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Networking and Cooperative Dynamics in Complex Physical Systems (Ⅲ)

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Abstract Phase transition and critical phenomena in some complex physical systems are examined from the viewpoint of networking and cooperative dynamics. Successive magnetic transitions of a hierarchical nature, observed in some graphite intercalation compound and identified as the characteristic phenomena of a 'ceramic' from the ceramic-like heterogeneous lattice structure, are reexamined in detail. The system is concluded to be in a spontaneously induced glassy phase in the intermediate temperature region between the upper and the lower critical temperatures. Possible mechanism for the formation of such a new ceramic phase is discussed, including the characteristic memory phenomena across the lower critical temperature.

1. Introduction

Phase transition and the cooperative dynamics in the natural world have long attracted a great attention of scientists. As mentioned in the preceding papers of the present series, random and frustrated systems are attractive from the viewpoint of networking and cooperative dynamics [1,2]. Spin glass is a perfectly random and frustrated system but homogeneous from the viewpoint of cooperativity. Heterogeneous system like ceramics is morphologically complex and should be more attractive from the following reasons.

A ceramic is generally composed of crystalline mesoscopic clusters, coupled mutually through the random interface boundaries [3]. It is therefore regular in microscopic scale but random and frustrated in mesoscopic scale and morphologically complex. Ordering of such a system will necessarily proceed successively from the intra- to inter-cluster direction in a hierarchical way, which should result in a characteristic 'ceramic' phase. It would practically be a literary intermediate phase in which the system is ordered inside each cluster but disordered among the clusters. Actually in some graphite intercalation compounds ($CoCl_2$- or $NiCl_2$-GIC) and in superconductive ceramics of $YBa_2Cu_4O_8$, phase transitions have been observed at two successive temperatures[3]. The intermediate state

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between the temperatures was then identified to be just such a 'ceramic' phase as discussed already in the previous papers[1].

In the present paper, the characteristics of successive phase transition of stage 2 $CoCl_2$-GIC i.e. nonlinear magnetic responses around the upper critical temperature T_{CU} and the characteristic memory phenomena across the lower critical temperature T_{Cl} and so on are reexamined in detail. Forming a contrast with the superconductive ceramic of $YBa_2Cu_4O_8$ [1], where the intermediate state is an intra-cluster Meisner and inter-cluster disordered state of paramagnetic nature, the intermediate state between T_{CU} and T_{Cl} is concluded to be an interesting 'ceramic' phase or an intra-cluster ferromagnetic and inter-cluster disordered state of glassy nature[1] and probably attributable to the possible inter-cluster interactions of RKKY-type.

2. $CoCl_2$-GIC as a Magnetic (Spin) Ceramic

Successive magnetic transitions were found in stage 2 $CoCl_2$-GIC at T_{CU}(= 9K) and at T_{CL}(=7K) by magnetic measurement [4]. Referring to the easy plane anisotropy, the intermediate state between T_{CU} and T_{CL} was first suspected to be a so called KT (Kosterlitz and Thouless) phase[5]. Detailed magnetic measurement at weak field limit [6] and neutron quasi-elastic scattering[7], however, revealed a small but finite thermoremanent magnetization and a true 2D order not of KT-type but of conventional type, respectively in the state. Taking the ceramic-like lattice structure into account that each intercalated $CoCl_2$ plane is not extended infinitely and divided into finite size clusters of mesoscopic scale, the experimental facts were reasonably explained by a hierarchical successive ordering [8]. The phase transition at T_{CU} is that from the paramagnetic into an intra-cluster (2D) ferromagnetic state with inter-cluster disorder. Such an intermediate state (schematically shown in Fig.1) could thus be called a 'ceramic' phase mentioned above.

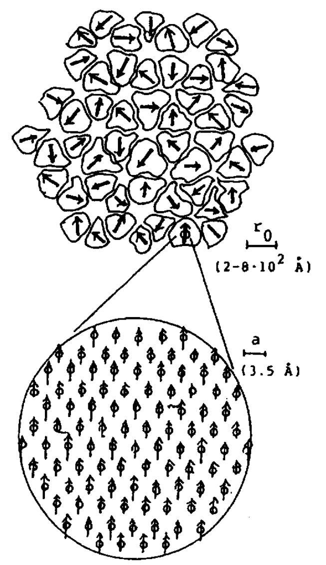

Fig.1 Schematic view of magnetic structure in the 'ceramic' phase.

In the intermediate state, however, many characteristic features of cooperative dynamics have been revealed, which can not be explained simply as those in the intra-cluster ferromagnetic phase. These are disagreement between the field cooled and zero-field cooled magnetizations, M_{FC} and M_{ZFC} [9], logarithmic slow decay of thermoremanent magnetization Mr[9], the characteristic anomalous memory of Mr[10], 1/ω-type magnetic fluctuation spectrum[11], and so on. All these facts suggested that the inter-cluster correlation is not simple as in the paramagnetic phase but in a disordered but correlated state, probably like a spin glass phase.

3. Nonlinear Magnetic Responses around Tcu

For the examination of such a disordered state, observation of nonlinear magnetic responses is expected to be useful[12]. Examination of the singularity of nonlinear susceptibility χ_2 at Tcu should give an important information to distinguish the first phase transition[12], analogously as in the case of spin glass ordering[13]. It is derived by the relation,

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

where $M'_{3\omega}$ is the third harmonic in-phase component of magnetic response M(t) to the excitation AC field h·exp(iωt).

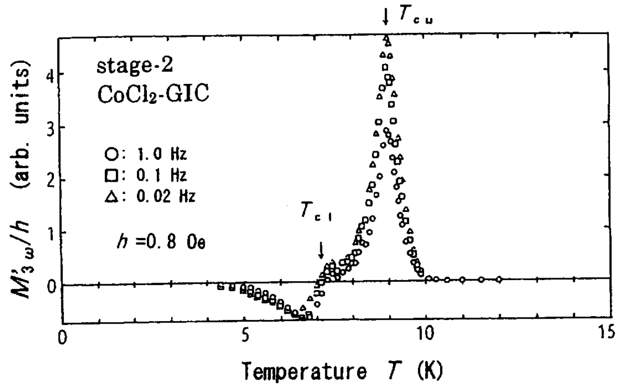

Fig.2 Temperature dependence of nonlinear magnetic response $M'_{3\omega}$ at low frequencies.

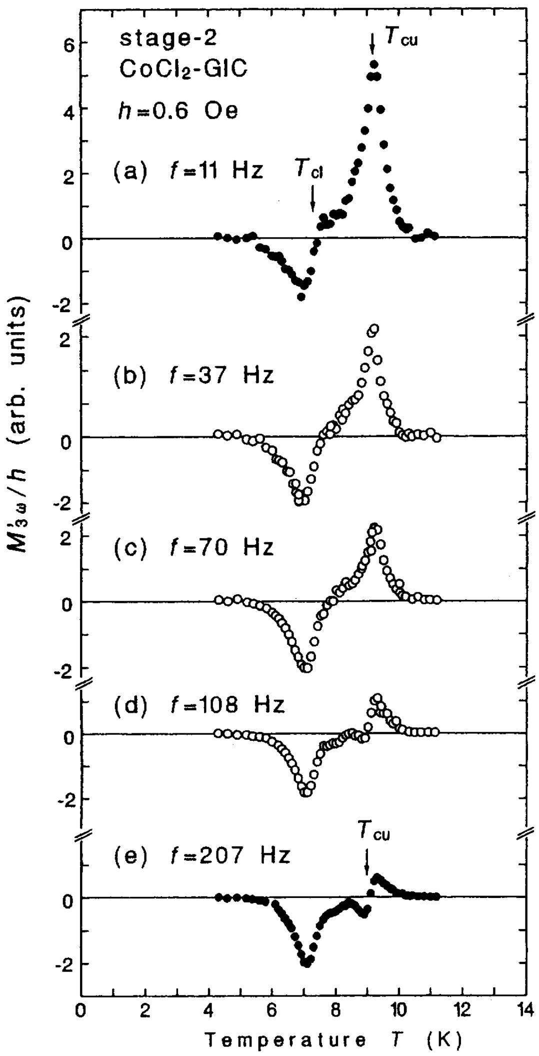

Fig.3 Dependence of $M'_{3\omega}$-T curve around Tcu on the observation frequency.

From the precise frequency dependence of $M'_{3\omega}$-T curve in the very low frequency region below 1 Hz (see e.g. Fig.2) down to 1 mHz, a negative divergence of χ_2 was concluded at Tcu[12], indicating the glassy disordered nature of the critical fluctuation at and below Tcu. Since a 2D ferromagnetic state is realized inside each cluster below Tcu, a crossover phenomenon should happen from the intra-cluster ferromagnetic into inter-cluster glassy disordered state around Tcu. Such a crossover phenomenon, if any, could be distinguishable as follows.

Generally, both intra- and inter-cluster critical fluctuation should contribute to the singularity of χ_2 at T_{CU}. Intra-cluster fluctuation could be separately observed from the inter-cluster one, if χ_2 is examined at different time scale, since the characteristic time scale of the latter is generally much longer than that of the former. As shown in Fig.3, it was confirmed that $M'_{3\omega}$-T curve changed the character at T_{CU} from the symmetric divergent feature against T_{CU} at lower frequencies to an anti-symmetric one as increasing the observation frequency[14]. Since χ_2 of ferromagnet shows an anti-symmetric divergence at the Curie point Tc (see Fig.4), the observed anomaly at high frequencies could be taken to reveal the intra-cluster ferro-magnetic critical fluctuation effect. From the fact, the state between T_{CU} and T_{CL} is confirmed to be a characteristic 'ceramic' phase in which the system is ferromagnetically ordered inside each cluster and disordered among the clusters but correlated in a way as in the spin glass phase[14].

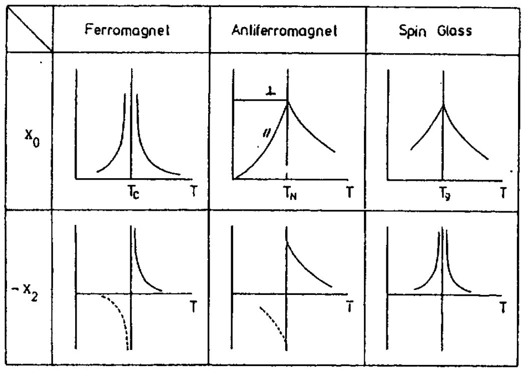

Fig.4 Singularity of linear and nonlinear Susceptibilities for magnetic systems.

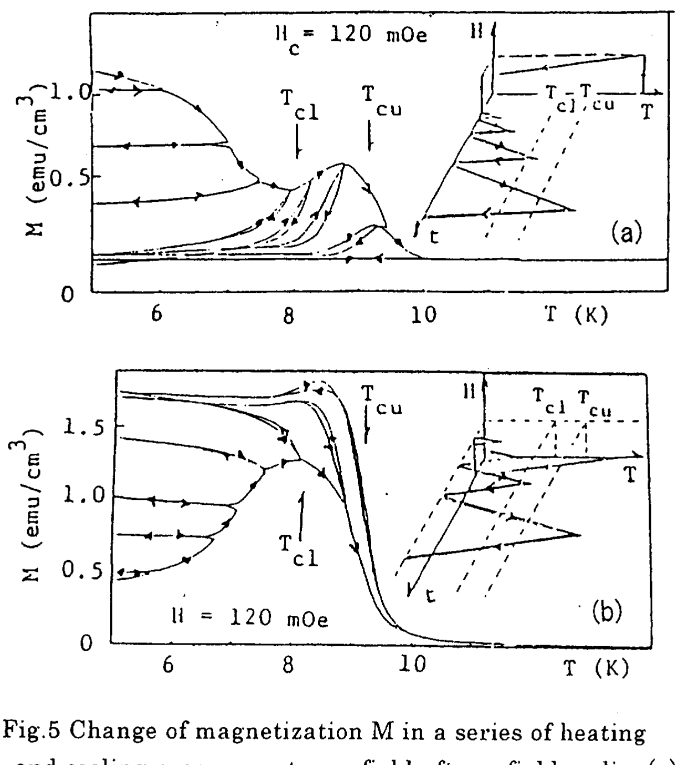

Fig.5 Change of magnetization M in a series of heating and cooling processes at zero field after a field cooling(a) and at a finite field after a zerofield cooling (b) to the lowest temperature, respectively.

4. Characteristic Memory Phenomena across T_{CL}

In the characteristic 'ceramic' phase in the previous paragraph, most of the dynamical and non-equilibrium phenomena in the intermediate state i.e. disagreement between M_{FC} and M_{ZFC}[9], logarithmic slow decay of Mr[9] and 1/ω-type magnetic fluctuation spectrum[11] could be understood reasonably. The problem to discuss now is therefore the origin of the characteristic anomalous memory phenomena across T_{CI}. Typical examples of the phenomena are shown in Fig.5(a) and (b)[10]. Figure 5(a) shows the change of magnetization M in a series of heating and cooling processes at zero field after a field cooling to the lowest temperature and (b) the change of M in the same process at a finite external field H after a zero-field cooling.

Now let us denote Tr as the temperature at which temperature sweep direction is changed from positive to negative. In the both figures (a) and (b), M is found little to change from the value at Tr in the following cooling process to lower temperatures, as far as Tr < T_{CI}. This process is reversible as far as the observation temperature does not come back to Tr. Such memory phenomena as in the present case for Tr < T_{CI} have been predicted theoretically for the spin glass[15] and actually observed experimentally in a spin glass like material, CuMn alloy below the spin glass ordering temperature or for Tr < Tg (see Fig.6)[10]. On the other side, the memory phenomena for Tr > T_{CI} are apparently different from those for Tr < T_{CI}. As seen in Fig.5(a) and (b), if the system is cooled down across T_{CI}, the value of M is found to decreases to almost zero at zero field and increases to a finite value at a field H, respectively, which are identified to be the thermal equilibrium values at the respective circumstances in the state below T_{CI}.

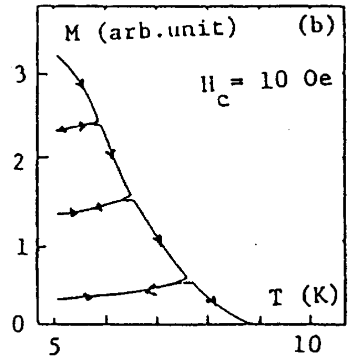

Fig.6 Memory phenomena of CuMn spin glass

Comparing the present characteristic situation with that of spin glass ordering across Tg, the system above T_{CI} looks apparently to be in the disordered phase of paramagnetic nature from the state below T_{CI}. However, if the system is heated up again across T_{CI} and to Tr in the situation of Fig. 4(a), the magnetization does not disappear but comes back to the original finite value. In such a way, the present system in the intermediate temperature range between T_{CU} and T_{CI} has both characteristics of ordered and disordered states. Therefore, the intermediate state in the present magnetic system may be called also a literary intermediate phase but in a different sense from the case of superconductive ceramics.

5. Inter-cluster Interactions for the Intermediate and Final Glassy Order

Possible origin for the appearance of such a characteristic glassy phase below T_{CU} could be speculated as follows. Candidates of the inter-cluster interaction are firstly the dipole-dipole interactions among the cluster moments and second the RKKY-type ones through the conducting π-electrons in the adjacent carbon layers. The former will be expected naturally to introduce interlayer antiferromagnetic correlation, which is, however, contrary to the experimental fact by neutron scattering[7]. The latter should, thus, be the origin of glassy inter-cluster coupling. Generally in chloride GICs, the electron transfer between the intercalant and adjacent carbon layers will takes place at the boundary regions of intercalant clusters. The inter-cluster interaction is thus given by the total sum of individual RKKY-type exchange interaction between the Co^{2+} ions at the boundary regions of different clusters. As the result, the sign of inter-cluster interaction of this type could be both plus and minus, which brings frustration in the inter-cluster coupling network and leads necessarily to a intermediate 'ceramic' phase of a glassy nature.

As for the origin of the transition at T_{Cl}, the dipole-dipole interactions among the cluster moments should be responsible from the distinct growth of 3D antiferromagnetic correlation below T_{Cl}[7]. In the case, temperature difference ΔT_c between T_{CU} and T_{Cl} is expected to increase with increasing the inter-plane distance or the stage number of GIC, which has been actually confirmed for $CoCl_2$-GICs and $NiCl_2$-GICs [4]. The detail of the transition characteristic into the low temperature glassy phase at T_{Cl} is, however, not very clear at present stage, including the question whether the transition occurs under a thermally equilibrium condition or not and remains to be an interesting future problem.

6. Summary

A stage 2 $CoCl_2$-GIC shows successive phase transition of a hierarchical nature at. T_{CU} and T_{CL}. The intermediate state between T_{CU} and T_{CL} is concluded to be a 'ceramic' phase, which is characterized by intra-cluster ferromagnetic order with inter-cluster disorder. The disordered state is found to have the characteristic not of paramagnetic but of glassy phase. The origin of such an inter-cluster glassy order is necessarily attributable to the frustration in the inter-cluster coupling network, which should be introduced by RKKY-type exchange interactions between the Co^{2+} ions along the adjacent cluster boundaries. The origin of the transition into the low temperature glassy phase would probably be the dipole-dipole interactions among the ferromagnetic clusters.

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