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Learning the Second-order Phase Transition Through Experiments: Targeting the Ferroelectric Phase Transition of Triglycine Sulfate (TGS)

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A method to learn the second-order phase transition experimentally was demonstrated. The targeted phenomenon was the ferroelectric phase transition of triglycine sulfate, and simultaneous measurements of heat flow and pyroelectric current were performed while changing the temperature. Two fractions of the phase transition were calculated as a function of temperature for each of the measurement data, and quantitative analysis was performed. The analytical result of the experimental data was compared with the theoretical result of the Ising model. In addition to achieving a deeper understanding, the reduction in apparatus cost is considered.

Keywords: Second-order phase transition, Ferroelectric phase-transition, Triglycine sulfate, Temperature-driven heat flow and pyroelectric current, Ising model.

1. Introduction

Second-order phase transition is a phenomenon in which the state of condensed matter changes dramatically by a slight change in surrounding conditions, and where many atoms or molecules move cooperatively. This phenomenon is a fascinating and important subject from the viewpoints of both theory and application, and it has attracted many researchers. University students should be attracted by this phenomenon as well and can learn much from this subject. A topic of the second-order phase transition is learned in the subject of statistical physics and material science at the undergraduate program; however, many of them have been conducted only by the lecture without experiments. Therefore, the learners mostly get only theoretical understanding.

It is known that a typical second-order phase transition occurs in the superfluid phase transition of ⁴He, the gas-liquid transition at the critical point, the magnetic phase transition, the ferroelectric phase transition, etc.^{1,2)} Experiments for undergraduate students are difficult to perform because the equipment costs, skill level, and time needed are high, for the experimental conditions of low temperature, high temperature, or high pressure.

At the University of Michigan, students conduct experiments to observe the ferroelectric phase-transition phenomenon of triglycine sulfate [TGS: (NH₂CH₂COOH)₃ · H₂SO₄]³⁾ in undergraduate program. TGS is known as a substance that causes an order-disorder type of phase transition, in which molecular electric-polarization aligns by a temperature decrease crossing the critical point from a random state in a hightemperature phase and expresses spontaneous polarization (ferroelectric phase).^{4,5)} TGS is suitable as an experimental material because its transition temperature, easily creating the observing conditions; furthermore, its crystal is easy to make and has low toxiity. The electrical characteristics (pyroelectric current and AC dielectric constant) are measured with changing temperature at the University of Michigan. From the pyroelectric current, the amount of electric polarization can be calculated. The anomalous increase in microscopic polar fluctuation is reflected in the dielectric constant, which becomes maximum at the phase transition temperature, the temperature dependence of which is well known to follow the Curie-Weiss law.^{1,2,6,7,8)}

From the viewpoint of thermal behavior, there exists an anomaly in specific heat in the vicinity of the second-order phase transition temperature.⁹⁾ The specific heat becomes maximum at the transition temperature, and the first derivative of specific heat by temperature is discontinuous at the critical temperature. This behavior is in contrast to the first-order phase transition, which occurs only at a phase transition temperature with latent heat. Combining the information obtained from thermal measurement with electric measurement makes it possible to understand the second-order phase transition more deeply.

In this work, an experiment for students is proposed in order to understand the behavior of the ferroelectric phase transition of TGS quantitatively. The experiment consists of novel simultaneous-measurements of heat flow and pyroelectric current in the vicinity of the phase transition temperature. From the combination of both the experimental data, quantitative consideration of the second-order phase transition is performed.

The educational goal of this laboratory activity is as follows: 1) recognize the behavior of second-order phase transition, a typical cooperative phenomenon, 2) pursue the quantitative relationship in the temperature dependences of the heat-flow and the electric-current, for deeper understanding, 3) learn the experimental skills; they are a) temperature control and the simultaneous measurements of the two observables with scanning the temperature, and b) numerical data analysis using a software. An additional goal for the learners who are unsatisfactory only by experimental observation and those who learn the second-order phase transition at university class is to compare the experimental result with the theoretical ones.

For popularization of the personal experiment, the equipment is small in size and low in cost, following the concept of a desk-assembly type experiment (personal desk lab, or PDL). ^{10,11}.

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2. Apparatus

2.1 Sample preparation

A single domain crystal for the sample was grown as described in the literature.^{12,13)} At first, a saturated aqueous solution of glycine sulfate was cooled naturally to get the seed crystals. Next, the saturated solution containing the seed crystals at 20 °C was cooled slowly to 5 °C for two weeks, and transparent single crystals at a size of about 3.5 mm were obtained. The grown crystal has the same thick plate shape shown in Fig.2 by R. Renugadevi *et al.*,¹³⁾ and a wide plane is perpendicular to the *b*-axis. When the parallel planes were selected as normal to the *b*-axis of the crystal, a large pyroelectric current flowed by the phase transition. A parallel-plate sample was obtained by shaping from the as-grown crystal using a steel cutter and the lapping. The electrodes were formed by coating the conductive epoxy (Stycast, Eccobond 56C) on both sides of the plate (**Fig.1**)



Fig.1 Sample with lead wires: this sample was placed on a substrate of a heat-flow sensor made of Peltier elements (unnecessary lead wires were cut off after setting).

2.2 Apparatus and method

The calorimeter used in this study was laboratory made,¹⁴⁾ and its basic structure was the same as that used by Wang *et al.*¹⁵⁾; however, it can be replaced by an ordinary one. A simple calorimeter suitable for student experiments will be described elsewhere.

If the scanning speed of the temperature is too fast, the substance cannot attain a stable state; thus, a warming/cooling rate of 1 mK s⁻¹ was chosen. The measurement was started at a temperature of 55 °C in the paraelectric state and cooled to 0 °C across the phase transition region; then, it was folded back to rise to 55 °C. This temperature condition can be attained by placing a calorimeter contained in a thermally insulated box in a freezer. It takes about 32 h for automated measurement to reciprocate the temperature. In the analysis described below, only data upon cooling are used; therefore, the measurement time can be decreased to a half.

For the measurement of pyroelectric current, a highly sensitive ammeter is used ordinally; instead, a shunt resistor and a general purpose digital voltmeter were employed here. A diagram of the configuration is shown in Fig.2. The shunt resistor used was a chip type metal-film resistor of 10 M Ω , and the digital voltmeter was a Keithley 2000 DMM whose input resistance could be set to a value beyond 10 G Ω . When the pyroelectric charge appeared between both electrodes of the sample, the current flowed through the resistor until the difference voltage was zero. A voltage resolution of 1 μ V that appeared at the shunt resistor corresponded to a current of 0.1 pA, which value was enough for the experiment. The amount of electricity that flowed between times 0 and t was equal to that which appeared on the electrode during that period. In the data analysis below, relative accuracy and stability of the current value were necessary, but high accuracy was not. Measurements of the current, heat-flow, and temperature were performed every 1 s and recorded.



Fig.2 Block diagram of the measurement circuit of pyroelectric current.

For the automation of measurement, the Visual Basic language attached in Excel was used. Also, the plotting of the figures and the analysis, including the determination of the regression line by the least-squares method, were conducted with N graph (free software; http://www2e.biglobe.ne.jp/%7Eisizaka/indexe.htm).

3. Experimental Result: Heat Flow and the Pyroelectric Current upon Temperature Scanning

The measured heat flow (black) and pyroelectric current (blue) are shown in **Fig.3**. The anomaly caused by the phase transition is shown in both properties. The first-order transition occurs from one phase to another through a coexistence state at a transition temperature, where the total amount of flown heat of the transition is known as the latent heat; however, the second-order phase transition occurs in an expanded temperature span.



Fig.3 Heat flow and pyroelectric current upon both cooling and warming at a rate of 1 mK s^{-1} of TGS. Each baseline is shown by red line.

The measured heat flow is in good agreement with the result given by Ema using AC calorimetry.⁹⁾ The reproducibility with cooling/warming cycles is excellent in the heat-flow measurement; however, the pyroelectric current decrease gradually by the repetition. The reason for this is the formation of polar domains¹⁶; hence, the virgin crystal is suitable for the test sample. The polar domains are known to be erased to the saturate polarization state by applying an electric field of 300 V mm⁻¹ at room temperature.

4. Analysis

It is characteristic that both the heat-flow curve and the current curve upon cooling and warming are vertically symmetrical with no hysteresis, respectively. This behavior indicates that the transition is reversible concerning the temperature rise and fall. The differential coefficients of each curve by temperature are discontinuous at the transition temperature. The phenomenon of the heat amount of an object changing discontinuously at a certain temperature is called the "first-order phase transition." However, when the heat amount changes continuously, and the first derivative of it by temperature becomes discontinuous, the phenomon is called the "second-order phase transition." Next, both the heat flow and the current rapidly change with a peak at 49 °C. Each change is sharp on the higher temperature side and gentle on the colder side. Looking at the whole, there is a temperature point at which the observed values and their derivatives with temperature exhibit singularities; thus, the anomalies decrease continuously by departing in temperature from the critical point. In short, the heat flow and the pyroelectric current change abnormally in the vicinity of the transition point and region.

It is not easy to separate the anomalous part exactly from ordinally part. Here, based on the scenario that this material has no polarization at the high-temperature side, and polarization occurs because of the transition caused by cooling, the temperature at which the pyroelectric current starts abruptly was determined as the upper limit temperature $(T_{\rm H})$ of this phase transition. It is difficult to determine precisely the lower-limit temperature of the transition, because the pyroelectric current decreases gradually with cooling and does not go to zero even at 0 °C. Here, the discussion is limited to capture the characteristics of the second-order phase transition that appeared in the vicinity of 49 °C; therefore, 0 °C was approximately determined as the lower-limit temperature, $T_{\rm L}$. By setting the pyroelectric current at 0 °C to zero, it is possible to determine a baseline (shown in Fig.3 by a red line), and the pyroelectric current caused by the phase transition, denoted by $I_P(T)$ as a function of temperature T, is calculated by subtracting the amount of the baseline.

Concerning the anomalous heat flow, it is more difficult to extract the anomalous part of the total because its variation with the temperature below the transition point is more gentle than that of the current. Furthermore, there is a slight difference in the amount of heat flow upon cooling and warming. Here, the analysis focuses on the behavior near the transition temperature, and the lower-limit temperature of the transition region, T_L is taken as 0 °C, which is the same one used in the case of the pyroelectric current.

For an observable X(T) at the temperature T, let a line connecting the point $[T_{\rm H}, X(T_{\rm H})]$ and the point $[T_{\rm L}, X(T_{\rm L})]$ on the figure be the baseline, $X_{\rm B}(T)$. At temperature T it is considered that the difference, $\Delta X(T)=X(T) - X_{\rm B}(T)$, is the part attributable to the phase transition. Hereafter, only the cooling process from the paraelectric phase to the ferroelectric one is considered.

Here, an amount of the fraction of transferred phase, $\rho(T)$, is defined as

$$\rho(T) = \int_{T}^{T_{\rm H}} X(T) dT / \int_{T_{\rm L}}^{T_{\rm H}} X(T) dT$$
(1)

which represents the fraction of the phase-translated part at temperature *T* evaluated by using the observable X,¹⁷⁾ where, $\rho(T_{\rm H}) = 0$ and $\rho(T_{\rm L}) = 1$.

4.1 Fraction of phase change calculated from the temperature dependence of pyroelectric current, $\rho_{\rm P}(T)$

When taking the pyroelectric current as the observable X in Eq.(1), the fraction denoted by $\rho_{\mathbf{P}}(T)$ is the ratio of the electric polarization at temperature T to the complete electric polarization attained at T_{L} . The graph of $\rho_{\mathbf{P}}(T)$ is shown in **Fig.4** by a black

line. This curve agrees with the order parameter in the literature. $^{4,5)} \label{eq:curve}$

4.2 Fraction of phase change calculated from the temperature dependence of heat-flow, $\rho_{\rm H}(T)$

Next, the fraction $\rho_{\rm H}(T)$ was calculated by taking the heat flow as the observed quantity X in Eq.(1), which represents the ratio of the heat released at T during the phase transition. The graph of $\rho_{\rm H}(T)$ is indicated by the blue line in **Fig.4**. The curves of $\rho_{\rm H}(T)$ and $\rho_{\rm P}(T)$ do not coincide. To investigate the relationship between $\rho_{\rm H}(T)$ and $\rho_{\rm P}(T)$, a figure of $\rho_{\rm H}(T)$ versus $[\rho_{\rm P}(T)]^n$ for some values of *n* is shown in **Fig.5**.



Fig.4 Fractions of ferroelectric phase determined by the pyroelectric current and heat flow, denoted by $\rho_{\rm P}(T)$ and $\rho_{\rm H}(T)$, respectively.



Fig.5 Relation between two kinds of fractions drawn as $\rho_{\rm H}(T)$ versus $[\rho_{\rm P}(T)]^n$: the three lines correspond to n = 1, 2, and 2.3.

The figure shows that there is a relation

$$\rho_{\rm H}(T) \doteq [\rho_{\rm P}(T)]^{2.3} \tag{2}$$

The reason for following this relationship is as follows. When electric polarization *P* occurs in the crystal, the electrical energy is proportional to P^2 . In general, the energy change caused by the ferroelectric phase transition could be structural rather than electrical. If the electric component occupies the major part in the total amount of energy change, $\rho_{\rm H}(T)$ is proportional to the square of $\rho_{\rm P}(T)$. The exponent *n* obtained from the experiment is approximately 2.3, which is slightly larger than 2. This difference in the value of *n* suggests that the orientational change of electric

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polarization may pose a change in molecular structure. This point is discussed later.

4.3 Temperature dependence of $\rho_{\rm H}(T)$

A traditional way for analyzing the specific heat in the vicinity of the second-order phase-transition-temperature is to determine a critical index α using the formula of $|T-Tc|^{-\alpha}$ or using the term of $\log(|T-Tc|)$. However, such diverging behavior was not observed in this experiment by approaching the temperature to Tc until 1 mK. An expression of the experimental data using a function is called an empirical formula; here, an empirical formula of $\rho_{\rm H}(T)$ is determined. The trial to find a regression formula with only one term and the singular temperature Tc as a parameter leads to be failed. However, an empirical formula with two terms is determined successfully as

$$\rho_{\rm He}(T) = 1 - \exp[-a(\Delta T)^{\alpha} - b(\Delta T)^{\beta}]$$
(3)

where $\Delta T = Tc - T$, $\alpha = 1$, $\beta = 3.24$, $a = 8.605 \times 10^{-2}$, $b = 1.0064 \times 10^{-5}$, Tc = 49.88 °C. The curve of $\rho_{\text{He}}(T)$ is shown in **Fig.6** by a red line and $\rho_{\text{H}}(T)$ by a black line. For the empirical formula in Eq.(3) and $\rho_{\text{H}}(T)$, the experimental curves are in good agreement with each other so as to be indistinguishable.



Fig.6 Plots of both $\rho_{\rm H}(T)$ and its empirical formula $\rho_{\rm He}(T)$ expressed by Eq.(3) as a function of temperature, using the black and red colors, respectively.

In the analysis of the second-order phase transformation, Landau's method has been widely used,^{3,8)} in which the function in Eq.(3) is expanded in series, and the coefficient of each term is obtained. However, it is not suitable for capturing the secondorder phase transition as a whole to approximate the exponential function shown in Eq.(3) into one or two Taylor expansion terms. The important points that Eq.(3) indicates are the transition behavior governed by an exponential formula as a function of ΔT and the function consisting of two terms of ΔT with different exponents. The latter point suggests the existence of different mechanisms there. The transition behavior would be separated into two regions by temperature. One region is near Tc at 42 °C < $T \leq 49.8$ °C ($0 \leq \rho_{\rm H}(T) < 0.5$), and a mechanism of ferroelectric phase formation governs the temperature dependence of $\exp[-a(\Delta T)]$. In the lower-temperature region at T < 42 °C (0.5 < $\rho_{\rm H}(T)$), another mechanism is added as a function of $exp[-b(\Delta T)^{3.24}]$. Concerning this point, there are essential reports of detailed X-ray experiments by Ito et al.^{18,19)} In their work, when the temperature is lowered below $T_{\rm C}$, the order-disorder-type transition progresses in which the electron

density distribution of N atoms becomes localized to one side from two equivalent positions; at the same time, the localized position moves gradually to the counter position; thus, the molecular structure changes. Considering the evidence, it is thought that the displacive movements of ordered atoms following an order-disorder-type mechanism promote the phase transition as expressed as the second term of ΔT in Eq.(3). Furthermore, the reason why the exponent n in Eq.(2) is larger than 2 could be that the molecular polarization is reduced by shifting the position of the N atom to the direction of the equivalent counter position. In response to the question of whether the phase transition mechanism of TGS is a displacement type or an order-disorder type, Ito et al. mentioned that the orderdisorder-type mechanism originates; however, the displacement mechanism is also involved. Therefore, it is not an ideal orderdisorder type of phase transition. The analytical result of the present experimental data supports their assertion.

5. Comparison with the theoretical results

This chapter is devoted for the learners who are unsatisfactory only by the experimental analysis described above and those who learn second-order phase transition in class. Theoretical efforts that explain the behavior of second-order phase transition and to understand the essence continue for nearly a century. These theories are learned at undergraduate program such as statistical physics and materials science; here we mention a model strongly related to TGS and their solutions.

To understand the second-order phase transition theoretically, the Ising model is useful.^{1,2,20,21,22)} In the Ising model, each element (the polarization of each TGS molecule, in this article) at each site is set as a unit by the variable σ_i , which takes only the value of +1 or -1 in the polarizing axial direction of the space, where a subscript *i* indicates the location of the site. It is assumed that the energy state differs depending on the combination of (1, 1), (1, -1) or (-1, -1) determined between the variable and its neighboring variables σ_i . Then, the value of the energy is set to -J, J, -J by the combination of (1, 1), (1, -1), and (-1, -1), respectively. When the interaction energy J is positive (corresponding to the ferroelectric), the energy becomes low and stable when the neighboring variables are ordered in the same direction. The energy E expressed by a formula becomes as follows: ^{20,22}

$$E = -J \Sigma \sigma_i * \sigma_j \tag{4}$$

The arrangement of the molecules in the space can be chosen variously, in which the two-dimensional square lattice is the most typical one. Onsager²³⁾ found in the model rigorously that a second-order phase transition occurs at a certain absolute temperature $T_{\rm C}^*$ (= $T_{\rm C}$ + 273.15), where the average value of the variable σ increases at $T_{\rm C}^*$ from zero continuously as the temperature lowered from the higher side. Although the calculation in the three-dimensional system has not yet been successfully solved, one can obtain a relational expression by using the method of the mean field approximation. The result is given as $<\sigma > = 0$ at absolute temperature $T^* > T_{\rm C}^*$, and

$$<\sigma(T^*)> = \tanh[<\sigma(T^*)>/(T^*/T_C^*)], (T_C^*=zJ/k_B)$$
 (5)

at $T^* < T_C^*$.^{21.22)} Here, *z* is the number of neighboring molecules, namely, the number of adjacent bonds per one molecule, and k_B is the Boltzmann constant. In this approximation, only *z* is taken into consideration as to the arrangement, and the dimension of space is not concerned; therefore, an inconsistency with reality may occur. The phase transition temperature T_C^* ($= Jz/k_B$) increases when the interaction *J* becomes stronger or increases in number of *z*. In another word, the stronger the interdipole interaction that forces the ordering in the same direction, the more the

ferroelectric ordering against the thermal disturbance is maintained until a higher temperature.

Here, we attempt to analyze the sharpness of the transition as an example, though other experimental observables can be considered similarly. To evaluate the sharpness of the transition on temperature, the normalized half-width W is defined as

$$W = \Delta T_{50} * / T c * \tag{6}$$

where ΔT_{50}^* is the temperature span until $\langle \sigma(T^*) \rangle$ changes from 0 to 0.5. The value of the normalized half-width W_m calculated from $\langle \sigma(T^*) \rangle$ for the Ising model using the mean-field approximation is 0.089; here, this value does not depend on the dimension of the model or on the number of nearest-neighbor sites.

On the other hand, the value of the normalized half-width determined by $\rho_{\rm F}(T^*)$ denoted by $W_{\rm P}$ is 0.0081, which is one order of magnitude smaller than $W_{\rm m}$; this difference is thought to be caused by the insufficiency of the mean field approximation, as described below.

The exact solution for the two-dimensional square lattice is given as $^{\rm 23,24)}$

$$\langle \sigma(T^*) \rangle = [1 - \operatorname{cosech}^4(\sinh^{-1}(1) (Tc^*/T^*))]^{(1/8)},$$

 $[Tc^* = 2J/(k_{\rm B}\sinh^{-1}(1))]$ (7)

Thus, the normalized transition width is given as $W_0 = 1 - \sinh^{-1}(1)/\sinh^{-1}(4/255^{0.25}) \Rightarrow 0.000785$.

The value of $W_{\rm O}$ is two orders of magnitude smaller than that of $W_{\rm m}$ (= 0.089) determined by the mean-field approximation.

Improvement of the approximation has been made by many researchers. Bethe made an advance by putting the average value to the variable at the next-nearest-neighbor site instead of that at the nearest-neighbor site, to the result

$$\langle \sigma(T^*) \rangle = \tanh(z\lambda/k_{\rm B}T^*)$$
 (8)

where λ is a parameter having a relation of ²⁵⁾

$$\tanh(\lambda/k_{\rm B}T^*) = \tanh(J/k_{\rm B}T^*) \times \tanh[(z-1)\lambda/k_{\rm B}T^*]$$
(9)

From these equations, the normalized transition width $W_{\rm B}$ is 0.0510. The value of *W* decreases and approaches to exact value by the improved approximation.

Although an exact solution of the three dimensional Ising model has not been obtained, plausible numerical values have been presented by computer simulation. Talapov and Blöte gave results using the Monte Carlo method for the cubic model as follows: ²⁶

$$<\sigma(t) > = t^{0.32694109} \times (1.6919045 - 0.34357731 \times t^{0.50842026} - 0.42572366 \times t),$$

$$t = (T_{\rm C}^* - T^*)/T_{\rm C}^*; \ T_{\rm C}^* = J/(0.2216544 \times k_{\rm B})$$
(10)

The normalized transition width W_{3S} obtained from this result is 0.0272.

Taken together, $W_{\rm O}$ (= 0.000785) < $W_{\rm P}$ (= 0.0081) < $W_{\rm 3S}$ (= 0.0272) < $W_{\rm B}$ (= 0.0510) < $W_{\rm m}$ (= 0.089). As the dimensions of the model increase from two to three, the value of W increases more than 30 times. This shows that the space in which the polarization can fluctuate spreads because of the increase of the dimension, and it becomes possible to fluctuate largely at a temperature farther from $T_{\rm C}$. Comparing $W_{\rm 3S}$ and $W_{\rm P}$, $W_{\rm P}$ is 0.3 times $W_{\rm 3S}$, and the temperature range where a large fluctuation exists is narrow; the reason for which is considered to be as follows. Whereas the Ising model considers the nearest-neighbor interaction, the electric dipole of the molecule interacts to farther sites. The long-range interaction strengthens the cooperativity and provides the suppression of the fluctuation and the decrease of W. This point is a difference from ferromagnets in which the magnetic interaction works mainly between nearest-neighbor sites. The differences between ferroelectric and ferromagnetic materials are described in Ref.2 (p.158).

The crystal structure of TGS was studied afterward, and the crystal was found to have two molecules facing each other on a mirror image plane to form one unit.²⁷⁾ If the positions of a glycine group symmetrical with respect to the mirror image plane are made to correspond to ± 1 of the variable σ the system would correspond to the Ising model. The values of W_P will be revealed in the future by computer simulation or the improved approximation.

6. Conclusion

The characteristic behavior of a ferroelectric second-order phase transition was clearly observed by the simultaneous measurements of both heat flow and pyroelectric current in TGS. From both experimental data of anomalous heat-flow and pyroelectric current, quantitative consideration of the process of the second-order phase transition as a function of temperature was performed. The analytical result agrees with the explanation of the transition mechanism given be the X-ray scattering experiment by Ito et al. A technique of simultaneous measurement of two physical quantities used here was proved to be a useful method to learn the second-order phase transition experimentally for students.

In addition to the above mentioned, in the advanced chapter 5, the experimental result was compared with the theoretical ones of a model of second-order phase transition. For the ease to compare the experimental result with the theoretical ones, the normalized transition temperature-width W is used. This index is useful for evaluating how the results depending on the model type and the approximation method agree with the experimental result. By theoretical consideration of the model, the essential mechanism of the cooperative phenomena can be understood, and the magnitude of the intermolecular interaction can be estimated.

In the present measurement of pyroelectric current, a shunt resistor and a general purpose voltmeter were used instead of a highly sensitive ammeter; the exchange cuts cost with enough sensitivity. In addition, although a laboratory-made sensitive calorimeter was used here for heat flow measurement, it can be replaced with an inexpensive calorimeter. These arrangements make it possible to do this experiment in higher education and as part of extracurricular activities in high school. The measurement is automated by PC control. Though it takes more than a day to conduct the measurement, this is inevitable for the precise observation of the second-order phase transition; though, the running time can be reduced by restricting the accuracy.

By the leaning content, the activities and the equipment mentioned above, many learners will understand the second-order phase transition deeply.

Note: Part of this content is Master Thesis, "ELECTRICAL AND THERMAL STUDY ON FERROELECTRIC PHASE TRANSITION OF TGS" (2013), Royal University of Phnom Penh, by Ms. Sun Limhuor.

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References

1) H. E. Stanley, Introduction to Phase Transitions and Critical Phenomena, Oxford University (1971); スタンリー,相 転移と臨界現象,東京図書 (1987).

- 中野藤生,木村初男,「相転移の統計熱力学」,朝倉書店 (1989); F. Nakano and H. Kimura, Statistical Thermodynamics of Phase Transitions, Asakura (1989). [only in Japanese]
- The Ferro-Electric Phase Transition and Critical Phenomena (2006), University of Michigan Advanced Physics Laboratory; http://instructor.physics.lsa.umich.edu/adv-labs/ Ferroelectrics/ phase_transitions.pdf (accessed 2019-1-07).
- S. Hoshino, Y. Okaya, and R. Pepinsky, *Phys. Rev.* 115, 323-330 (1959).
- 5) K. Itoh and T. Mitsui, Ferroelectrics 5, 235 (1973).
- 6) 三井利夫, 中村英二, 日本物理学会誌 24, 369-381 (1969); T. Mitsui and E. Nakamura, *Nihon Butsuri Gakkaishi* 24, 369-381 (1969) [only in Japanese].
- 7) Y. Tominaga and S. Iida, J. Phys. Soc. Jpn. 32, 1437 (1972).
- 8) H. V. Alexandru and C. Berbecaru, *Mater. Sci. in Semicond. Process.* **5**, 159–165 (2003).
- 9) K. Ema, J. Phys. Soc. Jpn. 52, 2798-2809 (1983).
- K. Sou, N. Ozaki, S. Matsuda, and K. Tozaki, Proc. ICPE2006, 218 (2008).
- K. Sou, T. Kato, K. Oto, T. Sakurai, K. Yamamoto, E. Omosa, and K. Tozaki, *AIP Conference Proceedings* **1263**, 175-178 (2010).
- 12) W. W. Duley and P. J. Finnegan, Am. J. of Phys. 41, 657-660 (1973).
- R. Renugadevi, G. Kanchana, and R. Kesavasamy, *Elixir Crystal Growth* 55A, 13033-13035 (2013).
- 14) K. Sou, K. Nishikawa, Y. Koga, and K. Tozaki, *Chem. Phys. Lett.* 506, 217-220 (2011),
- S. Wang, K. Tozaki, H. Hayashi, S. Hosaka, and H. Inaba, *Thermochim. Acta* 408, 31-38 (2003).
- 豊田博夫:日本物理学会誌 14, 588-589 (1959); A. Toyota, Nihon butsuri gakkai-shi 14, 588-589 (1959) [only in Japanese].
- 17) K. Sou, K. Nishikawa, Y. Koga, and K. Tozaki, J. Non-Cryst. Solids 358, 1313–1318 (2012).
- 18) K. Itoh, A. Nishikori, H. Yokomizo, and E. Nakamura, J. J. Appl. Phys. 24(s24-2), 594-596 (1985).
- 19) 伊東一幸, 日本結晶学会誌 28, 247-260 (1986); K. Itoh, *J. Cryst. Soc. Jpn.* 28, 247-260 (1986). [only in Japanese].
- 20) E. Ising, Z. Phys. 31, 253-258 (1925).
- 21) 小口武彦,「磁性体の統計理論」, 裳華房 (1970); Takehiko Oguchi, Statistical Theory of Magnetism; by SHOKABO (1970) [only in Japanese].
- 22) 八田一郎, 熱測定 29, 163-172 (2002); I. Hatta, Netsu Sokutei 29, 163-172 (2002) [only in Japanese].
- 23) L. Onsager, Phys. Rev. 65, 117-149 (1944).
- 24) J. M. Ziman, MODELS OF DISORDER, Cambridge University Press (1979); ザイマン: 乱れの物理学, 丸善 (1982).
- 25) H. A. Bethe, Proc. Roy. Soc. A 150, 552-575 (1935).
- 26) A. L. Talapov and H. W. J. Blöte, J. Phys. A: Math. Gen. 29, 5727 (1996).
- 27) J. M. Hudspeth, D. J. Goossens, and T. R. Welberry, J. Appl. Cryst. 47, 544-551(2014).

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