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Effect of the magnetic field on the ferroelectric transition of KD_2PO_4 measured by a high resolution and super-sensitive differential scanning calorimeter

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Abstract

The magnetic effect on the ferroelectric transition of single crystalline KD_2PO_4 (DKDP) was measured by using a high resolution and super-sensitive differential scanning calorimeter (DSC) working in a magnetic bore. The transition temperature of KD_2PO_4 with the magnetic field of 5 T along *a*-axis and along *c*-axis was 5.6 ± 0.8 and 2.8 ± 0.9 mK, respectively, higher than that without the magnetic field. The calculated temperature shifts of the transition due to the magnetic field along *a*-axis and along *c*-axis using the magneto-Clapeyron equation and the data of magnetic susceptibility were negative values, being contradictory to the experimental results. These results demand to consider another contribution in magnetic susceptibility. The high frequency term of magnetic susceptibility due to molecular motions was considered to play an important role in order to explain the positive experimental values.

Keywords: Heat flux; DSC; High resolution; Phase transition; DKDP; KD_2PO_4; Magnetic effect

1. Introduction

The development of refrigerator-cooled superconducting magnet has made possible easily to obtain a strong magnetic field, for example, 10 T. It has become possible to study the magnetic effect of paramagnetic and diamagnetic substances using such a magnet [1–6]. Since the magnetic energy at 10 T is still weaker than the thermal energy kT at room temperature, it is necessary to use a highly sensitive apparatus under the strong magnetic field in order to detect the magnetic effect of diamagnetic and paramagnetic substances. However, the magnetic effect on the dielectric substance has been scarcely reported.

Potassium dihydrogen phosphate KH_2PO_4 (KDP) belongs to a family of ferroelectric crystals where the molecular units are linked by hydrogen bonds. Their hydrogen bonds are preferably oriented in specific direction in the crystal lattice. In the KDP crystal, O–H bonds lie in the *c*-plane. Diamagnetic anisotropy was reported for the hydrogen-bonded ferroelectrics due to the anisotropy of spatial atomic distribution [7]. KDP is known to have a ferroelectric phase transition at about 120 K [8,9] from a ferroelectric orthorhombic structure to a paraelectric tetragonal structure. In the deuterated isomorph of KDP, KD_2PO_4 (DKDP), the transition temperature was reported to become about 220 K [10,11].

In the previous studies [12–17], we developed a high resolution and super-sensitive differential scanning calorimeter (DSC) capable of measuring a heat as small as the order of 20 nW with a temperature resolution less than 1 mK. We measured the magnetic effect on the phase transitions of

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diamagnetic materials such as $C_{32}H_{66}$, EBBA, MBBA, H_2O and D_2O using the DSC, which was placed in a magnetic bore. It has been shown that the transition temperature due to phase transitions and due to melting was shifted to a higher temperature side by several or several tens of mK for $C_{32}H_{66}$ [13], EBBA [14], MBBA [17], H_2O and D_2O [16] by applying the magnetic field of 5 or 6 T. In the case of H_2O and D_2O, the temperature shift due to the magnetic field is proportional to the square of the magnetic field, being compatible to the magnetic field. However, these temperature shifts did not obey the magneto-Clapeyron equation quantitatively.

Since the magnetic effect on the phase transition of diamagnetic materials has been scarcely measured, it is desirable to collect enough data on the phase transition of various kinds of diamagnetic materials in order to investigate the mechanism of the magnetic effect.

In the present study, we have measured the magnetic effect on the ferroelectric to paraelectric phase transition of KD_2PO_4 using the high resolution and super-sensitive DSC and discussed it using the magneto-Clapeyron equation.

2. Experimental

We have used a high resolution nW stabilized DSC working in a magnetic bore between 120 and 420 K, which was described previously [16]. The schematic drawing of the DSC is shown in Fig. 1. The calorimeter was set in a magnetic bore and was cooled by a refrigerating head, which was connected to the calorimeter through copper plates. The temperature of the sample was measured by the Pt thermometer, TS1. We calibrated the temperature of TS1 by measuring the resistance of TS1 as a function of the melting temperature of the standard materials, such as In, Ga, Hg, biphenyl and ice and the solid–solid transition temperature of cyclohexane. Then, we know the temperature of the sample by measuring the resistance of TS1. A single crystal of DKDP was purchased from Nippon Pastec Co. Ltd., Japan. The single crystal of DKDP with a size of 2.2 mm × 2.3 mm × 2.5 mm was put in a cylindrical aluminum pan with a diameter of 3.8 mm facing *a*-plane and *c*-plane to the bottom of the pan. The sample pan was set along the parallel direction to the ground and the magnetic filed was applied along the perpendicular direction to the ground. When the *a*-plane or *c*-plane of DKDP crystal was faced to (the bottom of) the aluminum pan, the magnetic filed was applied along *a*-axis or *c*-axis, respectively.

Before measuring the magnetic effect on the transition of DKDP, the magnetic effect on the Pt thermometer due to the magneto-resistance was measured. The magnetic effect at 5 T on TS1 was determined as described previously [16]. The DSC was kept at room temperature of 288.65 K without using temperature control and then the magnetic field of 5 T was applied three times to measure the magnetic effect on the Pt thermometer TS1 as shown in Fig. 2. In Fig. 2, the base temperature was corrected to be a flat line, since it drifted slowly due to the ambient temperature change. Fig. 2 shows

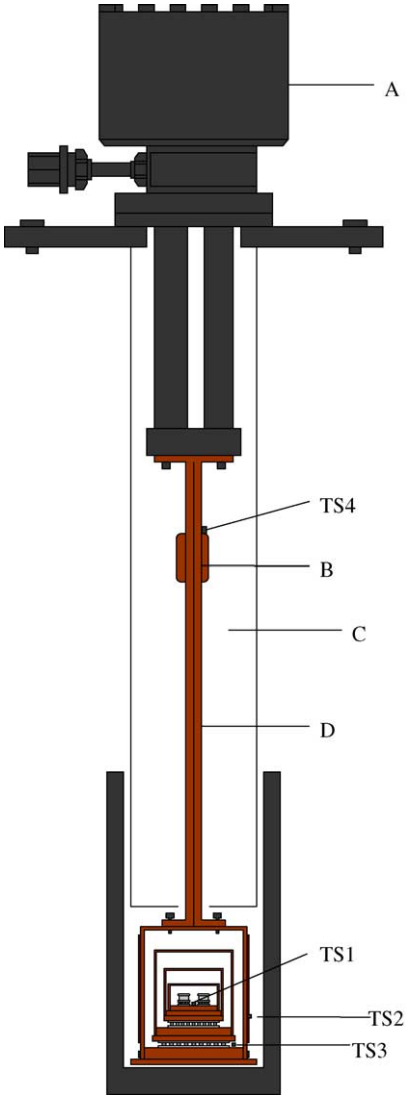

Fig. 1. Schematic drawing of the high resolution and super-sensitive DSC working in a magnetic bore between 120 and 420 K [16]. A, refrigerating head; B, thermal reservoir; C, thermal insulator; D, copper plates connected to the calorimeter, TS1–TS4; Pt resistance thermometers.

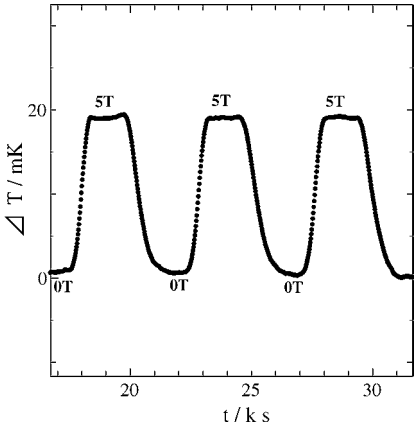

Fig. 2. The magnetic effect at 5 T at 288.65 K on the Pt resistance thermometer, TS1 [16].

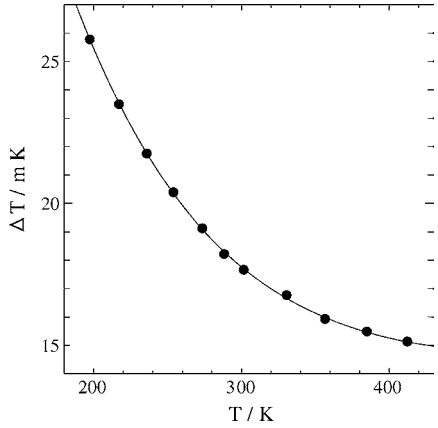

Fig. 3. The magnetic effect on TS1 at various temperatures at 5 T [16].

that the magnetic effect at 5 T on the Pt thermometer is reproducible and it is obtained to be 18.2 mK at 288.65 K. The magnetic effect on the Pt thermometer TS4 at a distant place from the maximum magnetic field of 5 T as shown in Fig. 1 was measured to be 0.4 mK, which is 2.2% of the magnetic effect on TS1. The magnetic effect on TS1 at other temperatures was measured with controlling the temperature to be constant using the thermometer TS4, similarly as shown in Fig. 2. After the small magnetic effect on TS4 was corrected, the magnetic effect at 5 T on TS1 at other temperatures was determined as shown in Fig. 3.

3. Results

The heat flux measurements on the ferroelectric transition of DKDP were made five times at a heating rate of 1 mKs^{-1} using the DSC. The results of repeated two measurements for the DKDP crystal facing *a*-plane to the aluminum pan (which is abbreviated to *a*-plane DKDP hereafter) are shown in Fig. 4, indicating almost the same results. The transition temperature can be reproducibly measured with the precision of ±0.5 mK. The transition temperature of the DKDP

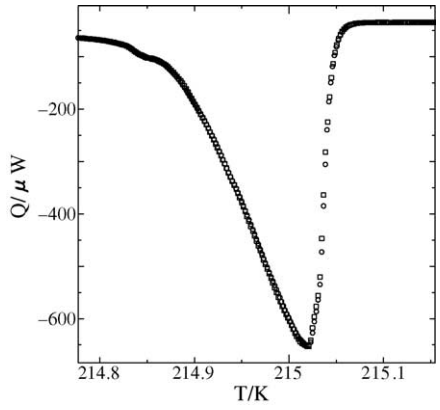

Fig. 4. The DSC curves on the ferroelectric transition of *a*-plane DKDP without magnetic field at a heating rate of 1 mKs^{-1}. The results of two measurements at the same condition are shown.

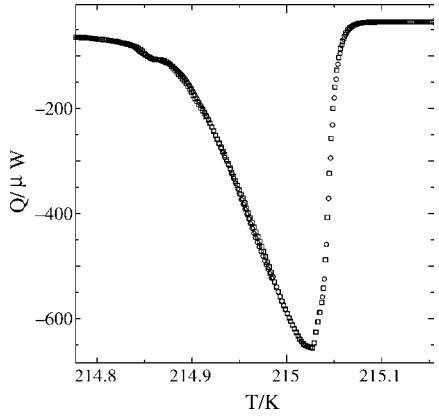

Fig. 5. The DSC curves on the ferroelectric transition of *a*-plane DKDP with the magnetic field of 5 T at a heating rate of 1 mKs^{-1}. The results of two measurements at the same condition are shown.

crystal facing *c*-plane to the aluminum pan (which is abbreviated to *c*-plane DKDP hereafter) can also be reproducibly measured with the same precision. The transition temperature of DKDP was 215.05 K, which is in the middle of the two reported values of 213 and 229 K [10,11]. The heat flux measurements on the ferroelectric transition of DKDP under the magnetic field of 5 T were made five times at a heating rate of 1 mKs^{-1} and the repeated two measurements are shown in Fig. 5 for *a*-plane DKDP. The heat flux measurements on the ferroelectric transition for *c*-plane DKDP under the magnetic field of 5 T can also be reproducibly measured with the precision of ±0.5 mK. The averaged results for *a*- and *c*-plane DKDP with the magnetic field of 5 T and without the magnetic field are shown in Figs. 6 and 7 for comparison, respectively. The transition temperature with the magnetic field of 5 T is slightly higher than that without the magnetic field as seen in Figs. 6 and 7. Since the shift of the transitional peak due to the magnetic field is slightly dependent on the peak position, the temperature shift was averaged over the whole range of the transitional peak. The resultant temperature shift was obtained to be 5.6 ± 0.8 mK for *a*-plane DKDP

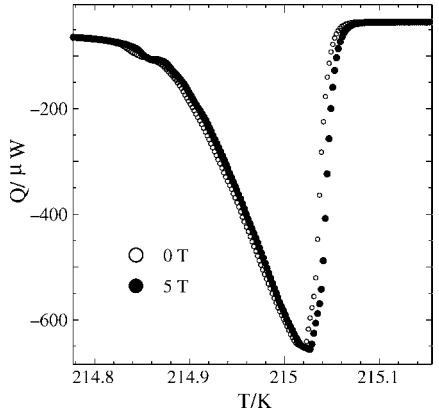

Fig. 6. The comparison between the averaged DSC curves of *a*-plane DKDP with the magnetic field of 5 T and without the magnetic field at a heating rate of 1 mKs^{-1}.

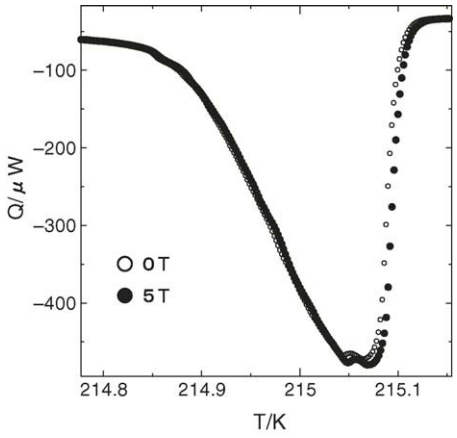

Fig. 7. The comparison between the averaged DSC curves of *c*-plane DKDP with the magnetic field of 5 T and without the magnetic field at a heating rate of 1 mKs^{-1}.

and 2.8 ± 0.9 mK for *c*-plane DKDP. The higher transition temperature of DKDP due to the magnetic field shows that the ferroelectric phase is stabilized by the magnetic field by some reason.

4. Discussion

The DSC curves with and without the magnetic field for the ferroelectric transition of DKDP show that the ferroelectric state becomes more stable than the paraelectric state by the application of the magnetic field. The relatively stable state in the low temperature phase has also been found in the phase transitions in $C_{32}H_{66}$, EBBA, MBBA, H_2O and D_2O [13,14,16,17]. The effects of an applied magnetic field on the phase transitions of these compounds were discussed on the basis of a simple extension of the Clapeyron equation [13,14,16,17].

When we consider a diamagnetic substance at temperatures near the phase transition, which has an angle θ with respect to the magnetic field, the molar Gibbs energy change dG including the magnetic effect is represented by the following equation:

$$\mathrm{d}G = -S\,\mathrm{d}T - \left(\frac{B}{\mu_0}\right)(\chi_\perp \sin^2\theta + \chi_= \cos^2\theta)\,\mathrm{d}B \qquad (1)$$

where S is the molar entropy, $\chi_\perp$ and $\chi_=$ are the diamagnetic susceptibility perpendicular and parallel to the molecular axis, respectively, and B is the magnetic flux. Since $\chi_\perp$ and $\chi_=$ are both negative values, the second term of Eq. (1) becomes positive and then the system becomes unstable by applying the magnetic field. When the phase transition is under way, the molar Gibbs energy at the high temperature phase is equal to the low temperature phase to give $\mathrm{d}G_\mathrm{h} = \mathrm{d}G_\mathrm{l}$, where subscript h and l mean the high temperature and the low temperature phase, respectively. Then the shift of the transition temperature by the application of the magnetic field, ΔT, becomes as by integrating of differential of Eq. (1) in the high and low temperature phases:

$$\Delta T = -\left(\frac{B^2}{2\mu_0}\right)\frac{((\chi_{\perp\mathrm{h}}-\chi_{\perp 1})\sin^2\theta + (\chi_{=\mathrm{h}}-\chi_{=1})\cos^2\theta)}{(S_\mathrm{h}-S_1)}. \qquad (2)$$

Since the absolute magnetic susceptibility in the direction of *a*-axis χ_a is larger than that in the direction of the *c*-axis χ_c for DKDP considering its crystal structure [7], χ_a and χ_c are regarded as $\chi_=$ and $\chi_\perp$, respectively. In the case of *a*-plane DKDP, where the magnetic field is applied along *a*-axis and θ is 0°, Eq. (2) becomes:

$$\Delta T = -\left(\frac{B^2}{2\mu_0}\right)\frac{(\chi_{\mathrm{ah}}-\chi_{\mathrm{a1}})}{(S_\mathrm{h}-S_1)} \qquad (3)$$

In the case of *c*-plane DKDP, where the magnetic field is applied along *c*-axis and θ is 90°, Eq. (2) becomes:

$$\Delta T = -\left(\frac{B^2}{2\mu_0}\right)\frac{(\chi_{\mathrm{ch}}-\chi_{\mathrm{c1}})}{(S_\mathrm{h}-S_1)} \qquad (4)$$

Using the unpublished values for the diamagnetic susceptibility of $(\chi_{\mathrm{ah}}-\chi_{\mathrm{a1}})$ and $(\chi_{\mathrm{ch}}-\chi_{\mathrm{c1}})$ for *a*-plane and *c*-plane [18], and the entropy change for the ferroelectric transition of DKDP: $S_\mathrm{h}-S_\mathrm{l} = 3.80\,\mathrm{J\,K^{-1}\,mol^{-1}}$ [19], ΔT for the ferroelectric transition of DKDP for *a*- and *c*-plane are calculated to be −0.5 and −1 μK at 5 T, respectively. The calculated values are both negative and the transition temperatures are expected to shift to the lower temperature. The experimental values for the shift of the transition temperature in the ferroelectric transition at 5 T, ΔT for *a*-plane DKDP: 5.6 mK and for *c*-plane DKDP: 2.8 mK, are both positive, contradicting the calculated values. Therefore, it is very difficult to make a theoretical explanation on the positive temperature shifts of the ferroelectric transition of DKDP due to the strong magnetic field.

These facts would show that the temperature shifts of the ferroelectric transition of DKDP due to the strong magnetic field cannot be explained by the simple application to Eqs. (3) and (4), if we use the values for the diamagnetic susceptibility of DKDP [18] and use the results of the entropy change [19]. Since the entropy change, $(S_\mathrm{h}-S_\mathrm{l})$, is definitely positive and its magnitude is considered to be correct, the difference between the experiment and the calculation may be due to directly using the data of diamagnetic susceptibility. There must exist another important contribution in the magnetic susceptibility under a strong magnetic field. One possible explanation would be the one made in the case of H_2O and D_2O [16]. According to Ramsey [20], the magnetic susceptibility χ of a diamagnetic molecule is expressed as:

$$\chi = \chi_\mathrm{static} + \chi_\mathrm{hf} \qquad (5)$$

where the first term is the usual diamagnetic susceptibility and the second term is the high frequency term due to molecular motions such as rotation and vibration under a strong magnetic field. He also gave a theoretical equation of χ_hf for

the rotational part of diatomic molecules [20]. Since the diamagnetic susceptibility is measured statically, such as using a microbalance and SQUID, the high frequency term is not included in the usual diamagnetic susceptibility. In the case of H_2O and D_2O [16], although the experimental temperature shifts ΔT were proportional to the square of the strong magnetic field, being compatible with the magneto-Clapeyron equation, the magnitudes were three orders of magnitude larger than the calculated ones. In order to explain the larger experimental values of H_2O and D_2O, the high frequency term expressed by Eq. (5) was taken into account. For a polarized molecule like H_2O, the charge of nucleus and electrons in the atoms cannot be cancelled completely. Then the thermal motion of the partially charged atoms of H_2O in the magnetic field gives rise to the Lorentz force at temperatures near the melting point, which contribute to make the high frequency term larger. The Lorentz force would suppress the thermal motion of the partially charged atoms, making the solid phase more stable.

The most generally accepted mechanism of the phase transition in DKDP is an order–disorder model of protons [21]. The bonding character of DKDP is considered to have some ionic character. Therefore, similarly as the case of H_2O, the thermal motion of the constituent ions of DKDP may be considered to give rise to the Lorentz force at temperatures near the ferroelectric transition in the magnetic field. The Lorentz force would suppress the thermal motion of the ions, resulting in the low temperature phase more stable. If we think that the thermal motion of partially ionized atoms contributing to the hydrogen bonding in the magnetic field gives rise to the Lorentz force, strengthening the hydrogen bonding can be considered to be brought by the Lorentz force acting on the moving ions. The reason why the temperature shift of the phase transition along *a*-axis as compared with *c*-axis is not clear at present.

5. Conclusions

The magnetic effect on the ferroelectric transition of single crystalline KD_2PO_4 (DKDP) was measured by using a high resolution and super-sensitive DSC working in a magnetic bore. The transition temperature of KD_2PO_4 with the magnetic field of 5 T along *a*-axis and along *c*-axis was 5.6 ± 0.8 and 2.8 ± 0.9 mK, respectively, higher than that without the magnetic field. The temperature shift of the phase transition due to the magnetic field was negative and about three orders of magnitude lager than the calculated one using the magneto-Clapeyron equation, if data of the static diamagnetic susceptibility are used. Instead, the high frequency magnetic susceptibility proposed by Ramsey is predominant, the experimental data are understandable using the magneto-Clapeyron equation. The thermal motion of constituent ions in DKDP is considered to be suppressed due to Lorentz force under the magnetic field, resulting in the low temperature phase to be more stable.

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