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Dedicated to Professor Bernhard Wunderlich on the occasion of his 65th birthday

THE ROLE OF THE ICE RULES IN THE THERMAL PROPERTIES OF POTASSIUM DIHYDROGEN PHOSPHATE*

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Abstract

Calorimetric properties of potassium dihydrogen phosphate are examined by analysis of the heat capacity data taken from the literature and from a recent measurement. The analysis is based on an extensive use of harmonic heat capacity functions to separate the effect of the phase transition from the vibrational contribution. The transition enthalpy and entropy derived are 421 J mol^{-1} and 3.79 J K^{-1} mol^{-1}, respectively. Characteristic temperatures of the lattice vibrations including the Debye temperature (254±18) K were determined. The transition entropy, exceeding the value compatible with the ice-rules, is consistent with the temperature dependence of the heat capacity. The implication of the result is discussed by comparison with the hydrogen bond networks in copper formate tetrahydrate and thallium dihydrogen phosphate.

Keywords: ferroelectricity, hydrogen bond, ice rules, potassium dihydrogen phosphate, transition entropy

Introduction

Potassium dihydrogen phosphate KDP is one of the earliest crystals identified as a ferroelectric [1]. It has been extensively studied experimentally and theoretically. There are still unsolved problems concerning the ferroelectricity and ferroelectric transition of this substance, even though practically every newly-available experimental method has been employed to examine its properties. Among the experimental techniques employed are calorimetry, X-ray

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diffraction, dielectric permittivity and polarization measurement, IR and Raman spectroscopies, nuclear magnetic resonance and neutron diffraction and scattering. Usually one experimental method focuses on one aspect of the properties of the substance. Consequently, a model conceived to explain one experimental observation may be inadequate when examined from other points of view. The difficulty may be serious or easily explained away.

The transition entropy is one of the less frequently quoted experimental quantities though it is an important property that connects structural and energetic aspects of the phase transition. An accurately evaluated transition entropy can be a significant test of models for the phase transition.

Stephenson and Hooley [2] measured the heat capacity of KDP between 13 and 300 K in a series of calorimetric studies on hydrogen bonded crystals. A conclusion they arrived at was that the transition entropy is about 3 J K^{-1} mol^{-1}. This is significant because the experimental transition entropy is much smaller than the largest possible value $2R\ln 2=11.6$ J K^{-1} mol^{-1} predicted by statistical independence of all of the hydrogen bonds in the crystal. Slater [3] proposed a model of the phase transition taking into account the short range correlation between the hydrogen bonds. He assumed that the four hydrogen bonds of a phosphate ion are correlated in such a way that just two of them have the hydrogen atom close to the phosphate ion. In this model the phosphate ions are always $(H_2PO_4)^-$ in the disordered high temperature phase and, a fortiori, in the low temperature phase as well. This correlation restricts the number of the allowed configurations of the hydrogen bonded system. He showed that the number of allowed configurations at $T\to\infty$ is equal to $w=(3/2)^N$ where N is the number of the phosphate ions. This calculation is the same as that used by Pauling [4] in the explanation of the residual entropy of ice Ih [5, 6]. It assumes that (1) a hydrogen bond provides a double minimum potential for a proton, (2) a hydrogen bond is occupied by one and only one proton, (3) a phosphate ion is engaged in four hydrogen bonds and (4) two of the four protons on the four hydrogen bonds extending from a phosphate ion lie in the closer and the other two in the farther of the minima. The ice-rules calculation was extended by Nagle [7] who found that the higher order terms contribute only a small correction term: $1.504^N < W < 1.506^N$. The transition entropy of the Slater model is equal to $(R\ln 2)/2=2.88$ J K^{-1} mol^{-1}. The experimental value 2.9–3.1 J K^{-1} mol^{-1} of Stephenson and Hooley is closer to this rather than $R\ln(3/2)=3.37$ J K^{-1} mol^{-1} expected at $T\to\infty$ though the difference is small. The model was generalized by Takagi [8] to include ionized phosphate ions.

Although the calorimetric data give support to the Slater model, its significance to the mechanism of the phase transition has not been appreciated in more recent work. There may be two reasons for this. First, the ice-rules correlation is difficult to incorporate in the interpretation of spectroscopic experiments with which the majority of recent experimental work is concerned. Most of the spectroscopic experiments have been explained as a dynamic response of a single hydrogen atom embedded in the environment of phosphate and potassium ions. Second, the experimental value of the transition entropy was determined on an assumption about the value of the vibrational heat capacity. The assumption appears rather arbitrary, being simply a linear interpolation of the high and low temperature heat capacities into the transition region [2]. Since the excess part is a small fraction of the total heat capacity in the pre-transition region, a small change in the assumed interpolation results in a significant variation of the entropy of transition.

In the present paper, we report a new measurement of the heat capacity in the transition region. Stephenson and Hooley's data were reproduced well. We show that an estimation of the vibrational heat capacity based on least squares adjustment of the vibrational characteristic temperatures gives a different transition entropy from the original value. The calculation of the vibrational heat capacity involves extensive use of the heat capacity function for harmonic oscillators and is closely related to the work of Professor Wunderlich [9] in polymer physics.

Experiment and result

A sample of KDP was prepared by recrystallization from an aqueous solution. The sample mass was 34.1950 g. It was sealed in a gold plated copper sample cell of an adiabatic calorimeter [10]. The heat capacity was measured in the normal intermittent heating mode in the temperature range between 80 K

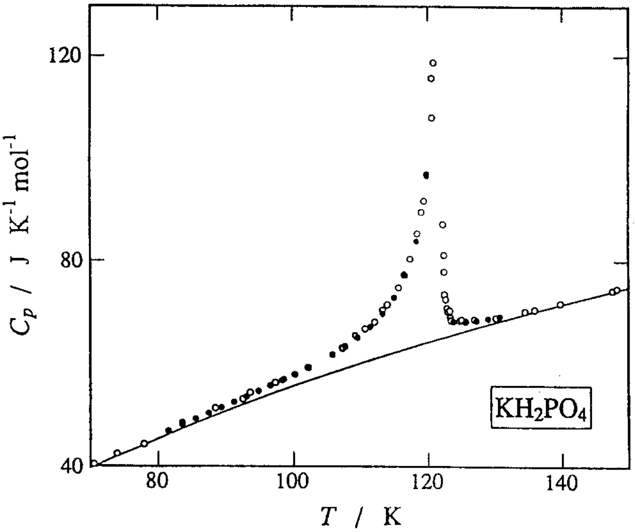

Fig. 1 The molar heat capacity of potassium dihydrogen phosphate. Open circles: from [2]. Closed circles: the present data. The curve represents the best-fit vibrational heat capacity

and 130 K. The temperature increment for a single heat capacity determination was 1 to 2 K. The inaccuracy of the measurement was estimated to be ±0.2%. The results are plotted in Fig. 1 along with Stephenson and Hooley's data. Agreement between the two sets of data is excellent.

Discussion

The vibrational heat capacity

At temperatures far away from the transition point, the experimental heat capacity contains solely the vibrational contribution. As the transition temperature is approached from below, the heat capacity increases gradually as a result of gradual disordering. At the transition temperature, the experimental heat capacity contains the latent heat of transition. Consequently, the apparent heat capacity increases to a large value that depends on the temperature increment employed for that particular datum point. However, the entire transition enthalpy and entropy are independent of the temperature steps taken in different series of measurements. The same applies for experimental data by different authors. Therefore different sets of data are best compared in terms of the temperature dependence of the enthalpy and entropy.

The experimental heat capacity contains contributions from the vibrational and transitional parts. We assume that they are separable from each other. We assume further that the vibrational degrees of freedom are represented as a collection of harmonic oscillators with a small correction for the difference between C_p and C_V. Thus the C_p(base) is given the following form:

$$C_p(\text{base}) = C(\text{Deb}) + C(\text{Ein}, 1) + C(\text{Ein}, 2) + a(C_V)^2 T \tag{1}$$

Table 1 Characteristic temperatures used for the calculation of the vibrational heat capacity from spectroscopy [11, 12] and the heat capacity (present data)

	Internal vibrations of PO_4^{-3} (from vibrational spectroscopy)	
Weight	Characteristic temp./K	
1	1318	ν_1
2	509, 529	ν_2
3	1463	ν_3
3	689, 768	ν_4
	Lattice vibrations (from heat capacity)	
3	254±18	Debye
3	129±5	Einstein
3	310±19	Einstein
6	1508±200	Einstein
	($A = (6\pm8)E\text{-}7\ J^{-1}$ mol, cf. Eq. (2))	

In this equation the first term represents the Debye part of the heat capacity and the second an Einstein part. These parts involve unknown characteristic temperatures. The third term contains all the spectroscopically accessible vibrational degrees of freedom. The last term represents the C_p–C_V correction. The unknown characteristic temperatures were determined by least squares fitting of C_p(base) to the experimental values outside the transition region. Normal mode frequencies from vibrational spectroscopy were used in the calculation of C(Ein, 2). They are summarized in Table 1. In the crystal, the degenerate modes split because of the lower site symmetries than the symmetry of the free phosphate ion.

In the fitted part, the Debye term C(Deb) contains three degrees of freedom and the Einstein term C(Ein,1) twelve. The latter are expressed by three Einstein functions of 3, 3 and 6 degrees of freedom. The Debye term represents the acoustic branch of the lattice vibration. The first two Einstein terms both with a weight of 3 are meant to account for the optical branches of the translational origin involving the motion of potassium ions and those of the rotational origin involving the phosphate ions. The last Einstein term (with a weight of 6) represents the motion of the hydrogen atom. The numbers of degrees of freedom contained in these terms sum up to 24, three times the number of atoms in a chemical unit.

The experimental heat capacities between 13 and 60 K and those between 200 and 300 K were employed for the fitting. The result of the fitting are given in Table 1. The base-line heat capacities calculated using the best fit parameter values are plotted in Fig. 1. The Debye temperature and two low Einstein temperatures are of reasonable values for lattice vibrations of an ionic and hydrogen bonded crystals. The highest Einstein temperature (1508 ± 200 K $=1048\pm140$ $\text{cm}^{-1}=$ 130 ± 18 meV) has counterparts in the neutron spectrum at 125, 160 and 160 meV [13]. In view of the large incoherent cross section of a proton against a neutron, these are the hydrogen vibrations parallel and perpendicular to the O–O vector connecting adjacent phosphate groups. It is to be noted that the short hydrogen bond happens to have the three vibrations (along the x, y and z directions) at close frequencies. This made it a good approximation to employ a single characteristic temperature to represent the three vibration of a hydrogen atom. It also helped that there are two hydrogen atoms in the chemical unit, because of which a large weight was assigned to the hydrogen mode. This allowed the characteristic temperature of the high energy mode to be determined with a reasonable accuracy from the low temperature heat capacity data. The coefficient A (Eq. (1)) may be calculated within quasi-harmonic approximation if all of the components of the thermal expansivity and elastic constants are available. This has not been done yet. Figure 2 shows the excess heat capacity plotted against the temperature. One sees that there does exist a gradual part below the transition temperature, but most of the anomaly is confined in a narrow interval of about 10 K covering the transition temperature.

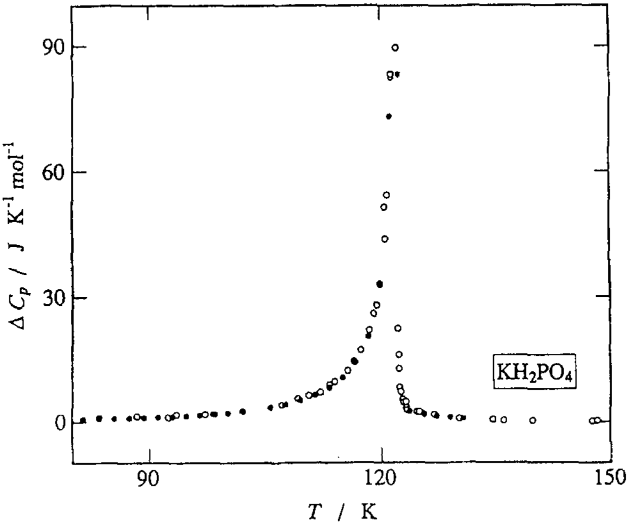

Fig. 2 The excess heat capacity of potassium dihydrogen phosphate. Open circles: from [2]. Closed circles: the present data

The transition enthalpy and entropy

Stephenson and Hooley [2] gave in their paper not only the heat capacity values but also the temperature increment for each of the datum points. This allows us to integrate their heat capacity data numerically by the trapezoidal rule. They gave two series of measurements covering the transitional region. These were integrated separately. The present experiment gives another set of data. The transition entropy was calculated by integration of $\Delta C_p(T)/T$. The result is shown in Fig. 3. For the transition enthalpy, the two series of data by Stephenson and Hooley gave 425 and 410 J mol^{-1} and the present data 421 J mol^{-1}. The transition entropies are 3.83, 3.72 and 3.790 J K^{-1} mol^{-1} for the two series of Stephenson and Hooley and for the present measurement. Stephenson and Hooley's original estimate of the transition enthalpy is ΔH=343–380 J mol^{-1} and ΔS = 2.87–3.22 J K^{-1} mol^{-1}. Both the enthalpy and entropy of transition calculated in the present paper are larger than the previous estimate. The previous estimate was smaller than the Slater value for $T \to \infty$, $\Delta S = R\ln(3/2) =$ 3.37 J K^{-1} mol^{-1}, whereas the present values are larger.

Mechanism of the ferroelectric transition

As pointed out in the Introduction, the transition entropy is considerably smaller than the $2R\ln 2 = 11.5$ J K^{-1} mol^{-1}. The re-analysis of the experimental data does not change this conclusion. The entropy value broadly supports the Slater model. However, it is substantially larger than the Slater value $(R\ln 2) =$

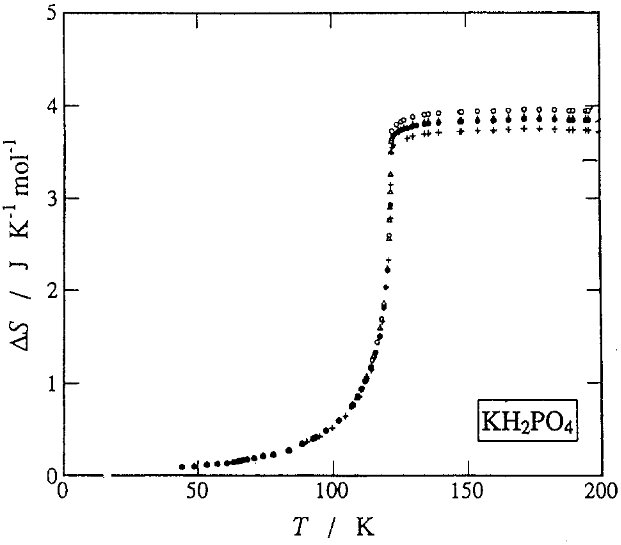

Fig. 3 The excess entropy of potassium dihydrogen phosphate. Open circles and plus signs: from the analysis of the data from [2]. Closed circles: the present data

2.88 J K^{-1} mol^{-1}. There are also indications that the ice rules may not be strictly followed. The transition entropy is 12% larger than the ice rule value.

We consider next the excess heat capacity below the transition temperature. As noted originally by Slater, the excess heat capacity in the low temperature phase is strictly zero if we enforce the ice rules strictly. This strong statement is related to the topological structure of the hydrogen bond network. If, in a perfectly ordered crystal of KDP, one displaces a proton to the other potential minimum of the same hydrogen bond on which the proton is sitting, the original phosphate ion is doubly ionized while the one accepting the displaced proton is neutralized. Strict application of the ice rules do not allow this to happen. To avoid this, the doubly ionized phosphate ion must accept a proton from one of the remaining three adjacent phosphate ions. Similarly, the neutralized phosphate ion must get rid of the excess proton to one of the remaining three neighbors. This process continues to infinity, separating the pair of the doubly ionized phosphate ion and neutral one by an infinite length of a string of displaced hydrogen bonds. This costs an infinite amount of energy. Therefore there can be no local excitation in the low temperature phase. However, there are infinitely many ways of making such string of displaced hydrogen bonds. This allows the transition to occur at a finite temperature as it actually does.

In the heat capacity curves shown in Figs 1 and 2, one finds an excess heat capacity in the low temperature phase, well reproduced in the two sets of data, as a precursory effect to the transition. From this experimental observation alone one has to conclude that there does exist a certain amount of local excitation in the ordered phase. This in turn shows that the ice rules are not strictly obeyed. The magnitude of the excess heat capacity should tell the extent to which the ice rules are violated.

Energy of the Takagi States

Takagi [8] discussed a generalization of the Slater model to include phosphate ions not conforming to the ice rule. We call them the Takagi States. In order to evaluate the energy of excitation from the ground "state" to such a state, we consider a displaced proton in an ordered crystal. At low enough temperature, the concentration of the displaced proton should be small so that they may be regarded as independent excitations against the background of the ordered state. The heat capacity of this system can be approximated by the Schottky anomaly in the low temperature limit. Thus,

$$\ln(T^2\Delta C) = \mathrm{Const} - \varepsilon/RT \tag{2}$$

where ε is the energy expended to create a pair of Takagi states. The equation shows that when the logarithm of $(T^2\Delta C_p)$ is plotted *vs.* $1/T$, it should give a straight line in the low temperature limit, the slope being equal to ε/R. Figure 4 shows such a plot. The slope of the straight line is equal to 813 K (=6.76 kJ mol^{-1}). Thus it costs 6.76 kJ to create a mole of H_3PO_4–$HPO_4^=$ pairs in the environment of the ordered configuration. It is interesting that the concentration of the Takagi states is about 0.2% at the transition temperature. But they still influence the heat capacity of the low temperature phase to a considerable extent.

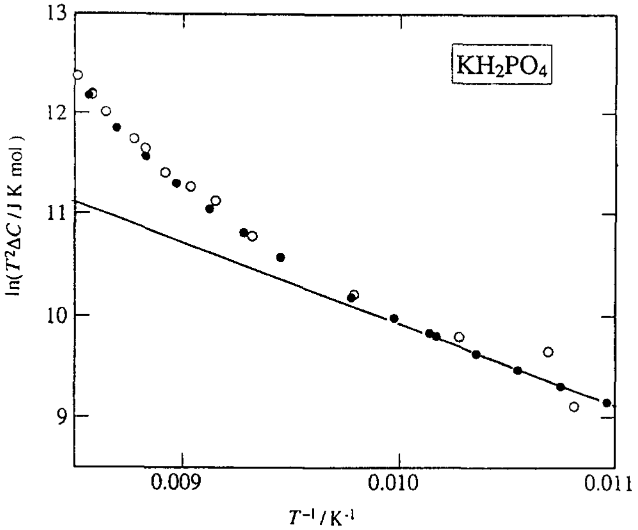

Fig. 4 Logarithmic plot of the excess heat capacity $T^2\Delta C$ from which the Takagi state energy is derived

We have thus shown that the transition entropy is larger than the maximum value compatible with the ice rules and that the heat capacity of the low temperature phase contains the contribution from the excitation to non-ice-rule states. The two aspects of the Takagi states should be related but the relation has not been worked out yet.

Comparison with other hydrogen bond systems

If the Takagi state costs a very high energy, it will be completely suppressed up to the transition temperature, resulting in a sharp first order transition. This actually occurs in copper formate tetrahydrate [14, 15]. In this crystal the vertex is simply an oxygen atom. Because of the small volume of the vertex, ionized states (H_3O^+ and OH^-) are at much higher energies than in KDP, and thus are not formed to any appreciable concentration at the transition temperature of 235 K.

In thallium dihydrogen phosphate, the hydrogen bond network is different from that in KDP. There are three types of them, of which one is symmetric and probably disordered [16]. The crystal undergoes a gradual transition at 230 K [17]. Difference in the types of thermal excitation is shown by the temperature dependence of the entropy plotted in Fig. 5. The entropy in this compound increases more gradually than in KDP (Fig. 3). This type of behavior is expected if each of the disordered hydrogen bonds takes one of the two states and if neighboring hydrogen bonds interact with each other through an Ising type mechanism without the restriction of the ice rules. The absence of the strong ice rules correlation allows localized excitation to occur more gradually than in their presence, hence the gradual increase of the entropy as plotted in Fig. 5.

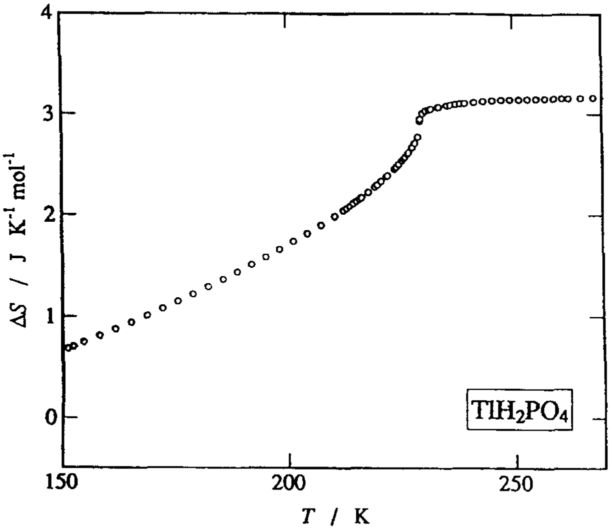

Fig. 5 The excess entropy of thallium dihydrogen phosphate [17]

The different behavior of the thallium and potassium compounds may be related to the difference in the hydrogen bond network and difference in the intrinsic properties of the hydrogen bonds themselves such as O–O distance and the distance between the two positions of the energy minima on a hydrogen bond.

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