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# The Ubbelohde effect in hydrogen-bonded crystalline $\text{K}_3\text{H}(\text{SO}_4)_2$

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**Abstract.** We present a new model reproducing the temperature dependence of hydrogen-bond lengths observed in  $\text{K}_3\text{H}(\text{SO}_4)_2$  (KHS) and  $\text{K}_3\text{D}(\text{SO}_4)_2$  (DKHS). The model also gives a consistent account of the Ubbelohde effect and the disappearance of an ordered phase in KHS.

## 1. Introduction

The substitution of deuterons for protons in hydrogen-bonded materials gives rise to an increase in hydrogen-bond lengths (oxygen–hydrogen–oxygen distances)  $u$ . Such a change in the geometry of hydrogen bonds has long been known as the Ubbelohde effect [1]. In addition to the Ubbelohde effect, a significant increase in the phase-transition temperature  $T_c$  upon deuteration is observed in many hydrogen-bonded materials: for example, in a typical hydrogen-bonded crystal  $\text{KH}_2\text{PO}_4$  (KDP), the increase in  $u$  upon deuteration is about 0.02 Å; that of  $T_c$  is about 100 K.

Ichikawa and co-workers [2] found a simple linear relationship between  $T_c$  and  $u$  on the basis of available data for KDP and asserted that the increase in  $T_c$  upon deuteration can be ascribed to an increase in  $u$ . They called this the ‘geometric isotope effect’. Nelmes [3] re-examined the high-resolution neutron diffraction results and confirmed that part, at least, of the increase in  $T_c$  is attributable to the geometric isotope effect. Similar relationships to the one described above are also observed for  $\text{H}_2\text{C}_4\text{O}_4$  [4] and  $\text{PbHPO}_4$  (LHP) [5]. Accordingly, it is necessary to clarify the physical origin of the increase in  $u$  upon deuteration and the influence of the increase in  $u$  on  $T_c$  if we are to achieve an understanding of the phase-transition phenomenon in hydrogen-bonded crystals. There is, however, no phase-transition model explaining the isotope effect on  $T_c$  as well as the Ubbelohde effect available so far. In this paper, we propose such a model.

For this purpose, we investigate here  $\text{K}_3\text{H}(\text{SO}_4)_2$  (KHS) and  $\text{K}_3\text{D}(\text{SO}_4)_2$  (DKHS). In these systems, a phase transition from an antiferroelectric phase to a paraelectric phase is observed at  $T_c = 85$  K in DKHS, whereas there is no phase transition in KHS [6, 7]. As regards the Ubbelohde effect, a temperature dependence is observed: for  $T > 85$  K, the increase of  $u$  upon deuteration is almost constant (about 0.02 Å) like for KDP and LHP, whereas it increases with the decrease in temperature for  $T < 85$  K [8]. This temperature dependence indicates that the order of the electric dipole moments influences the hydrogen-bond lengths. In this paper, we examine the properties of the phase transition and clarify the physical origin of the Ubbelohde effect in the KHS system, on the basis of a proton–dipole model, which has already been applied to the KDP and  $\text{CsH}_2\text{PO}_4$  (CDP) systems [9, 10].

## 2. The phase-transition model for the KHS system

Hydrogen bonds in KHS and DKHS are closed in a dimer in which two  $\text{SO}_4$  molecules are connected by a hydrogen bond with one proton (a deuteron). The interaction between dimers can, therefore, be assumed to be just the dipole–dipole interaction, which has a long-range character. So we consider  $N$  dimers interacting with each other by dipole–dipole interaction, under the assumption that (1) a proton strongly interacts with the distortion of the two  $\text{SO}_4$  molecules connected by the proton; (2) the distortion is proportional to the electric dipole moment of the  $\text{SO}_4$ ; and (3) the dipole moments of  $\text{SO}_4$  molecules lie along the same direction in a lattice.

The total energy in this dimer system can be written as follows:

$$E = \sum_i^N E_i + \frac{1}{2} \sum_{i,j}^{i \neq j} \sum_{\alpha,\beta=1}^2 D_{i,j}^{\alpha\beta} \mu_{i\alpha} \mu_{j\beta} \quad (1)$$

where the first term is the energy of the dimers and the second term is the electric dipole interaction between the dimers, in which the dipole moment of  $\text{SO}_4$  in dimer  $i$  is expressed as  $\mu_{i\alpha}$  ( $\alpha = 1$  or  $2$ ).

For the energy  $E_i$  of dimer  $i$  embedded in the lattice, we assume the following expression to apply:

$$E_i = \frac{A}{2} (\mu_{i1}^2 + \mu_{i2}^2) + \frac{B}{2} (u_i - u_0)^2 + C \mu_{i1} \mu_{i2} + E_p \quad (2)$$

where the first term is the distortion energy of two  $\text{SO}_4$  molecules, the second term is the elastic energy dependent on the hydrogen-bond length  $u_i$ , the third term is the dipole interaction in dimer  $i$ , and the fourth term is the ground-state energy for a proton in dimer  $i$  obtained by solving the Schrödinger equation:

$$\left[ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + U_p(x) + V_i(x) \right] \psi = E_p \psi. \quad (3)$$

In the expression above,  $m$  is the proton (deuteron) mass,  $x$  is the position of the proton (deuteron) measured from the centre of the hydrogen bond along the bond axis,  $U_p(x)$  is a potential acting on the proton (deuteron) when there is no distortion of the  $\text{SO}_4$  molecules,  $V_i(x)$  is the energy of the interaction between the proton (deuteron) and the distortion of the  $\text{SO}_4$  molecules and  $\psi$  is the ground-state wave function for the proton (deuteron). We took into account just the proton motion along the hydrogen-bond axis, for simplicity.

For  $U_p(x)$ , we adopt an empirical potential defined by

$$U_p(x) = f(u_i/2 - x) + f(u_i/2 + x) \quad (4)$$

using the Morse potential:

$$f(r) = f_0 [\exp[-2a(r - r_0)] - 2 \exp[-a(r - r_0)]] \quad (5)$$

The empirical potential has been widely used to examine the properties of hydrogen bonds [11]. Note here that this empirical potential has two minima for long  $u_i$ , whereas, for short  $u_i$ , it has one minimum: the potential profile changes drastically, depending on the value of  $u_i$ .

For  $V_i(x)$ , we assume the relation  $V_i(x) = K(\mu_{i1} + \mu_{i2})x$  to hold, where  $K$  is a coupling constant. This assumption for  $V_i$  was first introduced by Kojyo and Onodera [10] in order to examine the phase transition in the CDP system. We call it a proton–dipole model since a strong coupling between a proton and the dipole moments is assumed. An application of the proton–dipole model to KDP and DKDP was performed by Sugimoto and Ikeda [9]; it

was shown that properties of this system, including the isotope effect of the phase-transition temperature, are explained consistently. The success strongly indicates that the interaction between a proton and dipole moments plays an essential role in phase-transition phenomena in hydrogen-bonded materials. Thus we adopt the assumption of strong coupling for the KHS system. We emphasize here that the ground-state energy of a proton (deuteron) in our model is dependent on both  $u_i$  and  $\mu_{i1} + \mu_{i2}$ :  $E_p = E_p(u_i, \mu_{i1} + \mu_{i2})$ .

In order to proceed, it is convenient to introduce new variables defined by

$$s_i = \frac{1}{\sqrt{2}}(\mu_{i1} + \mu_{i2}) \quad \text{and} \quad t_i = \frac{1}{\sqrt{2}}(\mu_{i1} - \mu_{i2}).$$

By using these variables, equation (1) can be rewritten as

$$E = \sum_i^N \left[ \frac{A+C}{2} s_i^2 + E_p(u_i, s_i) + \frac{B}{2} (u_i - u_0)^2 + \frac{A-C}{2} t_i^2 \right] + \frac{1}{2} \sum_{i,j}^{i \neq j} [D_{ij}^{ss} s_i s_j + D_{ij}^{ts} t_i s_j + D_{ij}^{st} s_i t_j + D_{ij}^{tt} t_i t_j] \quad (6)$$

where

$$\begin{aligned} D_{ij}^{ss} &= (D_{ij}^{11} + D_{ij}^{12} + D_{ij}^{21} + D_{ij}^{22})/2 \\ D_{ij}^{ts} &= (D_{ij}^{11} + D_{ij}^{12} - D_{ij}^{21} - D_{ij}^{22})/2 \\ D_{ij}^{st} &= (D_{ij}^{11} - D_{ij}^{12} + D_{ij}^{21} - D_{ij}^{22})/2 \\ D_{ij}^{tt} &= (D_{ij}^{11} - D_{ij}^{12} - D_{ij}^{21} + D_{ij}^{22})/2. \end{aligned}$$

We adopt here the mean-field approximation for the dipole–dipole interaction between dimers. This approximation is valid for an interaction with a long-range character such as the dipole–dipole interaction.

As seen from equation (6), the fields acting on  $s_i$  and  $t_i$  in dimer  $i$  are regarded as

$$\sum_j^{j \neq i} [D_{ij}^{ss} s_j + D_{ij}^{st} t_j] \quad \text{and} \quad \sum_j^{j \neq i} [D_{ij}^{ts} s_j + D_{ij}^{tt} t_j]$$

respectively. In the mean-field approximation, using the mean fields  $\bar{s}$  and  $\bar{t}$ , these quantities may be expressed as

$$\sum_j^{j \neq i} [D_{ij}^{ss} s_j + D_{ij}^{st} t_j] = D_{ss} \bar{s} + D_{st} \bar{t} \quad (7)$$

and

$$\sum_j^{j \neq i} [D_{ij}^{ts} s_j + D_{ij}^{tt} t_j] = D_{ts} \bar{s} + D_{tt} \bar{t} \quad (8)$$

where

$$\begin{aligned} D_{ss} &= \sum_{j(\neq i)} D_{ij}^{ss} & D_{st} &= \sum_{j(\neq i)} D_{ij}^{st} \\ D_{ts} &= \sum_{j(\neq i)} D_{ij}^{ts} & D_{tt} &= \sum_{j(\neq i)} D_{ij}^{tt} \end{aligned}$$

are assumed.

The mean fields introduced above,  $\bar{s}$  and  $\bar{t}$ , are determined from the self-consistency conditions:  $\bar{s} = \langle s_i \rangle$  and  $\bar{t} = \langle t_i \rangle$ , where  $\langle X_i \rangle$  means the thermal average of the quantity  $X_i$  defined by

$$\langle X_i \rangle = \left( \int \int \int ds_i du_i dt_i X_i \exp[-(E_s + E_t)/kT] \right) \times \left( \int \int \int ds_i du_i dt_i \exp[-(E_s + E_t)/kT] \right)^{-1} \quad (9)$$

with

$$E_s = \frac{A+C}{2} s_i^2 + E_p(u_i, s_i) + \frac{B}{2} (u_i - u_0)^2 + (D_{ss}\bar{s} + D_{st}\bar{t})s_i \quad (10)$$

and

$$E_t = \frac{A-C}{2} t_i^2 + (D_{tt}\bar{t} + D_{ts}\bar{s})t_i. \quad (11)$$

The thermal average of the quantity  $t_i$ ,  $\langle t_i \rangle$ , can easily be calculated by performing the integration of equation (9). Using this result and the self-consistency condition for  $\bar{t}$ , we obtain the following result:

$$\bar{t} = \frac{-D_{ts}}{A-C+D_{tt}} \bar{s}. \quad (12)$$

Substituting this relation into equation (10), we can express  $E_s$  as follows:

$$E_s = \frac{A_s}{2} s_i^2 + D_s \bar{s} s_i + E_p(u_i, s_i) + \frac{B}{2} (u_i - u_0)^2 \quad (13)$$

where

$$A_s = A + C \quad \text{and} \quad D_s = D_{ss} - \frac{D_{ts}D_{st}}{A-C+D_{tt}}$$

are used.

By using equation (13), the thermal average of a quantity  $F$  dependent on only  $s_i$  and  $u_i$  can be calculated by performing the following integration:

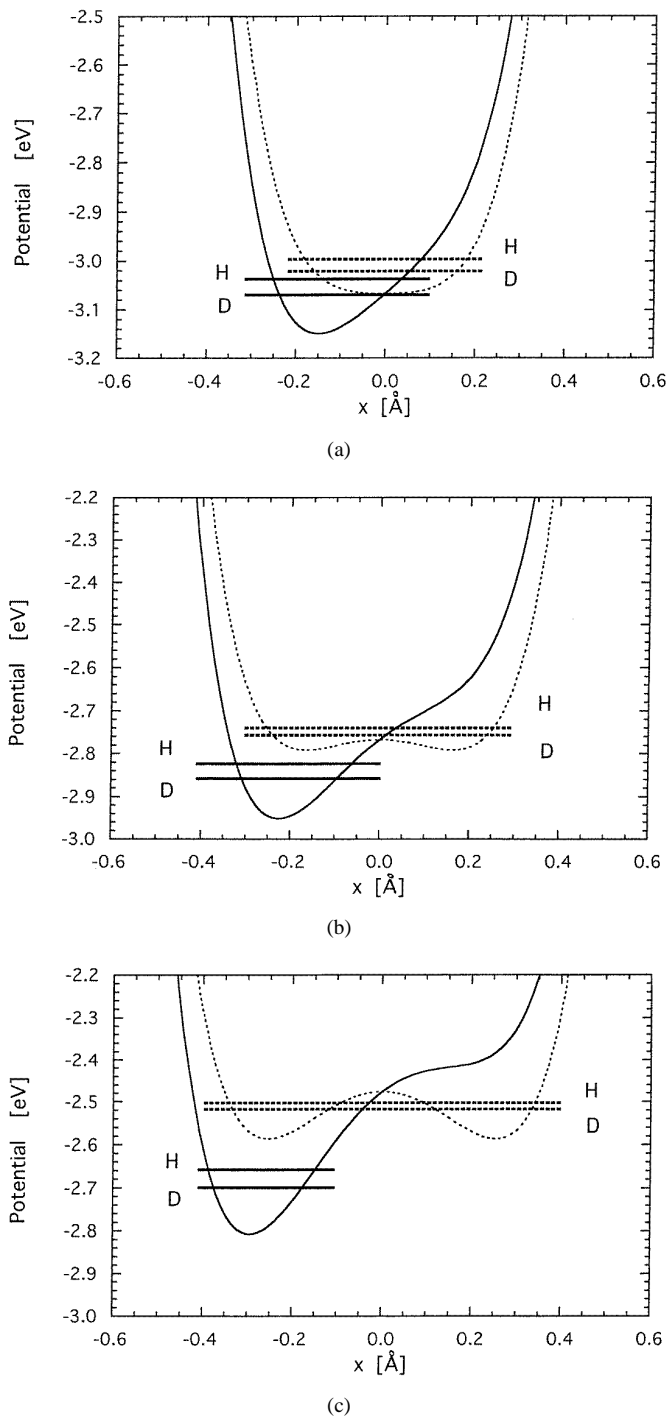
$$\langle F \rangle = \left( \int \int ds_i du_i F(s_i, u_i) \exp[-E_s/kT] \right) / \left( \int \int ds_i du_i \exp[-E_s/kT] \right). \quad (14)$$

**Table 1.** The values of the parameters used in our calculations. Here,  $s_0$  is the unit of  $s_i$ .

$f_0$	$a$	$r_0$	$K\sqrt{2}s_0$	$A_s/s_0^2$	$D_s/s_0^2$	$B$	$u_0$
2 eV	3 Å <sup>-1</sup>	0.98 Å	0.8 eV Å <sup>-1</sup>	0.2 eV	-0.018 eV	13.2 eV Å <sup>-2</sup>	2.66 Å

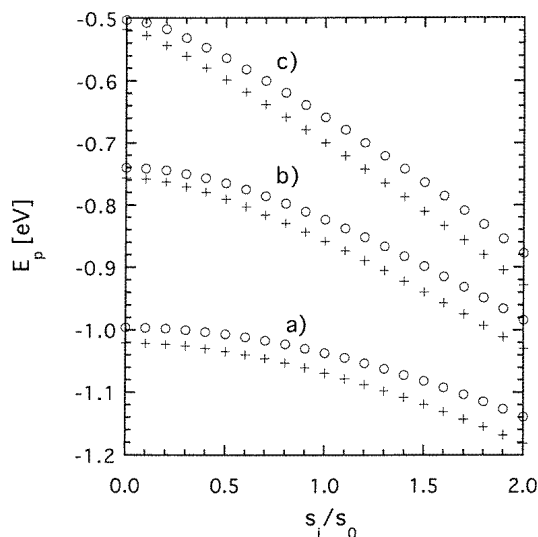
### 3. The phase transition and the Ubbelohde effect

In table 1, the parameter values used in this paper are listed. The parameters adopted in the empirical potential  $U_p$  ( $f_0$ ,  $a$  and  $r_0$ ) were those used in the calculation for KDP [9], since we have no knowledge of the values of these parameters for the KHS system. The remaining parameters,  $K$ ,  $A_s$ ,  $D_s$ ,  $B$  and  $u_0$ , were determined so as to reproduce both the transition temperature  $T_c$  and the hydrogen-bond length at  $T_c$  in DKHS.



**Figure 1.** The profiles of the potential,  $U_p(x) + V_i(x)$ , at (a)  $u_i = 2.4$  Å, (b)  $2.5$  Å and (c)  $2.6$  Å. The profiles at  $s_i/s_0 = 0$  and  $1.0$  are shown by broken and full curves, respectively. The horizontal lines in the figures indicate the ground-state energies for the proton (H) and deuteron (D).

In figure 1, we show the potential acting on a proton (deuteron),  $U_p(x) + V_i(x)$ , at  $s_i/s_0 = 0$  and 1.0 with the ground-state energies obtained by solving the Schrödinger equation (equation (4)) numerically. With the parameter values of the empirical potential chosen here, the potential at  $s_i/s_0 = 0$ , i.e.,  $U_p(x)$ , has one minimum at the centre of the hydrogen bond ( $x = 0$ ) for  $u_i < 2.42$  Å, whereas it has two minima for  $u_i > 2.42$  Å. Note that the difference between the ground-state energy for the proton and that of the deuteron increases with increase in  $s_i$ .



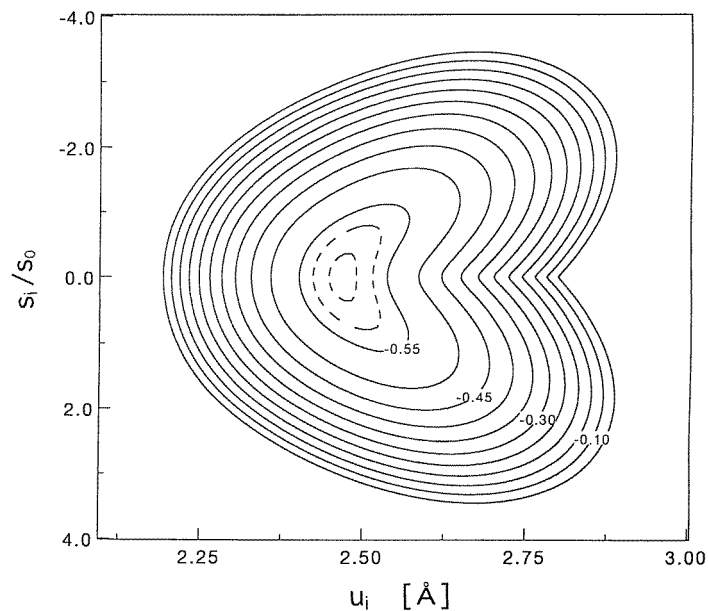
**Figure 2.** The dependencies of  $E_p(u_i, s_i)$  on  $s_i$  for (a)  $u_i = 2.4$  Å, (b)  $2.5$  Å and (c)  $2.6$  Å. The results for the proton and deuteron are represented by open circles and crosses, respectively.

The  $s_i$ -dependence of the ground-state energy is shown in figure 2. As seen in this figure, the decrease in  $E_p$  with the increase of  $s_i$  is more rapid for a deuteron than for a proton. The isotope dependence of  $E_p(s_i, u_i)$  obtained here is due to deformation of the potential profiles induced by changes of  $s_i$  and  $u_i$ . We emphasize here that the isotope dependence of  $E_p$  is the origin of all of the isotope effects that are obtained below.

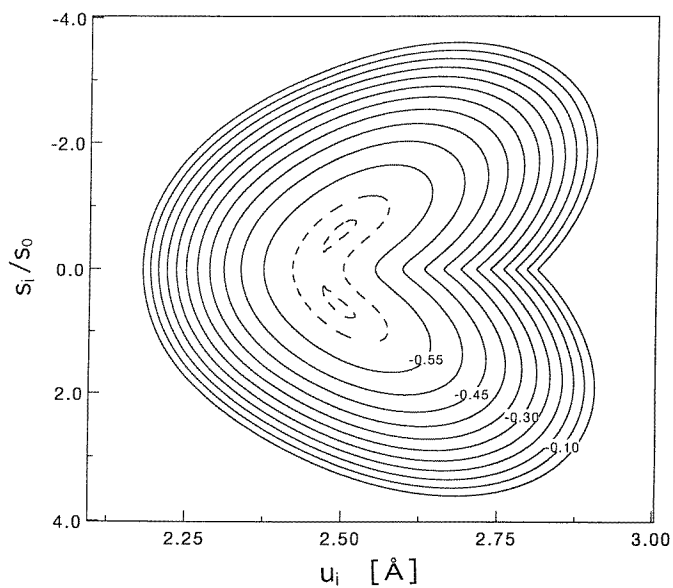
Energy-contour maps of  $E_s$  at  $\bar{s} = 0$  obtained from equation (13) are shown in figures 3(a) and 3(b) for a proton and a deuteron, respectively. The striking feature in these figures is that  $E_s$  for the proton has one minimum at  $s_i = 0$ , whereas, in the case of the deuteron, there are two minima at  $s_i/s_0 = 0.8$  and  $-0.8$ .

In figure 4 we show the temperature dependence of  $|\langle s_i \rangle|$  for the deuteron obtained by using the self-consistency condition. We can see from this result that there is an ordered phase at low temperatures, which undergoes a second-order phase transition at  $T_c \simeq 85$  K. For the proton, on the other hand, the only self-consistent solution is  $|\langle s_i \rangle| = 0$ : no ordered phase exists for protons. These results are in agreement with observations for the KHS system. Although the parameters were chosen so as to reproduce  $T_c$  for DKHS, the agreement indicates that our model proposed here is valid for achieving an understanding of the phase-transition phenomenon in the KHS system.

In figure 5, we show the temperature dependence of  $\langle u_i \rangle$  for both the proton and the deuteron. As seen in this figure, the features of the temperature dependence obtained are as follows: (1)  $\langle u_i \rangle$  decreases with decrease in temperature in the paraelectric phase,



(a)

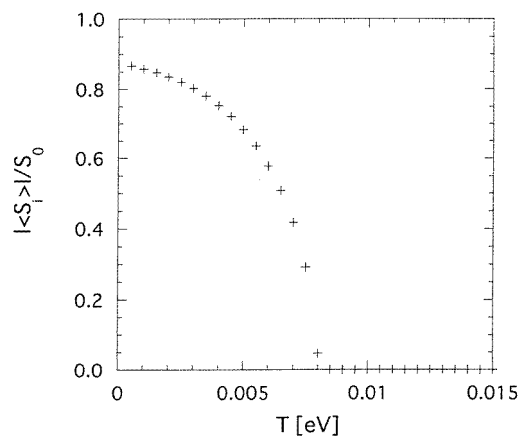


(b)

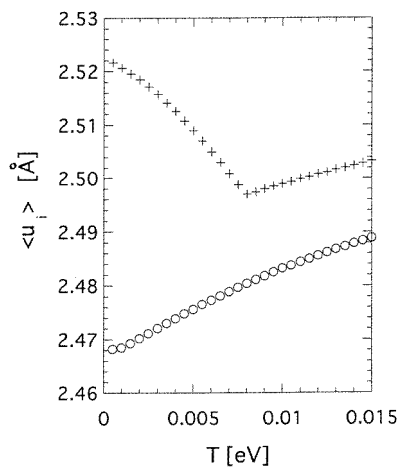
**Figure 3.** Energy-contour maps of  $E_s(s_i, u_i)$  at  $\bar{s} = 0$  for (a) the proton and (b) the deuteron. The numbers in the figure are the energy values in eV.

whereas, in the ordered phase,  $u_i$  increases with decrease in temperature; and (2) in the paraelectric phase, the difference between  $\langle u_i \rangle$  for the proton and that for the deuteron is almost independent of the temperature and its value is about 0.02 Å. These features are completely in agreement with the recent observations for the KHS system made by Noda





**Figure 4.** The temperature dependence of the order parameter  $|\langle s_i \rangle|$  for the deuteron. For the proton,  $\langle s_i \rangle = 0$  holds in all temperature regions.



**Figure 5.** Temperature dependencies of  $\langle u_i \rangle$ . Open circles and crosses are used for the proton and deuteron, respectively.

*et al* [8]: our model reproduces the Ubbelohde effect in the KHS system completely. Finally, we emphasize that all of the isotope effects obtained here arise just from the difference in mass between the proton and the deuteron.

#### 4. Discussion

First we make a comment concerning the disappearance of the ordered phase in KHS. In the mean-field approximation, the condition for an ordered phase to be stabilized is that there is a region of  $\bar{s}$  in which the relation  $\langle s_i \rangle > \bar{s}$  is satisfied. The appearance of the ordered phase in the present calculation is, therefore, caused by the fact that  $E_s$  for the deuteron has two minima at  $s_i/s_0 = 0.8$  and  $-0.8$  when  $\bar{s} = 0$  because, in this case, states stabilized by applying the mean field ( $\bar{s}$ ) can have large dipole moments. In the case of the proton, on the

other hand, dipole moments induced by  $\bar{s}$  are small, because  $E_s$  at  $\bar{s} = 0$  has a minimum at  $s_i = 0$ . This property of  $E_s$  is the origin of the disappearance of ordered phases in KHS.

The position of the energy minima in  $E_s$  at  $\bar{s} = 0$  varies with the values of the parameters. Accordingly, there is a possibility that the stabilization of an ordered phase at low temperatures can be realized for protons by using other sets of the parameters. Since the parameters, especially  $K$ ,  $A_s$ ,  $D_s$ ,  $B$  and  $u_0$ , are expected to be dependent on the materials involved, there must be hydrogen-bonded materials in which an ordered phase is realized for protons. In fact, a phase transition is observed at 20 K [16] for  $K_3H(SeO_4)_2$ . More detailed discussion concerning the properties of the phase transition for materials in which the hydrogen bond closes in a dimer will be presented in a forthcoming paper.

To explain the isotope effect on  $T_c$  in hydrogen-bonded materials, the tunnelling motion of protons (deuterons) has been introduced by Blic [12] and by Tokunaga and Matsubara [13]. Hydrogen-bonded materials exhibiting an isotope effect on  $T_c$  have mainly been investigated from this point of view. For the KHS system, Moritomo *et al* [14] asserted, on the basis of an analysis of their observations, that proton tunnelling plays a dominant role as regards the phase transition and related properties. Although the introduction of the tunnelling motion provides an explanation for the large isotope effect on  $T_c$ , there is no observation of direct evidence for the tunnelling motion of protons (deuteron), in spite of recent careful experiments [15]. Accordingly, there is some doubt as regards the existence of tunnelling motion of protons in hydrogen-bonded materials. In addition, this model could not give a consistent account for the Ubbelohde effect.

We emphasize here that tunnelling motion of protons (deuterons) is not assumed in our model explicitly. Both the Ubbelohde effect and the isotope effect on  $T_c$ —that is, the isotope effects of  $\langle u_i \rangle$  and of  $\langle s_i \rangle$  obtained—arise just from the isotope dependence of  $E_p$ . This isotope dependence of  $E_p$  is caused by the fact that the potential profile varies with  $s_i$  and  $u_i$ . Accordingly, the physical origin of the isotope effect in this system is ascribable to deformation of the potential profile induced by the interaction between a proton (deuteron) and  $SO_4$  tetrahedra, not the tunnelling motion of a proton (deuteron).

We again emphasize that our model gives a consistent account of not only the Ubbelohde effect but also the isotope effect on  $T_c$  in the KHS system. Since the hydrogen-bond network in this system is closed in a dimer, it is impossible for the mechanism of the phase transition to be based on the configuration energy determined by the proton (deuteron) configurations, introduced by Slater [16] and refined by Takagi [17]. On the other hand, the proton–dipole model gives a consistent account of the properties of KDP and DKDP including the isotope effect on  $T_c$ , as shown by Sugimoto and Ikeda [9, 18]. These facts are considered to be strong evidence of the validity of the present model based on the proton–dipole model.

Finally, we note that there is ambiguity concerning the determination of the parameters. Accordingly, there might be another set of parameter values with which the KHS system is well described. However, the ambiguity has no influence on the conclusions obtained from the present calculation.

## 5. Conclusion

With the new model proposed here, a consistent account has been obtained of the Ubbelohde effect as well as properties of the phase transition in the KHS system. This success strongly indicates that the model is valid for the description of the physics of hydrogen-bonded materials in which the hydrogen bond closes in a dimer.

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