

CALORIMETRIC STUDY ON PHASE TRANSITION OF LANTHANUM PERCHLORATE OCTAHYDRATE\*

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ABSTRACT

Heat capacities of lanthanum perchlorate octahydrate  $\text{La}(\text{ClO}_4)_3 \cdot 8\text{H}_2\text{O}$  have been measured from 11 to 320 K by an adiabatic calorimeter. Two phase transitions were observed at 115.5 K and 285.2 K, respectively. The enthalpy and entropy of the upper phase transition amounted to  $17.97 \text{ kJ mol}^{-1}$  and  $62.98 \text{ JK}^{-1}\text{mol}^{-1}$ . Anomalously large entropy change can be interpreted by a statistical model including a combined positional and orientational disorder of the hydrate water molecules, in accord with an unusually high crystal symmetry of the room temperature phase.

INTRODUCTION

The crystal structure of the room temperature phase of lanthanum perchlorate hexahydrate was determined by the X-ray diffraction method (1). It belongs to the isometric system (space group  $\text{Fm}\bar{3}\text{m}$ ) and crystallizes in the ideal anti-cryolite structure. This is in sharp contrast to a great number of other hydrate crystals studied so far, most of which belong to the low symmetry systems, e.g. monoclinic or triclinic system. One suspects that the high symmetry of the crystal is due to disorder of the water molecules coordinated to  $\text{La}^{3+}$ . However, even though water molecules do exist in disordered state in a few hydrate crystals (2) and notably in the ice itself (3), the extent of the disorder inferred from the crystal structures and evaluated from the entropy is rather small and never so great as to produce an orientationally disordered cubic phase. In view of the unusual high symmetry of the crystal, we measured its heat capacity from 11 to 320 K.

EXPERIMENTAL

The sample was prepared by dissolving  $\text{La}_2\text{O}_3$  in the ten percent excess of the equivalent amount of 60 % perchloric acid. The solution was evaporated slowly in a vacuum desiccator over  $\text{P}_2\text{O}_5$ . The crystal so obtained was purified by recrystallization from an aqueous solution in the same way. The crystal with thickness of about 15 mm was obtained. They were stored in a desiccator together with partially dehydrated crystals to remove excess water. Chemical

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analysis leaving the hydration number as the only unknown gave 8.38 water molecules per  $\text{La}^{3+}$ . The same quantity reported so far ranges between 5.4 and 9 (1)(4)(5). The rapid deliquescence of the substance may explain part of the large variation of the stoichiometry.

The heat capacity measurement was performed in a double-jacketed adiabatic calorimeter described elsewhere (6). The sample appropriately crushed in He gas atmosphere was sealed in a Mylar bag and put in a calorimeter cell together with 1 atm He gas as the heat exchanger. The calorimeter cell was made of gold-plated Cu and had an internal volume of  $8 \text{ cm}^3$ . The sample mass was 8.4312 g in vacuo. The temperature increment of one measurement was 0.7 to 2.5 K except in the temperature range near the heat capacity anomaly. In the first series of measurement anomalies were found at 244.7, 277.0 and 285.2 K. The first two anomalies disappeared in the second series of measurement after the excess water was carefully removed by evacuation. The sample mass used at the second measurement was 8.3321 g in vacuo. In addition to the phase change at 285.2 K, a first order phase transition occurred at 115.5 K. This phase transition was liable to undercool. It developed fully only after annealing at 90-100 K.

## RESULTS AND DISCUSSION

Figure 1 shows the molar heat capacity of lanthanum perchlorate octahydrate

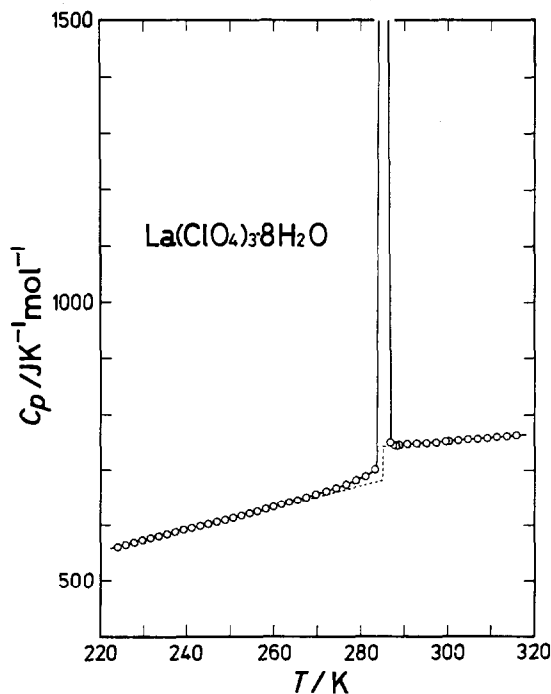


Fig. 1 Heat capacity of  $\text{La}(\text{ClO}_4)_3 \cdot 8\text{H}_2\text{O}$  around the upper phase transition.

in the temperature range 220-320 K. The strong first-order phase transition at  $285.2 \pm 0.1$  K occurred practically isothermally without any precursory effect (see also Fig. 2). The heat capacity above the transition temperature is appreciably larger than below. The difference  $\Delta C_p$  amounts to  $60 \text{ JK}^{-1}\text{mol}^{-1}$  (8.4 %). This large  $\Delta C_p$  causes some difficulty in estimating the normal heat capacity in the transition region. A step function was assumed for it as is shown by dotted line in Fig. 1. The enthalpy of transition based on this normal heat capacity was determined by the following method. The enthalpy increases due to the normal heat capacity and the heat capacity of the cell were subtracted from the total energy supplied between an initial temperature below the transition and a final temperature above, and the correction for the heat leak was made. Then multiplication by an appropriate molar factor gave the enthalpy of transition. The enthalpy and the entropy of transition obtained were  $17.967 \text{ kJ mol}^{-1}$  and  $62.98 \text{ JK}^{-1}\text{mol}^{-1}$ , respectively. These values were obtained from the measurement in which the transition was traversed in several steps of heat input. The enthalpy of transition obtained from a total heat measurement in which the transition was traversed in one step was  $17.962 \text{ kJ mol}^{-1}$ . The entropy of the transition at 115.5 K was  $5.51 \text{ JK}^{-1}\text{mol}^{-1}$ .

The anti-cryolite structure determined by Glaser and Johansson is that of the hexahydrate, while the sample we studied was the octahydrate. Therefore we can not expect exact correspondence between the structural and calorimetric data. Nevertheless, we will discuss the entropy change on the basis of the cubic disordered structure because it is large enough to warrant this.

The coordination of eight ligands occurs in square antiprisms, dodecahedra or bicapped trigonal prisms(7). But no example of these occurring in an isometric crystal is known. If we assume, in spite of this, all the eight water molecules to be coordinated to  $\text{La}^{3+}$  and equivalent with each other, then one water molecule has 2.59 different orientations [ $R \ln (2.59)^8 = 62.98 \text{ JK}^{-1}\text{mol}^{-1}$ ]. Here, we

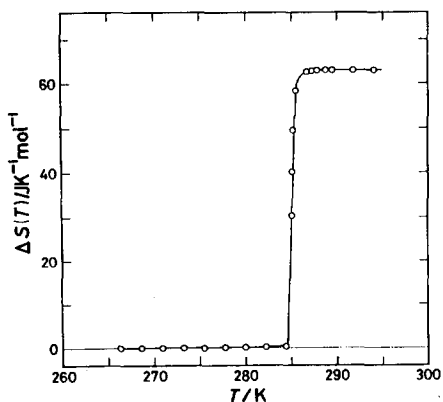


Fig. 2 Entropy change associated with the phase transition at 285.2 K.

ascribed the entropy of the transition at 115.5 K to the orientational disorder of one (4b in the Wykoff notation) of the three perchlorate ions in the anti-cryolite structure because its value is very close to  $R \ln 2 = 5.76 \text{ JK}^{-1} \text{ mol}^{-1}$ . The other two perchlorate ions are in the tetrahedral site and thus ordered.

Another model is to place six water molecules on the 4-fold axes of the unit cell following Glaser and Johansson, and allow each of them two possible orientations as the site symmetry requires. Of the total entropy change  $62.98 \text{ JK}^{-1} \text{ mol}^{-1}$ ,  $34.58 \text{ JK}^{-1} \text{ mol}^{-1}$  is explained by the disorder of the six water molecules. The remaining part of the entropy is ascribed to the two water molecules. Suppose there are 8 positions available to the water molecules. Then the entropy will be  $R \ln (8!/2!6!) = 27.70 \text{ JK}^{-1} \text{ mol}^{-1}$ . This is very close to  $62.98 - 34.58 = 28.40 \text{ JK}^{-1} \text{ mol}^{-1}$ . In fact such a spatially disordered water molecules are known to exist in  $\text{KTI} \text{Br}_4 \cdot 2\text{H}_2\text{O}$  (8)(9). If the spatial disorder of the proposed kind occurs in  $\text{La}(\text{ClO}_4)_3 \cdot 8\text{H}_2\text{O}$ , the molecular distribution should be smeared out and may not be found by the structural study.

In proteins, lipid bilayers and other biological substances, water molecules are important building blocks because of their ability to form hydrogen bonding on one hand and to be disordered in a liquidlike state on the other. In the ordinary hydrate crystals they usually form rigid lattices with little tendency to disorder. The water molecules in  $\text{La}(\text{ClO}_4)_3 \cdot 8\text{H}_2\text{O}$  are in an intermediate state between the liquidlike and the rigid crystalline states as the present entropy data show and may bridge the two extreme cases.

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