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Abstract

The crystal structure of an organic weak-ferroelectrics, tricyclohexylmethanol (TCHM), was re-examined by single-crystal x-ray diffraction at room temperature. TCHM forms a dimer through hydrogen bonding at the centre of the dimer, where two hydroxyl groups are arranged in tandem and their direction is disordered in two possible orientations, which brings about a dipolar Ising nature. The heat capacity measured by adiabatic calorimetry from 6 to 400 K shows three anomalies including fusion at 368 K. The entropy of the ferroelectric transition is 1.9 J K^{-1} mol^{-1}, supporting the order–disorder mechanism of dimer dipoles. A broad anomaly at 348 K is related to the breakage of the intra-dimer hydrogen bond. Detailed analysis of the temperature dependence of heat capacity due to the phase transition showed the presence of a broad hump in the excess heat capacity around 160 K. The temperature dependences of the excess heat capacity and the existing dielectric constant can be analysed in terms of a highly anisotropic Ising model.

1. Introduction

The static and dynamic structure of protons within hydrogen bonds (H-bonds) is behind some major issues in the science of condensed matter. The residual entropy of ice is probably one of the most famous ones [1, 2]. The 'ice problem' is a typical example of interparticle correlation in interacting particle systems [3, 4]. Equivalent issues have been discussed extensively in the fields of dielectric materials (H-bonded dielectrics [5–7]) and magnetism ('spin ice' due to geometrical frustration [8]). The important role of H-bonds is also of current interest in biological science.

Recently, organic ferroelectrics having H-bonds, complexes, phenazine-chloranilic acid and phenazine-bromanilic acid were reported [9]. This discovery renewed the interest in H-bonded molecular dielectrics [10]. The title compound, tricyclohexylmethanol ((C_6H_{11})$_3$COH, abbreviated as TCHM hereafter) is, as far as the authors know, the first organic ferroelectrics to have moving protons within the H-bonds [11]. In contrast to most crystals involving H-bonds, where the H-bond forms an infinite network and/or chain, the TCHM crystal consists of H-bonded dimers [12]. The absence of an infinite network/chain is due to the bulkiness of the molecule. Namely, the bulky cyclohexyl groups inhibit the formation of interdimer H-bond(s). The formation of H-bonds within the dimer has been proved by spectroscopy [13–15]. The dimers are almost broken in the liquid.

The proton dynamics in the TCHM crystal has been studied for a long period. The first report [16] appeared in 1956 before the crystal structure was known. After an interval, attention was re-focused in 1980s. The mechanism of dielectric relaxation has been discussed by Bator *et al* [11, 14, 17]. They suggested that H-bond reversal occurred through the formation of a closed dimer, though there is no structural evidence to support this.

Through these studies, a phase transition has been found around 103 K [17]. The existence of spontaneous polarization was recently demonstrated for the low-temperature phase [11]. Although the ferroelectric transition was clearly detected by dielectric studies [11, 17], it was accompanied by only a slight signal in differential scanning calorimetry (DSC) [11]. A pronounced critical slowing down was observed in the dielectric relaxation time around the ferroelectric transition, suggesting a higher-order nature of the transition, which probably rationalizes the failure to detect a clear thermal anomaly by DSC.

It is important that the crystal under consideration does not belong to the class of so-called isolated H-bonded ferroelectrics [18–21], though the dimer in the crystal of TCHM is certainly isolated. In isolated H-bonded ferroelectrics only a proton is involved in the H-bond, resulting in quantum tunnelling between two minima [22]. In contrast, the H-bond in the present system is formed between two hydroxy groups (–OH). That is, another proton exists outside the H-bond. Concerted transition is necessary for tunnelling as long as the local 'ice rule' is required.

Study of ferroelectrics and related materials has a long history in condensed matter physics [23]. A ferroelectrically (or antiferroelectrically) ordered state usually appears on cooling through a structural phase transition, which is often classified into two limiting cases, the displacive type as in $BaTiO_3$ and the order–disorder type in $NaNO_2$, though real systems lie somewhere in between [24–26]. Order–disorder transitions can conveniently be described utilizing the parallelism between a pseudo spin variable and spin in magnetism. In such treatments, the main part of the interaction between pseudo spins is not a long-ranged dipolar one but a short-ranged one mediated by lattice degree(s) of freedom. In this context, it is natural to ask what type of order and phase transition are possible in purely dipolar systems. This issue also has a long history, dating back to 1912 [27]. By restricting the orientation of dipoles into two opposing directions, a dipolar Ising model (DIM) is obtained [28, 29]. Extensive studies have been performed concerning the critical behaviour of the DIM [29–32].

The DIM is one of the most intuitive models in (anti)ferroelectrics. Most crystals consist of simple polar molecules such as HCl [33]. However, the separation of charge inside a molecule is not negligible in comparison with the interdipole distance and strong coupling with lattice degrees of freedom is expected. Rather strong coupling is also expected even for clathrates because of the asymmetric shape of the clathrated molecule, although some interesting properties were reported probably related to the long-ranged nature of the dipolar interaction [34, 35].

In this paper, the details of the ferroelectric phase transition of TCHM crystal are studied from structural and thermodynamic points of view. It is shown that the crystal fits the definition

Table 1. Summary of structure analysis.

Chemical formula	$(C_6H_{11})_3COH$
Formula mass	278.46
Temperature	295(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	$P\bar{1}$
a, b, c (Å)	10.9102(6), 9.5173(5), 9.2980(5)
α, β, γ (deg)	115.765(1), 86.779(1), 96.784(1)
V (Å^3)	863.38(8)
Z	2
D_{calc} (Mg m^{-3})	1.071
Absorption coefficient	0.063 mm^{-1}
F (000)	312
Crystal size	$0.18 \times 0.14 \times 0.13$ mm^3
Index ranges	$-14 \leqslant h \leqslant 14$
	$-12 \leqslant k \leqslant 12$
	$-12 \leqslant l \leqslant 12$
No. of reflections	12 036
No. of independent reflections	4127 [$R_{int} = 0.0292$]
Completeness (to $\theta = 27.9°$)	99.9%
Absorption correction	Empirical
Max. and min. transmission	0.9918 and 0.9887
Refinement	Full-matrix least squares on F^2
Data/restraints/parameters	4127/0/322
Goodness-of-fit on F^2	1.032
Final R [$I > 2\sigma(I)$]	$R_1 = 0.0594, wR_2 = 0.1490$
R (all data)	$R_1 = 0.0806, wR_2 = 0.1646$
Largest diff. peak and hole	0.291 and $-0.155e$ Å^{-3}

of a dipolar Ising system and that physical properties far from the critical point seem to be well approximated by a highly anisotropic Ising model.

2. Experimental details

TCHM was purchased from Tokyo Chemical Industry, Co. and purified by fractional sublimation in a vacuum. To avoid possible formation of a metastable crystalline phase, the sublimed specimen was melted once under a helium atmosphere and then recrystallized. This recrystallization revealed the easy formation of liquid quenched glass.

A single crystal for x-ray crystallography was grown from an ethanol solution of the purified specimen. X-ray measurement was made on a SMART APEX diffractometer (Bruker AXS KK). Data collection was performed at room temperature. Unit-cell refinement and data reduction were carried out using the SAINT program [36]. The program SHELXTL [37] was used to solve and refine structures. The experimental conditions and the crystallographic parameters are tabulated in table 1.

The sample for calorimetry was sealed in a gold-plated copper calorimeter vessel with helium gas under atmospheric pressure. The mass of the sample was 1.9268 g (6.9192 mmol) after the buoyancy correction.

The working thermometer mounted on the calorimeter vessel was a platinum resistance thermometer (Minco, S1059). Its temperature scale is based upon ITS-90. The details and operation of the adiabatic calorimeter are described elsewhere [38].
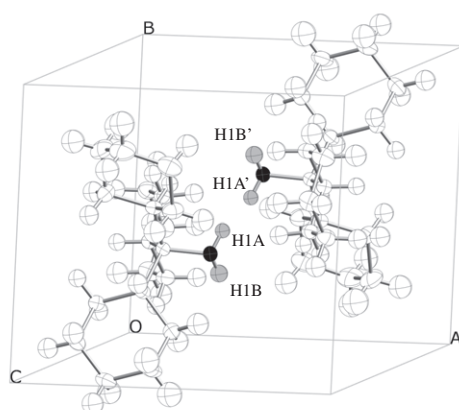
Figure 1. Crystal structure of TCHM at room temperature. Alcoholic hydrogen atoms (shadowed) attached to the oxygen atom (filled) were split into two (H1A and H1B) with a nearly equal occupancy due to positional disorder.

The measurement was carried out by the so-called intermittent heating adiabatic method. The temperature increment due to a single energy input (Joule heating) was less than 1% of temperature. Thermal equilibrium inside the vessel was attained within a normal time (1–10 min depending on temperature) after energy input. The sample contributed 20% of the total heat capacity, including that of the vessel, at 50 K, 17% at 100 K, 22% at 200 K, 26% at 300 K and 30% at 375 K.

The temperature, enthalpy and entropy of fusion were determined as 367.2 K, 23.8 kJ mol^{-1}, and 64.9 J K^{-1} mol^{-1}, respectively. The chemical purity of the calorimetric sample was determined as 99.7 mol% by using the fractional melting method, which utilizes the melting point depression.

3. Results and discussion

3.1. Crystal structure of the room-temperature phase and dipole moment

The crystal structure of TCHM at room temperature was reported previously [12]. Although the space group implies positional disorder for the alcoholic hydrogens, no detailed analysis was performed there. The present analysis confirmed that the reported result is essentially correct.

The previous report [12] stated that all hydrogen atoms are located in the difference Fourier synthesis map and the hydrogen atom on the hydroxyl group is located at a single site with a large isotropic thermal parameter. On the other hand, the present refinement shows that two remarkable peaks of electron density exist close to the oxygen atom of the hydroxyl group in the difference Fourier synthesis map. The structure refinement assuming the disorder of the hydrogen atom of the hydroxyl group was carried out and converged successfully with the hydrogen atom occupying each site (H1A and H1B) nearly equivalently (figure 1). This finding readily leads to the conclusion that the ferroelectric transition would have an order–disorder character.

The hydrogen atoms on the hydroxyl groups constitute a dimer of TCHM through a H-bond. The distance between H1A and H1A′ in figure 1 is about 0.126 nm. Simultaneous occupancy of two inner sites is geometrically forbidden at a normal energy, because the distance between them is too short. Considering the coordination and strength of the hydrogen bond, it

is reasonable that the two hydroxyl groups in the dimer are arranged in tandem (O–H$\cdots$O–H). The crystal can therefore be regarded to consist of dipoles on dimers. They have only two configurations and change their orientations concertedly. Since concerted tunnelling is scarcely found, the quantum effect can safely be ignored in the present compound. The entropy of transition is then expected to be $\frac{1}{2}R\ln 2 \approx 3$ J K^{-1} mol^{-1} (R, the gas constant) assuming a pure order–disorder mechanism.

The dipole moment of an isolated dimer was estimated by a quantum chemical calculation under the restricted Hartree–Fock (RHF) level using the 6-31G* basis set in the GAUSSIAN98 program [39]. The experimental geometry of the dimer was assumed. The electric dipole moment per dimer is estimated to be about 7.9×10^{-30} C m along the orientation of the tandem hydroxyl groups. The large dipoles, which are restricted to two orientations like an Ising spin are arranged in a lattice with a cell size of about $10 \times 10 \times 10$ Å^3.

The TCHM crystal consists of H-bonded dimers. The electric dipole is the sum of that of each TCHM molecule. Since the direction of the OH bond is restricted by the H-bond between the adjacent molecules, the direction of the dipole of a dimer is restricted to two orientations along the H-bond. Then, the following Hamiltonian seems appropriate.

$$\mathcal{H} = -\sum_i J_{\text{intra}} s_{i\text{A}} \cdot s_{i\text{B}} - \sum_{\langle i,j \rangle} J_{\text{inter}}(s_{i\text{A}} + s_{i\text{B}}) \cdot (s_{j\text{A}} + s_{j\text{B}}), \qquad (1)$$

where s_i is an Ising spin variable ($\pm\frac{1}{2}$) that specifies the direction of the dipole of each TCHM molecule. The first term describes the coupling inside a dimer consisting of two molecules (A and B). The sum is over $N/2$ dimers. The second term describes dipolar coupling between dimers. The relation $|J_{\text{intra}}| > |J_{\text{inter}}|$ is required for the physical consistency of the model.

At sufficiently low temperatures (in comparison with $J_{\text{intra}}/k_{\text{B}}$), equation (1) is reduced to

$$\mathcal{H} = -\sum_{\langle i,j \rangle} J_{ij} \sigma_i \sigma_j. \qquad (2)$$

Dipoles are assumed to be like Ising spins having two orientations ($\sigma = \pm 1$) and the interaction has the form of an interdipole one. This Hamiltonian is just the dipolar Ising model (DIM) without exchange interaction [29, 30, 40–42]. Although the crystal is certainly anisotropic with a triclinic cell, the interdimer distances along the three crystallographic axes do not differ significantly, as seen in table 1. The assumption of isotropy is therefore not far from the truth.

The reported spontaneous polarization in the low-temperature phase (about 10^{-4} C m^{-2} [11]) is much smaller than that expected from the completely ferroelectric order of dimer dipoles (about 1×10^{-2} C m^{-2}). This clearly shows that the TCHM crystal is essentially an antiferroelectric. Indeed, in general, purely dipolar systems do not have a ferroelectrics ground state on a simple lattice [28, 40, 41]. The net polarization should be attributed to a canted antiferroelectricity or to ferrielectrics. From the ratio between the experimental spontaneous polarization and the expected dipole moment of a dimer, the canting angle may be roughly estimated as $\arcsin 10^{-2} \approx 0.6°$. If this was due to the rotational displacement of a molecule, the rotation angle would be of the same order of magnitude. In any way, a precise crystallographic study is necessary at low temperatures.

3.2. Excess heat capacity and entropy

Heat capacity of the crystalline TCHM was first measured after annealing around 360 K to improve crystallinity. After completing the measurements at the ferroelectric transition around 100 K, measurements across the melting temperature were carried out. The results are shown in figure 2. A small anomaly around 100 K is attributed to the ferroelectric transition found previously in dielectric measurements [11]. A sharp anomaly around 370 K is due to fusion.
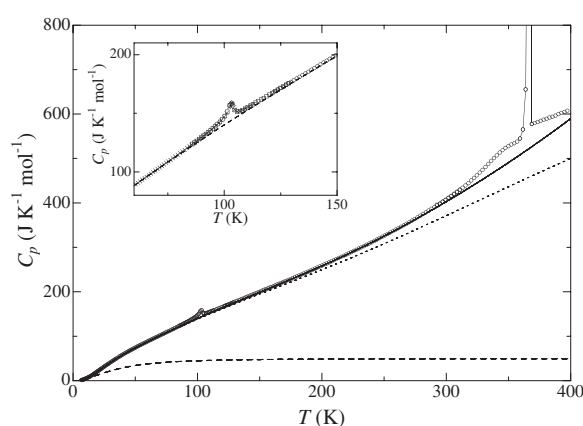
Figure 2. Measured heat capacities of crystalline (below 370 K) and liquid (above 370 K) TCHM. An assumed 'normal' portion, to separate the excess heat capacities, is indicated by solid line. Broken and dotted lines show the contributions of lattice and intramolecular vibrations, respectively, to heat capacity.

Below the fusion there is a broad hump, which seems to be interrupted by fusion before returning to a baseline.

The heat capacity around the ferroelectric transition is shown in the inset of figure 2 on an enlarged scale. An anomaly with a maximum around 103 K is clearly seen. Since the temperature of the anomaly is reasonably close to the reported transition temperature, the anomaly is attributed to the ferroelectric transition. Neither latent heat nor supercooling was detected around the peak of the anomaly. This fact suggests that the paraelectric–ferroelectric phase transition is of second or higher order. The heat capacity has a maximum at 103 K. In contrast to the notable critical phenomenon detected in the dielectric relaxation time [11], the diverging trend in the excess heat capacity is not strong.

To separate excess heat capacities attributable to the hydrogen dynamics, it is necessary to subtract the contribution of the intramolecular vibrational degrees of freedom (156 modes), the external lattice vibration (three translational and three librational branches) and the so-called C_p–C_v correction term from the total heat capacity.

A quantum chemical calculation was carried out for an isolated molecule to estimate the first contribution. Gaussian98 [39] was used for this purpose. The molecular geometry was optimized under the RHF level using the 6-31G* basis set. Vibrational analysis was then performed. The resultant frequencies obtained through such calculation usually deviate systematically from the experimental ones. The deviation can be corrected by multiplying by a correcting factor. Since the estimation of the second and third contributions requires curve fitting, the correcting factor was included in a set of fitting parameters.

The second contribution (of the external lattice vibrations) is assumed to be described by Debye and Einstein models. The three degrees of freedom are assumed to be involved for translational and librational degrees of freedom, respectively. The C_p–C_v correction is assumed to be approximated by the Lindemann relation: C_p–$C_v \propto AC_pT^2$.

The normal heat capacity to be subtracted from measured one was determined by performing a least squares fitting on the measured heat capacity in the regions of 6–60 K and 200–230 K while assuming the intramolecular vibrational frequency correction factor, Debye and Einstein temperatures and the *A* parameter as free parameters. The resultant normal heat capacity is drawn in figure 2 by a solid line. Subtraction of this normal heat capacity from the
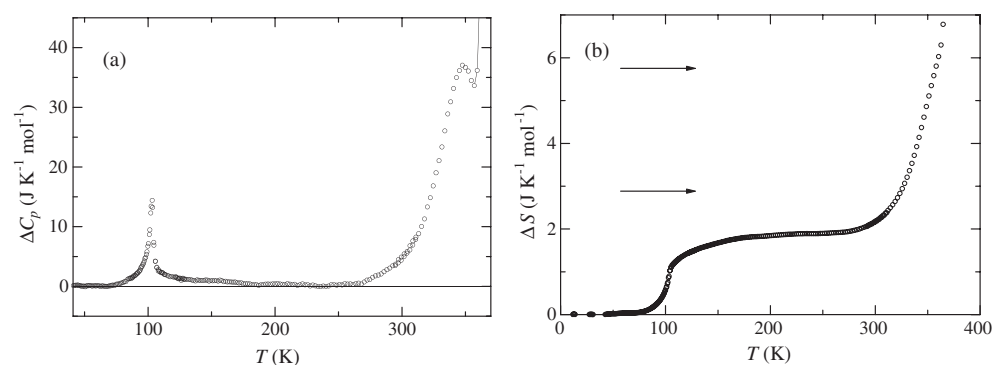
Figure 3. (a) Excess heat capacities of crystalline TCHM. (b) Temperature dependence of excess entropy of crystalline TCHM. The expected magnitudes for complete disorder of dimer dipoles ($\frac{1}{2}R\ln 2$) and molecular dipoles ($R\ln 2$) are indicated by arrows.

measured heat capacity yields the excess heat capacities shown in figure 3(a). The small scatter around zero in the regions of 6–60 K and 200–230 K demonstrates the goodness of the fit.

Numerical integration of the excess heat capacities was carried out between 70 and 190 K to estimate the enthalpy and entropy of phase transition. The results are $\Delta_{\text{trs}}H = (176 \pm 1)$ J mol^{-1} and $\Delta_{\text{trs}}S = (1.9 \pm 0.1)$ J K^{-1} mol^{-1}. The entropy of transition is, though slightly smaller, comparable to the the expected magnitude for an order–disorder transition of dimer dipoles ($\frac{1}{2}R\ln 2 \approx 2.9$ J K^{-1} mol^{-1}).

By integrating the excess heat capacity in figure 3(a), temperature dependence of the excess entropy was evaluated as shown in figure 3(b). There are two plateaus: one around 2 J K^{-1} mol^{-1} and the other around 6 J K^{-1} mol^{-1}. The latter magnitude is reasonably close to the expected one ($R\ln 2 \approx 5.8$ J K^{-1} mol^{-1}) for complete disordering of molecular dipoles. This indicates that the separation of the excess heat capacity was essentially successful.

The present result demonstrates that two protons within a dimer change their positions concertedly. Since clear critical slowing down is observed in dielectric relaxation in the kHz range [11], though the diverging trend in heat capacity is not strong, high-frequency ac calorimetry may detect correlated proton dynamics. This possibility is currently being pursued in this laboratory.

Figure 3(a) clearly shows that a broad anomaly lies near the fusion of TCHM in addition to that due to the phase transition. This anomaly has a large long tail on low-temperature side and a maximum at 348 K. A broad hump is expected for the destruction of intradimer correlation from a model Hamiltonian (equation (1)). Considering this, the broad hump between 310 and 360 K can possibly be attributed to this phenomenon. This assignment is consistent with the existing IR result [15] and the fact that no significant difference is found for the entropy of fusion between TCHM and similar compounds such as triphenylmethane [$(C_6H_5)_3CH$] [43].

Although the integrated entropy (figure 3 (b)) is consistent with the assumption of the destruction of the dimer upon heating, the temperature dependence of the excess heat capacity is more prominent than that expected for a simple two-state (two-level) system. Indeed, the simple model predicts the maximum excess heat capacity of about 1.8 J K^{-1} mol^{-1} (3.6 J K^{-1} (mol of dimer)$^{-1}$) in contrast to about 40 J K^{-1} mol^{-1}. This clearly shows that some cooperativity is occurring in this process. To describe such a moderate cooperativity, Sorai *et al* [44] have proposed a 'domain model' [45]. Although this model works well in general [46], the application was abandoned because of the severe overlap of the anomaly with the low-temperature tail of fusion. The origin of the strong correlation among dimers is unclear
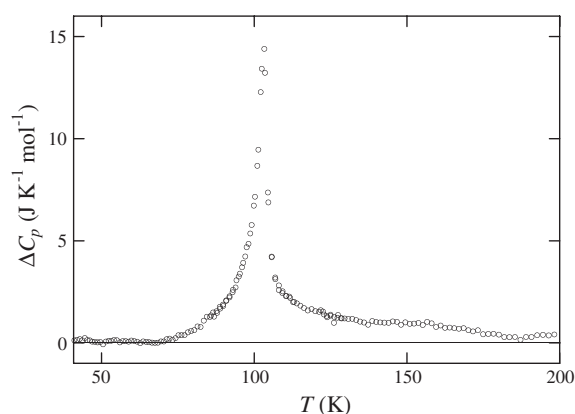
Figure 4. Excess heat capacities of crystalline TCHM due to the paraelectric–ferroelectric phase transition.

at present. This is to be pursued in context of the 'strong correlation effect' in molecular solids [3].

3.3. One-dimensional correlation of dipoles

Figure 4 represents an enlarged plot of the excess heat capacity in the temperature range from 60 to 200 K. There is a broad hump around 160 K. Although its magnitude is less than 1% of the total heat capacity, inclusion of the temperature region around 180 K into the 'normal region' in the fitting dramatically reduced the goodness of the fit. This strongly suggests that the hump around 160 K is not an artefact but an intrinsic one. The shape of the anomaly just around the transition temperature is not so far from a typical λ-shaped anomaly. Detailed analysis of the critical behaviour is, however, beyond the scope of this paper because of the insufficient temperature resolution of adiabatic calorimetry. A study using ac calorimetry is planned in this laboratory.

The abnormal temperature dependence of the excess heat capacity above the transition temperature is rationalized by assuming the occurrence of the so-called dimensional crossover on cooling. Indeed, a similar temperature dependence of the excess heat capacity is often seen in phase transitions of some one-dimensional magnets with strong anisotropy, such as $CoCl_2 \cdot 2NC_5H_5$ [47], decamethylferrocenium tetracyanoethenide [48] and decamethylferrocenium tetracyanoquinodimethanide [48]. Those materials have a one-dimensional chain structure and Ising anisotropy in the magnetic interaction. Since the temperature dependence of the heat capacity of a one-dimensional Ising chain (with an interaction of the form $-J\sigma_i\sigma_j$) is the same as a two-level system with a gap $\Delta = 2J$, a broad hump (Schottky anomaly) is observed around $0.4\Delta/k_B$. It was pointed out that the dipolar Ising model shows one-dimensionality along the dipole direction [41, 51, 52], though no estimate of the effective coupling constant was given. If the hump around 160 K is regarded as a symptom of this, the magnitude of J is roughly estimated as 200 K.

The low-frequency dielectric constant above 100 K reported by Bator *et al* [17] can also be fitted very well as shown in figure 5 to

$$\epsilon - \epsilon_\infty = \frac{A/T}{\exp\left(-2J_\parallel/k_BT\right) - 2zJ_\perp/k_BT}, \tag{3}$$

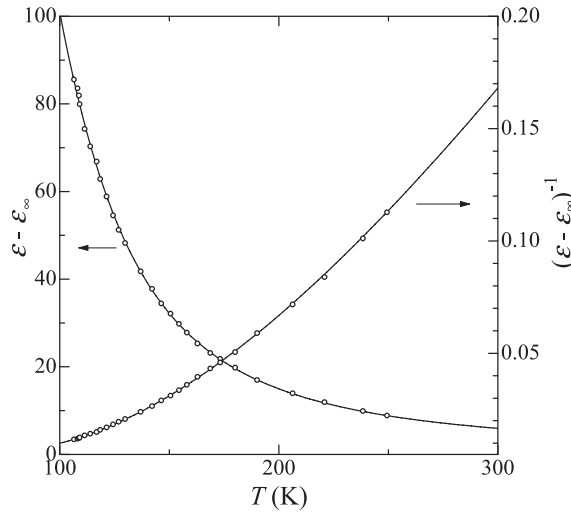which was developed for quasi-one-dimensional ferroelectrics [49, 50]. The resultant

Figure 5. Fit of the reported dielectric constant [17] of TCHM crystal to the quasi-one-dimensional model formula (equation (3)).

parameters are, while assuming nearest neighbour couplings, $J_{\parallel}/k_B = 166$ K and $zJ_{\perp}/k_B = -1.2$ K according to equation (2). Here z is the number of neighbouring chains.

The mean field theory for a quasi-one-dimensional model [49, 50] predicts the anisotropy ($z|J_{\perp}|/J_{\parallel}$) dependence of the transition temperature as

$$\exp\left(-\frac{2J_{\parallel}}{k_B T_{trs}}\right) = \frac{2z|J_{\perp}|}{k_B T_{trs}}. \tag{4}$$

Although a transition temperature is not a good test for any mean field theories, this equation gives $z|J_{\perp}|/k_B = 2$ K if $J_{\parallel}/k_B = 170$ K is assumed. The resultant anisotropy is reasonably close to that deduced from the temperature dependence of the dielectric constant.

The above analysis shows that the physical properties of the TCHM crystal, which can be regarded as a dipolar Ising system, are in general well approximated by a highly anisotropic Ising model in which only the nearest neighbour interaction is considered. Since it is hard to find any symptom of structural one-dimensionality, it is natural to assume that this behaviour originates from the anisotropic nature of the dipolar interaction. Although an extensive study was made for the dipolar Ising model and its critical behaviour in 1970s [29–32], only a little has been reported on the high-temperature behaviour [41, 51, 52]. It is interesting to note that the excess heat capacity reported for a clathrate (quinol–HCN) exhibited a broad hump far above a transition temperature [34].

4. Concluding remarks

The re-examination of the crystal structure of the high-temperature phase of TCHM revealed the presence of positional disorder concerning the H-bond orientation. This suggested a naive dimer model as a basic mechanism for the ferroelectric phase transition at 103 K. Structural features implied that TCHM crystal is a dipolar Ising system [29, 30, 40–42].

Precise adiabatic calorimetry successfully detected the heat capacity anomaly due to the phase transition. Careful and detailed analysis of the temperature dependence of the heat capacity was performed utilizing a quantum chemical calculation. The resultant excess entropy

due to the phase transition supported the dipole Ising nature of the system. The analysis revealed the presence of a broad hump in the excess heat capacity around 160 K. The hump was attributed to the presence of one-dimensional correlation of the dipoles of H-bonded dimers, which was expected for a dipolar Ising system [41, 51, 52]. The quasi-one-dimensional model well reproduced the temperature dependence of the dielectric constant while considering the nearest neighbour coupling.

The present authors have previously demonstrated that molecular systems can be the best stage for studies of structural phase transitions in dielectrics. Namely, a unified model for displacive and order–disorder transitions [24] could be tested in a clean (neat) system and a compound showing an intermediate transition could be prepared [25, 26]. Besides, on such well-characterized systems, effects of well-defined impurities could be studied [53–55]. The present study is presented as another example in the same spirit: typical systems for condensed matter physics can be found in molecular crystals because of the richness of their variety.

Acknowledgment

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