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Networking and Cooperative Dynamics in Complex Physical Systems (II)

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Abstract

Phase transition and critical phenomena in some complex physical systems of layer structure are examined from the viewpoint of networking and cooperative dynamics. There are included critical phenomena at the phase transitions of a Heisenberg-type antiferromagnet $Cu(HCOO)_2.2H_2O.2CO(NH_2)_2$ and of an organic superconductor κ-$(BEDT\text{-}TTF)_2Cu(NCS)_2$. The characteristic features are all concerned with highly developed short range order coming from the two-dimensional lattice structure and also with a remarkable effect of weak interlayer coupling near the critical point. Such characteristic critical phenomena of these systems suggest an occurrence of phase transitions associated with a symmetry breaking on chiral degree of freedom.

1 .Introduction

Phase transition and cooperative dynamics in the natural world have long attracted a great attention of scientists. For the study of ordering characteristics, low dimensional systems are interesting because the cooperativity is strongly reduced geometrically[1]. Among these, a two-dimensional (2D) system especially with frustration and/or quantum fluctuation in the interaction network may be interesting further, because the cooperative action would be suppressed more extensively by the factors. Indeed, a triangular (△) antiferromagnet[2] and a quadratic Heisenberg (□H) antiferromagnet[3] have been predicted theoretically not to show any spin long range order (LRO) at a finite temperature. Spin glass with isotropic interaction (XY- or H-type)[4] and superconductive ceramics[5] are also interesting from the analogous cooperative situation in the systems.

Experimentally, in any spin systems which approximate such a model mentioned above, a phase transition into a 3D LRO has been observed at a finite temperature, although with somewhat peculiar critical phenomena[1]. It has usually been taken to be the effects of weak interlayer interaction and/or partial elimination of frustration by small lattice distortion and of quantum fluctuation by small Ising(I)-type anisotropy in the real systems. Some of the critical phenomena, however, have been still remained so far to be solved, which may bring a finding of a new type of phase transition into a novel orderd state. In this paper, two such

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examples are discussed, (1) a S=1/2 layer antiferromagnet $Cu(HCOO)_2.2H_2O.2CO(NH_2)_2$ and (2) a layered superconductor κ-(BEDT-TTF)$_2$Cu(NCS)$_2$. A possible appearance of phase transitions associated with a symmetry breaking on chiral degree of freedom is suggested in the both systems.

2.Critical Phenomena of $Cu(HCOO)_2.2H_2O.2CO(NH_2)_2$

2-1.General Feature

$Cu(HCOO)_2.2H_2O.2CO(NH_2)_2$ is a layer structure compound[6], as shown in Fig.1. Each antiferromagnetic copper formate layer are separated by H_2O and $CO(NH_2)_2$ molecules. The exchange interaction J' between the layers is thus much weaker than the intralayer one J (=33 K)[7]. The anisotropy energy of I-type is estimated much smaller than the exchange one[8]. The system is thus a typical example of a 2DH antiferromagnet of S=1/2, which has been theoretically predicted not to order at all even with a small anisotropy probably by the large quantum fluctuation[3].

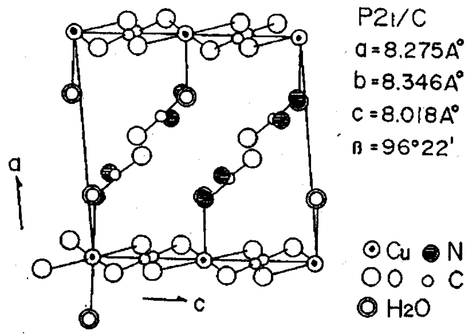

Fig. 1 Crystal structure of $Cu(HCOO)_2.2H_2O.2CO(NH_2)_2$

Contrary to the prediction, a phase transition was identified to appear at a rather high temperature (~ 0.5J/k) by the distinct peak of magnetic susceptibility χ at zero DC field[7]. A negligibly small but finite anomaly of heat capacity was observed at the critical temperature T_N[7]. A spontaneous staggered magnetization was observed to appear below T_N[9]. The distinguishable increase of χ above T_N[7], which is never observed in usual antiferromagnets, was then identified to show the critical divergence of staggered susceptibility of the compound, through the staggered field effect coming from the in-equivalence of g-tensors at the different sub-lattice points[10]. The appearance of antiferromagnetic LRO was first speculated due to a weak interlayer interaction or an I-type anisotropy in the system. From the viewpoint of scaling law and universality, the values of critical exponents are considered useful information to examine the origin of the phase transition.

2.2.Spontaneous Staggered Magnetization

In order to examine the characteristic of the phase treansition, spontaneous staggered magnetization was derived by detailed analysis of proton NMR frequencies at the formate radical[10]. The obtained temperature dependence of NMR frequencies is shown in Fig.2(a). It shows a single exponential grow up of staggered magnetization below T_N with a critical

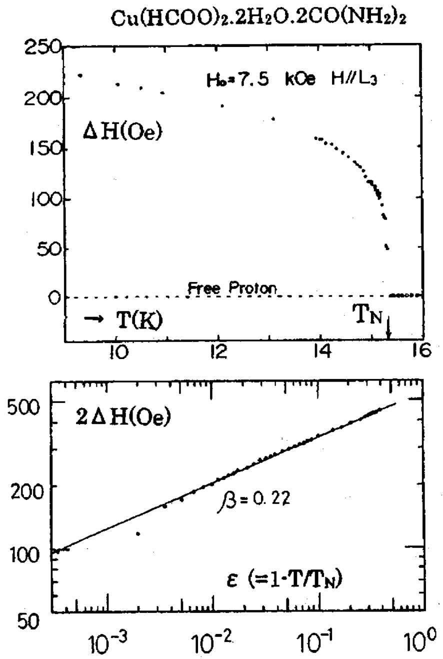

Fig. 2 Temperature dependence of spontaneous staggered magnetization

exponent β = 0.22 over the whole measured temperature range as shown in Fig.2(b) with the value of T_N quite consistent with the susceptibility measurement. The remarkable fact that the value of β is quite different from both 0.3 for 3DH model or 0.125 for 2DI model, and out of the experimental error, which suggest that the origin of the phase transition is not simply attributable to possible inter layer interaction and/or I-type anisotropy.

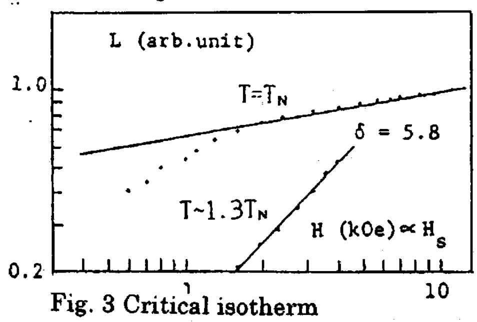

Fig. 3 Critical isotherm

2-3. Critical Isotherm of Staggered Magnetization

For the present system, the critical isotherm of staggered magnetization is observable by using the staggered field effect mentioned above, while it is quite impossible in usual antiferromagnets. For further examination of critical phenomena, the observation of critical isotherm was carried out by proton NMR in the external magnetic field, much weaker than the exchange field[11]. The result is shown in Fig.3. The derived critical exponent $\delta = 5.8$ is quite different from both for 3DH model and for 2DI model, as in the case of β for spontaneous staggered magnetization .

2-4.Discussion

If the scaling hypothesis is applicable in the present system, the values of other critical exponent can be derived by using the so called scaling laws from the obtained β and δ values. The exponents for heat capacity and staggered susceptibility α and γ are estimated 0.46 and 1.1, respectively. Unfortunately, the comparison of α with experiment is impossible because of too weak heat capacity anomaly at T_N. The obtained value of γ is found rather consistent with the susceptibility measurement. The obtained values of critical exponents for the present system are summarized in Table 1 with the theoretical value for 3DH and 2DI models. The comparison apparently reveals that the universality class of the phase transition in the present system is qualitatively different from those for the simple

Table 1 Critical exponents

	α	β	γ	δ
2DI	0	0.125	1.75	15
3DH	-0.1	0.35	1.33	4.8
present	(0.46)	0,22	(1.1)	5.8
SO(3)	0.4	0.25	1.1	5.4

( ): estimated value by scaling laws

magnetic systems studied so far.

Meanwhile, the ordering of a single △ antiferromagnet of H- type has been examined theoretically. The system was predicted to show a phase transition at a finite temperature into a new ordered state not of collinear spin degree of freedom but of a chiral degree of freedom[12]. Afterwards a layered △ antiferromagnet of H- or XY-type was also examined theoretically by Kawamura[13]. The phase transition was found to belongs to a new universality class (SO(3)), associated with symmetry breaking of a chiral degree of freedom as well as a usual collinear spin degree of freedom. The predicted critical exponents are included in Table 1 for a comparison. According to the theory, the layered □H antiferromagnet with spin canting interaction is found also to belongs to the same chiral universality class[13]. From the location of T_N, which is much higher than that expected from the possible interlayer interaction and/or I-type anisotropy, and from the obtained values of critical exponents, the phase transition of the present system is suggested to belongs to a chiral universality class and stimulated mainly by highly developed short range order (SRO) on the chiral degree of freedom.

If such a speculation is the case, a considerable amount of spin reduction i.e. a diminution of staggered magnetization below T_N is expected in the ordered state in addition to the spin reduction by usual spin wave excitation in the □H antiferromagnet. Experimentally, a large spin reduction, which amount to about 50 %, was derived by precise analysis of proton NMR frequencies at low temperature[14]. For further confirmation, a direct observation of chiral fluctuation by e.g. neutron scattering experiment is requested.

3. Critical Phenomena of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$

3-1.General Feature

κ −(BEDT-TTF)$_2$Cu(NCS)$_2$ is an organic superconductor of a layer structure[15]. As shown in Fig.4, each conductive BEDT-TTF layer is separated from the others by an insulating Cu(NCS)$_2$ layer. An ideal 2D superconductor is predicted to show a Kosterlitz and Thouless (KT) type phase transition into a quasi LRO with a divergence of correlation length ξ of superconductive local order parameter at a finite temperature. Experimentally, the electric resistivity ρ decreased rapidly around 10 K and disappeared perfectly at about 9 K indicating an appearance of

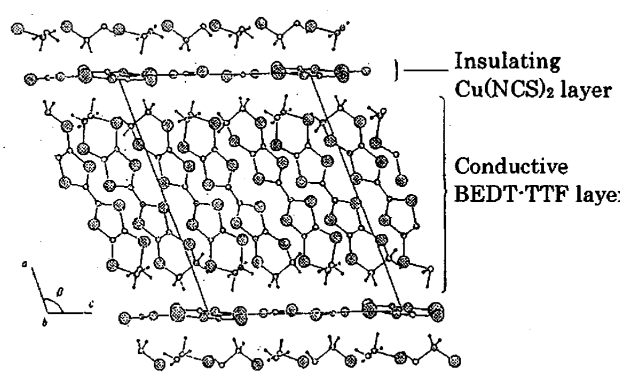

Fig. 4 Crystal Structure

superconductivity over the whole system. Indeed, AC susceptibility measurement at a weak field amplitude shows that linear susceptibility χ_0 decreases rapidly around 9 K showing diamagnetism below the temperature. The onset temperature Tc of the 3D superconductive LRO is thus reasonably estimated to be about 9 K.

Meanwhile, a similar two step behavior has been observed in the superconductive ceramic of $YBa_2Cu_4O_8$[18]. In the case, it was reasonably described as successive superconductive transitions from the intra- to inter-grain ordering based on the ceramic structure. The transition into the superconductive LRO over the whole system is established in the Josephson coupled inter-grain network. Theoretically, such a Josephson coupled network is equivalent to 3D random XY model and therefore to a XY spin glass, if there is some frustration in the network. For the latter, a chiral glass ordering or a phase transition into a glassy ordered phase on chiral degree of freedom was theoretically predicted to occur[5]. The transition is then predicted to be identified by negative divergence of nonlinear magnetic susceptibility χ_2[5], analogously with the case of spin glass ordering. The interlayer interaction of the present system is certainly of a Josephson type through the intermediate insulating layer. The examination of χ_2 anomaly around Tc would be interesting.

3-2.Linear and Nonlinear Susceptibility

By AC magnetic measurement, χ_0 and χ_2 are derived simultaneously from the fundamental and third-harmonic in-phase Fourier components M'_ω and $M'_{3\omega}$ to AC excitation field $h\exp(i\omega t)$ by the relations,

$$\chi_0 = \lim_{h,\,\omega\to 0} M'_\omega/h, \quad \text{and} \quad \chi_2 = -4\lim_{h,\,\omega\to 0} M'_{3\omega}/h^3, \qquad (1)$$

respectively. Measurements at low frequencies and at weak field amplitudes are thus essential. As a typical examples, the temperature dependences of $M'_\omega/h(=\chi')$ and $M'_{3\omega}/h^3$ (at $\omega/2\pi = 300$ Hz and at h =0.1 Oe) are shown in Fig. 5(a) and (b), respectively[19]. Consistently with previous measurements so far, χ' shows an inflection at about 9 K, indicating the onset of diamagnetism. At the temperature, $M'_{3\omega}/h^3$ shows a sharp peak suggesying a negative divergence of χ_2 at Tc. Indeed the peak value is found to increase with decreasing h[19]. It will, therefore, show an intrinsic critical phenomenon of the present system.

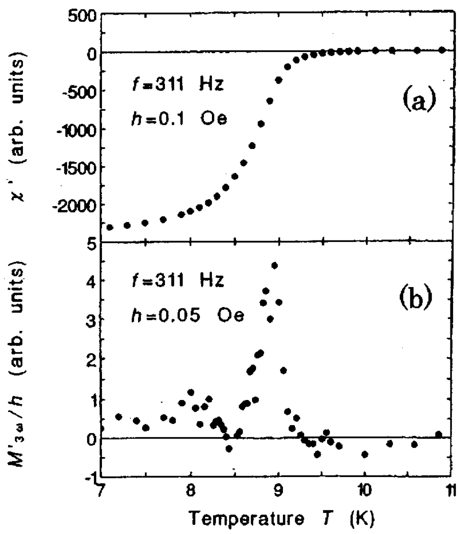

Fig. 5 Linear and nonlinear magnetic responses

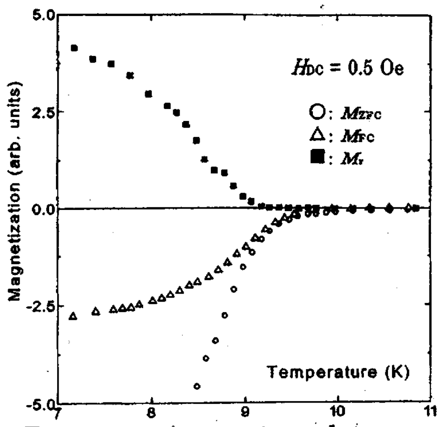

Fig. 6 Temperature dependence

3-3.DC Magnetization

The necessary condition for the onset of chiral glass ordering in superconductive ceramics is an inclusion of frustration in the Josephson coupled network among the grains. Any such a frustration can not be expected in a simple regular quasi 2D systems. For further information, DC magnetization measurement was systematically carried out in detail[20]. Experimental results at a DC field of 0.5 Oe, is shown in Fig. 6 as an example. As seen in the figure, the thermoremanent magnetization Mr disappears at about 6 K as increasing temperature. Correspondingly, the field cooled and zero field cooled magnetizations, M_{FC} and M_{ZFC} agree at the temperature. A remarkable fact is that both M_{FC} and M_{ZFC} do not disappear around T_C, further increase continuously above T_C and disappear gradually around 10 K. Such a diamagnetic behavior above T_C could not be simply explained by so called Meissner effect, because it should be attributed to a superconductive SRO.

3-4.Discussion

As mentioned above, it is difficult to reconcile the negative divergence of χ_2 well with other experimentally observed critical behaviors, if we assume a simple quasi-2D lattice structure that each conductive layer is perfect and extended infinitely. In the case, any frustration could not be introduced in the ordering process above T_C. Then, we assume here a modulated quasi 2D lattice structure, in which each conductive layer is divided into many clusters of finite size. The ordering situation will then be quite different.

In a 2D superconductor, a KT type Phase transition will appear at a finite temperature $T^{(2)}$. Then the correlation length ξ of local superconductive order parameter increases divergently towards $T^{(2)}$ as temperature decreases. If each 2D layer is not perfect, the growing up of ξ once stops at a certain geometrical length r_0. Further growth of ξ should be brought by inter-cluster interaction through the boundary region within each layer. If the intercluster coupling is of a Josephson type, the Josephson coupled network will be formed among the short range ordered clusters above T_C. As the result, the ordering process will crossover successively, from the 2D to Josephson-coupled 2D and finally to Jpsephson coupled 3D regimes. According to the highly developed SRO, the final ordering situation near $T^{(2)}$ could be similar to that for the superconductive ceramic near the inter-grain transition point. Such a qualitative similarity of ordering situation of a modified quasi 2D system to the superconductive ceramic may describe the chracteristic critical phenomena of the present system including the negative divergence of χ_2, suggesting a chiral glass ordering. For further confirmation, a nonlinear resistivity measurement is recommended, which will show a divergent singularity at the chiral glass ordering temperature[21].

4.Summary

In this paper, the ordering characteristics in two complex physical systems of layer structure are examined from the viewpoint of networking and cooperastive dynamics. In both cases, the phase transition and the critical phenomena are different from those for usual simple systems. In $Cu(HCOO)_2.2H_2O.2CO(NH_2)_2$, suppression of cooperative action by large quantum fluctuation could be overcome by some spin canting mechanism in the interaction network, which can result in the phase transition associated with a chiral symmetry breaking. In κ-(BEDT-TTF)$_2$Cu(NCS)$_2$, an imperfect lattice structure i.e. an inclusion of cluster structure in each 2D layer could introduce a frustration in the interaction network, which can result in the phase transition into a chiral glass phase.

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