Ber. Bunsenges. Phys. Chem.* **90**, 284 (1986).
- [16] F. S. Rys and H. E. Müser, *Ber. Bunsenges. Phys. Chem.* **90**, 291 (1986).
- [17] G. M. Schwab and E. Schwab-Agallidis, *Svensk Kem. Tidskr.* **58**, 161 (1946).
- [18] M. Brehm, H. Finkelmann, and H. Stegemeyer, *Ber. Bunsenges. Phys. Chem.* **78**, 883 (1974).
- [19] R. Lipowsky, *Phys. Rev. Lett.* **49**, 1575 (1982).
- [20] S. J. Kennedy and J. S. Walker, *Phys. Rev.* **B30**, 1498 (1984).
- [21] Y. Iwata, N. Koyano, and I. Shibuya, *J. Phys. Soc. Japan* **49**, 304 (1980).
- [22] H. Matsunaga, K. Itoh, and E. Nakamura, *J. Phys. Soc. Japan* **48**, 2011 (1980).
- [23] K. Itoh, P. Ozaki, and E. Nakamura, *Acta Cryst.* **B37**, 1908 (1981).