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Potentiality of an ac calorimetric method in the study of phase transitions

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Abstract

To manifest potentiality of an ac calorimetric method, successful application of a light-irradiation ac calorimetric method is introduced in the studies of phase transitions of quartz, ferroelectric $BaTiO_3$, and two-dimensional antiferromagnetic K_2NiF_4-family. In quartz, the α-to-incommensurate and the incommensurate-to-β phase transitions, which lie in a narrow temperature range, were clearly separated by this method. In $BaTiO_3$, the heat capacity at first-order transition was measured with high precision and, therefore, it was found that the detailed behavior at the first-order transition is well-expressed in terms of the free energy expansion. As a result, in a stress-clamped crystal in which the phase transition becomes second order, the discontinuity of the heat capacity at the phase transition was estimated to be $0.19\ k_B$. This result stimulated further theoretical investigation. From this study, it was revealed that $BaTiO_3$ is classified as a typical displacement-type ferroelectric. In order to study crossover phenomenon from a two-dimensional Ising system to a two-dimensional Heisenberg system in the K_2NiF_4 family, the critical amplitude of the heat capacity was measured as a function of the strength of Ising-like anisotropy. Based upon the analysis for the results, the existence of an asymptotic transition temperature in a two-dimensional Heisenberg system is proposed. © 1997 Elsevier Science B.V.

Keywords: ac Calorimetry; Critical behavior; Crossover; Heat capacity; Phase transition; Temperature modulated calorimetry

1. Introduction

A light-irradiation ac calorimetric method has been successfully applied for the measurement of heat capacity at phase transitions. Using this method, we can measure the heat capacity with a temperature resolution of 1 mK. Such a characteristic is strongly desired for the study of phase transitions, especially for that of critical behavior. As another advantage, this method requires only a small sample, whose weight is less than a few milligrams. In the study of phase transitions, it is also important to perform the heat capacity measurement very close to the transition temperature. For a detailed measurement of heat capacity, therefore, we need a high-quality sample. Thus, we usually perform the measurement on a small piece of a good single crystal.

In a light-irradiation ac calorimetric method, by first applying which heat capacity at the magnetic transition of Ni has been measured [1], alternatively chopped light is applied to the surface of a plate-like sample. Usually, the sample surface is coated with a black material, for instance, sprayed carbon, an evaporated film of bismuth, etc. so as to absorb light efficiently. The thickness of the sample should be

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sufficiently smaller than thermal diffusion length and, then, the temperature is uniform over the sample during the temperature modulation, which requires the high-frequency limit for the measurement. Furthermore, when chopped light is applied, the temperature of the sample increases constantly; moreover, it practically reaches a saturated temperature because there is heat-loss due to radiation, conduction, convection, etc. In connection with these facts, the surrounding of the sample is positively filled by gas so as to reduce the increase of the temperature. Therefore, the measurement can be performed at a stationary temperature when the temperature is changed stepwise, for instance, by 1 mK. Consequently, there is the low-frequency limit required for the measurement so as not to lose the ac part of applied thermal energy.

In the proper frequency range [2,3], the heat capacity C is given by

$$C = \frac{Q}{\omega T_{\mathrm{ac}}} \tag{1}$$

where Q is the amplitude of the applied thermal energy, ω is the measuring angular frequency and T_{ac} is the amplitude of the ac temperature. As already mentioned, from the high-resolution detection of ac temperature we can obtain the detailed behavior of heat capacity using a light-irradiation ac calorimetric method.

In the present paper, studies on three typical phase transitions will be discussed, to which a light-irradiation ac calorimetric heat capacity measurement was usefully applied [2,3]. These studies are comprise the separation of two successive phase transitions in a quartz (SiO_2) single crystal which lie close to each other, the typical behavior at the first-order phase transition of a $BaTiO_3$ crystal, and the critical behavior in two-dimensional antiferromagnets of the K_2NiF_4 family.

2. Phase transitions of quartz

The α-to-β transition of quartz has been studied by many researchers after the discovery by Le Chatelier in 1889 [4]. In 1983, Gouhara et al. have found an intermediate phase between the α- and β-phases by X-ray diffraction topography [5] and a fine-beam X-ray Laue method [6]. Independently, Dolino et al. also have reported the intermediate phase by differential scanning calorimetry (DSC) [7] and by neutron diffraction [7,8]. From the X-ray diffraction and neutron diffraction studies, the intermediate phase is identified as an incommensurate (IC) phase. Using an ac calorimetric method, the separation of two successive transition temperatures, α-to-IC (T_c) and IC-to-β (T_i) transition temperatures, was clearly shown and furthermore, the nature of these phase transitions was revealed [9–11].

A sample was prepared from the Y-cut plates of a Y-bar synthetic quartz crystal (Kinseki, Japan). The Z-growth sector was used as a sample, because the Z-growth sector contains less OH impurity than the other sectors. In fact, the plate of the Z-growth sector was characterized by X-ray diffraction topography prior to the preparation of a sample, and the best part was chosen where fewer dislocations exist. After thinning and etching, a sample for the heat capacity measurement was finally obtained, with dimensions of $\sim$4 mm^2 in area and $\sim$50 mm in thickness.

The ac temperature of a sample was measured by a thermocouple composed of Chromel and Alumel wires of 50 mm diameter (Omega Engineering, USA) that was glued to the sample with silver paste. The sample, which was suspended in a vessel, was periodically heated by a chopped-light beam from a halogen lamp [1–3]. The sample was suspended by a pair of thermocouples as shown in [2]. A pair of thermocouples was connected to relatively thick copper lead wires in the vessel: one served for the detection of ac temperature and the other for the measurement of the dc temperature increment beyond the temperature of the vessel as shown in [2]. The amplitude of the temperature oscillation was about 3 mK. The validity of Eq. (1) was tested by measuring T_{ac} as a function of angular frequency ω at a fixed temperature, since the derivation from Eq. (1) took place at frequencies lower than the low-frequency and higher than the high-frequency limit, and then, the chopping frequency was set at 4 Hz. A similar apparatus could be used for the following measurements for a $BaTiO_3$ crystal and a K_2NiF_4 family, since there was no significant difference among the measurements of ac temperature using a Chromel/Alumel thermocouple. As seen in Eq. (1), to obtain the absolute value of heat capacity, it is necessary to determine the value of Q given by light irradiation or calibrate the

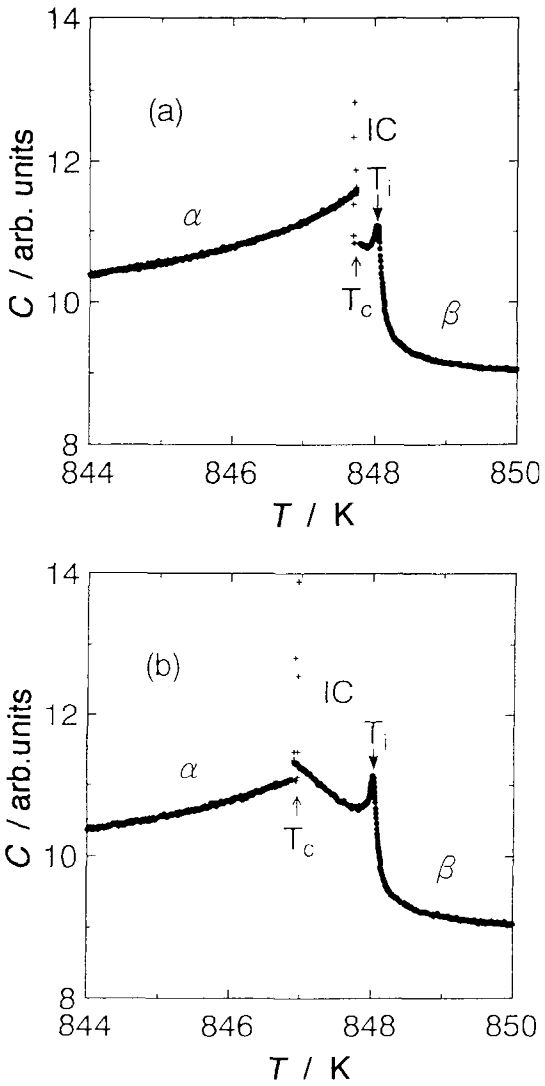

Fig. 1. Heat capacity of a quartz (SiO_2) crystal in the α-, incommensurate(IC)- and β-phases. (a) Heating. (b) Cooling. Both heating and cooling rates were 0.05 K min^{-1}. At the α-to-IC transition, + indicates the apparent heat capacity at the mean temperature. Note that the curve obtained by connecting the crosses is not straight due to the existence of latent heat. Comparing between the results on heating and cooling, we can see large thermal hysteresis at the α-to-IC transition, and on contrary, coincidence near the IC-to-β transition and above this transition temperature.

heat capacity by the other method and in fact, in the measurements for a $BaTiO_3$ crystal and the K_2NiF_4 family it was performed in the way discussed in the following sections.

The detailed heat capacity near T_c and T_i for a high-quality crystal is clearly shown as a function of temperature in Fig. 1(a) and (b) in heating and cooling, respectively, although the two transition temperatures are close to one another [11], namely, the temperature region of the IC phase ($= T_i - T_c$) is less than 0.5 K and, furthermore, the separation of the two phase transitions is shown clearly. This situation is quite similar to that for the successive phase transitions of $NaNO_2$ [12]. In the above figures, the ordinates are scaled in arbitrary units, but both the results can be compared with each other since the intensity of light is common. For the present purpose, this plot is sufficient. As will be discussed later, in a light-irradiation ac calorimetric method, to get the absolute value of heat capacity, the other experiment to calibrate the heat capacity or the estimation of the value of Q is necessary.

In quartz, the heat capacity at T_c exhibits a distinct jump and some contribution of latent heat appears (see crossed points in Fig. 1(a) and (b)) in both heating and cooling. Furthermore, there is hysteresis of T_c in heating and in cooling. These facts indicate that α-to-IC transition is of the first order. On the other hand, no thermal hysteresis appears at T_i. Therefore, the heat capacity exhibits critical behavior at T_i and, consequently, the shapes of the curves are identical in heating and in cooling. These facts indicate that the IC-to-β transition is of the second order. In a further study, it is of interest to analyze the heat capacity from the viewpoint of critical behavior in a three-dimensional XY system.

3. Phase transition of ferroelectric barium titanate

In $BaTiO_3$, it has been well established, from the various experiments, that the ferroelectric-to-paraelectric transition is of the first order [13]. However, the results of the heat-capacity studies do not give clear evidence for the behavior at the first-order transition. An ac calorimetric method has potentiality in the study of the detailed behavior of the heat capacity, if a high-quality crystal is used.

A sample was cut from the crystal grown by a top-seeded solution technique, from which we could expect to obtain a good single crystal with less impurities. The dimensions were ~4 mm^2 in area and ~50 mm in thickness. The detailed behavior of the heat capacity at the transition temperature T_c, obtained by a light-irradiation ac calorimetric method is shown in Fig. 2 [14]. The scale of the ordinate was calibrated by the heat capacity obtained by Todd and Lorenson [15] at 301.23 K, which is far lower than the transition temperature.

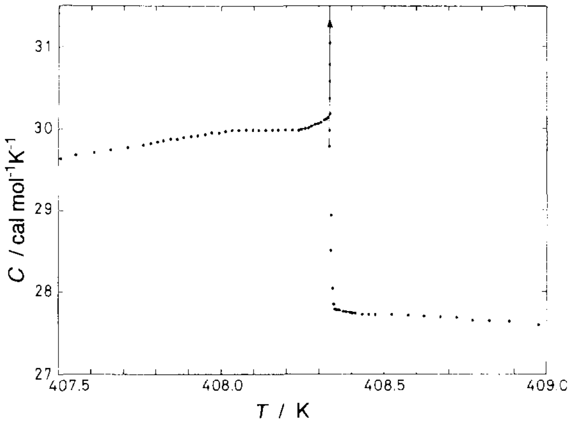

Fig. 2. Temperature dependence of the heat capacity near the transition temperature for a $BaTiO_3$ crystal grown by a top-seeded solution technique.

A clear anomaly indicating first-order transition appears at T_c, i.e. the heat capacity exhibits a distinct jump and in addition a contribution of latent heat at T_c [14]. The same behavior is observed at the first-order transition of quartz as mentioned earlier. Therefore, it can be concluded that it is a common characteristic of first-order transitions. It is noteworthy that this is just the behavior predicted from the thermodynamic theory. A similar experiment was carried out in a sample cut from a $BaTiO_3$ crystal obtained by a flux method. The behavior of heat capacity is quite similar to that for a crystal grown by a top-seeded solution technique, but a gradual decrease in the heat capacity above T_c appears and T_c is slightly lower than that of a crystal grown by the top-seeded solution technique. The slope of heat capacity above T_c might be due to the dispersion of transition temperature arising from the impurities in the crystal, which are usually fluorine of up to 0.3% and potassium of several hundred ppm.

The above-mentioned behavior is well expressed in terms of the coefficients of the series expansion of the free energy for a stress-free crystal against the polarization, where the coefficients have been obtained from the analysis of the data of the dielectric constant and spontaneous polarization. These facts indicate that the measured quantities are consistently well expressed in the free energy. Furthermore, it means that the phase transition of $BaTiO_3$ can be considered within the framework of molecular field theory. For further theoretical consideration, we need to know the heat capacity for a stress-clamped crystal, because usually the theory is constructed under this condition. For this purpose, the coupling terms – between the polarization and the stress – which have been obtained from the other experiments are added to the free energy. As a result, in a stress-clamped crystal of $BaTiO_3$ the phase transition becomes of the second order. The discontinuity ΔC of the heat capacity at the second-order transition is estimated from the experimental results as

$$\Delta C = 0.19 k_B, \quad (2)$$

where k_B is the Boltzmann constant. This is far smaller than $(3/2)k_B$, which is the discontinuity at the order–disorder limit.

In connection with the aforementioned facts, it is of interest to consider whether ferroelectric $BaTiO_3$ belongs to displacement or order–disorder type. In this context, Onodera and Kojyo [16] have carried out a theoretical study, in which they have proposed that the relation between the ratio μ_c/μ_s, of the paraelectric dipole moment μ_c to the saturation dipole moment μ_s, and the discontinuity ΔC of the heat capacity at the transition temperature gives further evidence for the type of ferroelectric phase transition. Based upon a coupled anharmonic-oscillator model, the paraelectric dipole moment μ_c, which is defined through the Curie constant, and the saturation dipole moment μ_s, obtained from the spontaneous polarization, has been calculated in the molecular-field approximation and, thus, the ratio, μ_c/μ_s, has been defined [16]. In the order-disorder type, $\mu_c/\mu_s \approx 1$ and, on the other hand, in the displacement type, $\mu_c/\mu_s > 1$. To obtain further evidence for the type of ferroelectric phase transition, Onodera and Kojyo have pointed out that the relation between μ_c/μ_s and ΔC is effective, which is shown in Fig. 3 together with the results of $BaTiO_3$ obtained from the experiments.

As discussed in the paper of Onodera and Kojyo [16], in Fig. 3 the curve starts at the point, $\mu_c/\mu_s = 1$ and $\Delta C = (3/2)k_B$, which corresponds to the order–disorder limit. When μ_c/μ_s increases, the curve rises steeply and ΔC becomes smaller, that is, the behavior is close to that characteristic of the displacement type. The data point obtained experimentally lies close to the point for the displacement type, as seen in Fig. 3, in other words, ferroelectric $BaTiO_3$ is characterized as the displacement type not only from the discontinuity ΔC but also from the ratio μ_c/μ_s.

Finally, it should be stressed that, from the detailed behavior of heat capacity, we can make clear the type of the phase transition mechanism.

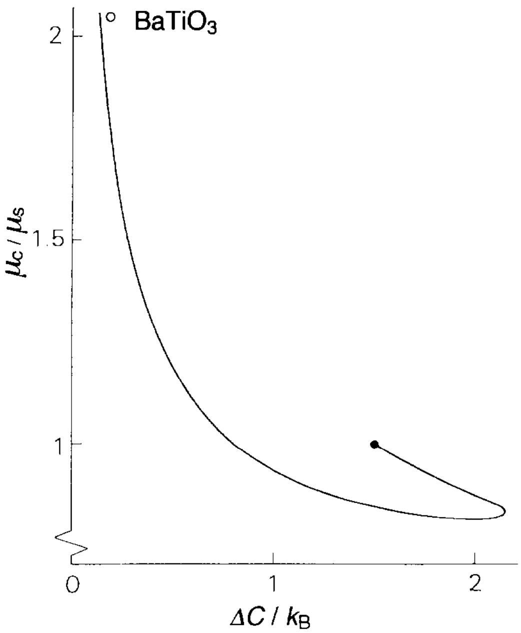

Fig. 3. Relation between the ratio μ_c/μ_s and ΔC in terms of the Onodera–Kojyo model. The empty circle at the top left refers to the experimental data for $BaTiO_3$.

4. Critical behavior of a two-dimensional system

The K_2NiF_4 family is a typical two-dimensional (2d) antiferromagnet. The magnetic Ni atoms are arranged in a quadratic lattice in a NiF_2 layer lying between KF layers. The ratio of the interlayer exchange energy J' to the intralayer exchange energy J, $|J'/J|$, is estimated to be 10^{-6}. Therefore, the critical behavior of the K_2NiF_4 family is characterized as a 2d Ising-like anisotropic Heisenberg system.

I have focused my attention to the crossover phenomena from a 2d Ising system to a 2d Heisenberg system [17]. For this purpose, we have carried out the ac calorimetric measurement of the critical heat capacity for the crystals of the K_2NiF_4 family with a variety of the strength of Ising-like anisotropy [18]. The spin Hamiltonian in the antiferromagnetic K_2NiF_4 family is given in [18]

$$H = 2J\sum_{i,j}[(1-\Delta)(S_i^x S_j^x + S_i^y S_j^y) + S_i^z S_j^z] \quad (3)$$

where the summation runs over all pairs of nearest-neighbor spins at ith and jth sites on the quadratic

Table 1
Anisotropy parameters Δ in the 2d anisotropic Heisenberg antiferromagnets studied.

	Heisenberg model	K_2NiF_4	K_2MnF_4	$Rb_2Mn_{0.5}Ni_{0.5}F_4$	Rb_2NiF_4	Ba_2NiF_6	K_2CoF_4	Ising model
Δ	0	0.0020	0.0039	0.0071	0.0084	0.03	0.488	1

lattice and Δ the anisotropy parameter. When $\Delta=0$, Eq. (3) becomes the spin Hamiltonian of a 2d Heisenberg system and, on the other hand, when $\Delta=1$, Eq. (3) becomes the spin Hamiltonian of a 2d Ising system. The antiferromagnets of the K_2NiF_4 family studied are K_2NiF_4, K_2MnF_4, Rb_2NiF_4, Ba_2NiF_6, and K_2CoF_4 whose anisotropy parameter, together with that for $Rb_2Mn_{0.5}\,Ni_{0.5}F_4$ is presented in Table 1.

According to universality, the critical exponent of the heat capacity for the K_2NiF_4 family is always the same as that for a 2d Ising system, i.e. the heat capacity diverges logarithmically at the transition temperature. In fact, the heat capacities observed for all of the above antiferromagnets exhibit logarithmic divergence, that is, $\alpha_I = \alpha_I' = 0$ where α_I and α_I' are critical exponents above and below the transition temperatures, respectively. For example, Fig. 4 exhibits the typical heat capacity for Ba_2NiF_6 near the transition temperature. The data can be well expressed by a logarithmic divergent equation as

$$C = A|\ln|t|| + B + Et \quad (4)$$

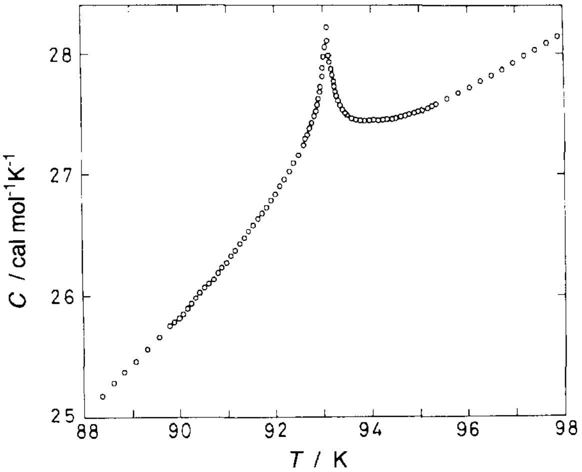

Fig. 4. Heat capacity of two-dimensional antiferromagnet Ba_2NiF_6 near T_c where 1 cal=4.1855 J.

above the transition temperature T_c, and by the same equation with primed coefficient below T_c, where,

$$t = (T - T_c)/T_c$$

and A, A', B, B', E and E' are coefficients. Consistent with the 2d Ising critical behavior, the relation, $A = A'$, holds.

I will discuss the experiment briefly. The high-quality single crystals used in the ac calorimetric measurements have a weight less than 10 mg. Thus, the systematic ac calorimetric measurement could be performed over a small amount of the high-quality single crystals. The absolute value of the heat capacity was measured using the thermal relaxation method for the same crystals [19]. The heat capacity could be determined within an accuracy of 5%. In the heat capacity, the contribution of the addenda such as coated black material, thermocouple, glue, etc. were included, however, none of these was troublesome for the study of the critical behavior because it only put an additional background to $B + Et\,(\text{or}\,B' + E't)$ and, thus, the critical amplitude was not affected.

My attention has been drawn to the fact that, although the critical heat capacity of the antiferromagnets studied shows 2d Ising critical behavior, the critical amplitude A $(= A')$ depends markedly on the anisotropy parameter Δ. Therefore, to study crossover phenomenon from a 2d Ising system to a 2d Heisenberg system, it is of interest to clarify the relation between the critical amplitude and the anisotropy parameter. The relation is depicted in Fig. 5. The antiferromagnets indicated in Table 1 have a variety of spin numbers and, then, in Fig. 5 the ordinate is normalized at $S = 1/2$ for the quantitative comparison. In Fig. 5, the exact solution for a 2d Ising system is also plotted. The experimental results are well expressed a priori by

$$A/R = (2/\pi)[\ln(\sqrt{2} + 1)]^2\Delta^{1/2} \quad (6)$$

where R is the gas constant. It is quite surprising that

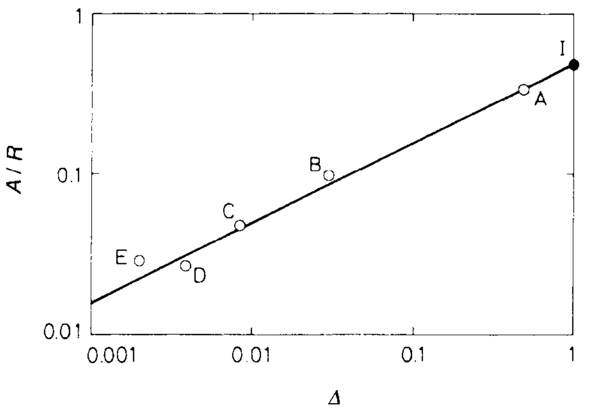

Fig. 5. A double logarithmic plot of the critical amplitude of the heat capacity vs the anisotropy parameter. Closed circle (*I*) shows the point for the exact solution in a 2d Ising system. A: K_2CoF_4, B: Ba_2NiF_6, C: Rb_2NiF_4, D: K_2MnF_4, and E: K_2NiF_4. The straight line shows an empirical relation.

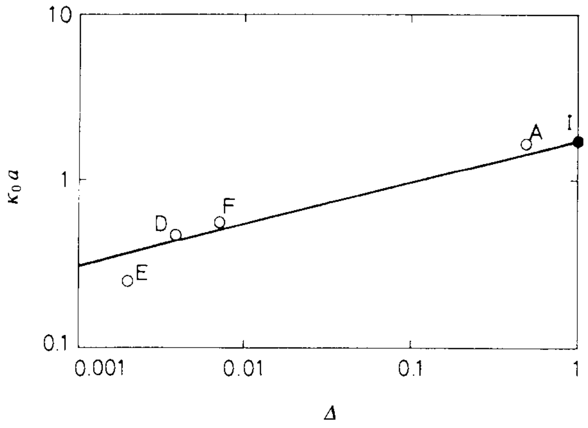

Fig. 6. A double logarithmic plot of the coefficient of the inverse correlation length vs. the anisotropy parameter. Closed circle (I) shows the point for the exact solution in a 2d Ising system. A – K_2CoF_4; D – K_2MnF_4; E – K_2NiF_4; and F – $Rb_2Mn_{0.5}Ni_{0.5}F_4$. The straight line shows an empirical relation.

such a simple relation holds over the wide range of the anisotropy parameter Δ from 0.0020 to 1.

To obtain further evidence, let us reconsider the inverse correlation length κ. When $\Delta = 1$ (i.e. in a 2d Ising system),

$$\kappa = \kappa_0 |t|^{\upsilon_{\mathrm{I}}} \text{ with } \upsilon_{\mathrm{I}} = 1 \tag{7}$$

$$\kappa_0 a = 2\ln(\sqrt{2} + 1) \tag{8}$$

where a is the lattice spacing of the quadratic lattice. Under the scaling relation $d\upsilon_{\mathrm{I}} = 2 - \alpha_{\mathrm{I}}$ with $d = 2$, Stauffer et al. [20] have proposed the two-scale-factor universality,

$$\frac{A/R}{(\kappa_0 a)^2} = \frac{1}{2\pi} \tag{9}$$

in a 2d Ising universality class. This means that Eq. (9) can be applied not only to a 2d Ising system (Δ=1) but also to a 2d Ising universality class (Δ>0). In Eq. (9), *A*/*R* is given by Eq. (6) and as a result, $\kappa_0 a$ depends on Δ. Then, from Eqs. (6) and (9) we can predict the following relation:

$$\kappa_0 a = 2\ln(\sqrt{2} + 1)\Delta^{1/4} \tag{10}$$

In this way, I re-examined the empirical relation between $\kappa_0 a$ and Δ in a 2d Ising-like anisotropic Heisenberg system, based on the data obtained from neutron diffraction. As seen in Fig. 6, the experimental results are consistent with Eq. (10). This is the further surprising result.

Under the assumption that, when Δ becomes close to naught, T_c tends to an asymptotic transition temperature and the crossover scaling function leads to

$$A/R \sim \Delta^{(\alpha_{\mathrm{I}} - \alpha_{\mathrm{H}})/\phi} \tag{11}$$

$$\kappa_0 a \sim \Delta^{(\upsilon_{\mathrm{H}} - \upsilon_{\mathrm{I}})/\phi} \tag{12}$$

where ϕ is the crossover exponent of the transition temperature from a 2d Ising system to a 2d Heisenberg system [21]. Comparing Eq. (6) and Eq. (10) with Eq. (11) and Eq. (12), respectively, we can obtain

$$-\frac{\alpha_{\mathrm{H}}}{\phi} = \frac{1}{2} \tag{13}$$

$$\frac{(\upsilon_{\mathrm{H}} - 1)}{\phi} = \frac{1}{4} \tag{14}$$

since $\alpha_I = 0$ and $\upsilon_I = 1$. Eqs. (13) and (14) satisfy the following relation:

$$d\upsilon_{\mathrm{H}} = 2 - \alpha_{\mathrm{H}} \text{ with } d = 2 \tag{15}$$

The foregoing results are consistent with the fact that there is an asymptotic transition in a 2d Heisenberg system.

Until now, there is no widely accepted theory which undoubtedly indicates the existence of the asymptotic transition temperature in a 2d Heisenberg system. In such a situation, the simple and meaningful relations of Eq. (13) and Eq. (14) should be interpreted theoretically.

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