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HIERARCHIC NATURE OF ORDERING IN $Mn(HCOO)_2 \cdot 2H_2O$ AND ITS DILUTED SYSTEMS

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The critical phenomena of a quasi two-dimensional (2D) antiferromagnet $Mn(HCOO)_2 \cdot 2H_2O$ and its diluted systems are studied. The critical exponent of susceptibility $\gamma = 1.7$ indicates a 2D nature of staggered mode fluctuation. While, $\beta = 0.30$ for the staggered magnetization shows the onset of a 3D order. The single transition at T_N is furcated systematically into three successive ones by dilution at T_0, T_{p1} ($< T_0$) and T_{p2} ($< T_{p1}$), respectively. Such phenomena suggesting a hierarchy of ordering is discussed, refering the sandwich-like heterogeneous inter-plane structure of the systems.

1. Introduction

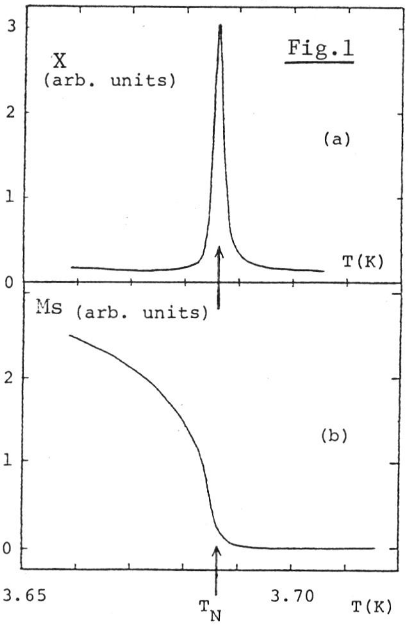
Critical phenomena of the phase transition for the second kind have been well understood theoretically to be subject to the scaling law and universality and independent of the detail of the system. Experimentally, the fact is known to be confirmed in a few simple magnetic systems like e.g. K_2CoF_4. [1].

Here we examine the critical phenomena of a quasi 2D Heisenberg-like canted antiferromagnet $Mn(HCOO)_2 \cdot 2H_2O$ (MnF2H) and its diluted systems in detail through magnetic measurements by a SQUID magnetometer, proton NMR and neutron diffraction. The observed hierarchic natures of ordering in the systems are discussed taking the quasi 2D charactor of the lattice and the inter-plane structure of the system into account.

2. Critical Phenomena of MnF2H

Figure 1 shows the temperature dependences of magnetic susceptibility X and spontaneous magnetization Ms across the Néel temperature T_N. Measurements are done in almost zero fields or static field H_0 less than 3 mOe and exciting AC field H_1 of about 1 mOe. So called cooling in field method is applied to obtain the spontaneous magnetization in the cooling field Hc of 120 mOe. Both X and Ms are measured simultaneously with increasing temperature. A divergent anomaly of X is seen at T_N. Correspondingly, Ms disappears at T_N as temperature increases.

The divergent part ΔX ($= X - X_{af}$) is proportional to the staggered susceptibility Xs [2]. As shown in Fig.2(a), ΔX or Xs follows an exponential law with a critical index $\gamma = 1.7 \pm 0.1$ down to the temperature ε ($= T/T_N - 1$) $\cong 4 \cdot 10^{-4}$. The value of γ is in agreement with 1.75 for 2D Ising system within experimental error, which



may suggest that the critical fluctuation is essentially of 2D systems and that the phase transition is caused by only intra-plane interactions. On the other hand, the spontaneous magnetization Ms, which is proportional to the staggered one L [2], follows an exponential law with a critical index $\beta = 0.30 \pm 0.02$ in the range $5 \cdot 10^{-4} < \varepsilon < 2 \cdot 10^{-2}$ as shown in Fig.2(b). The spontaneous staggered magnetization L derived from proton NMR is also plotted in Fig.2(b), which is in agreement with Ms in the temperature range $\varepsilon < 2 \cdot 10^{-2}$ confirming the proportionality of Ms with L. The value of β is in agreement with that for 3D systems, which may indicate the 3D nature of ordering process below T_N.

In such a way, the universality class of γ for $T > T_N$ is apparently different from that of β for $T < T_N$. The anomalous critical phenomena, which is inconsistent with the scaling law, rather suggest a hierarchic nature of ordering from 2D to 3D. One may think that it is attributable to so called dimensionality crossover effect from 2D to 3D behaviours. Then the crossover temperature ε^* of Xs should be equal to that of L as predicted theoretically [3]. Actually, however, ε^* for susceptibility is less than $4 \cdot 10^{-4}$ and ε^* for magnetization is $\sim 2 \cdot 10^{-2}$. Such a remarkable asymmetry of ε^* against T_N can hardly be expected for simple quasi 2D systems. So we should examine the phenomena concerned with the inter-plane structure of the system, which is qualitatively different from other simple quasi 2D systems.

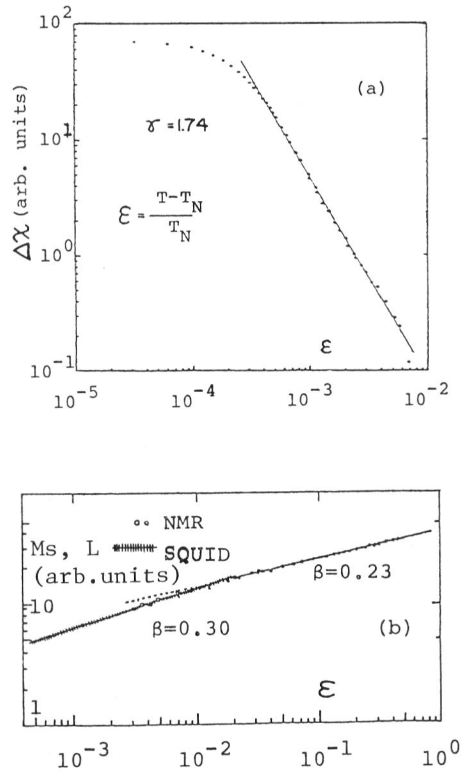


Fig.2 X-ε (a) and L-ε (b)

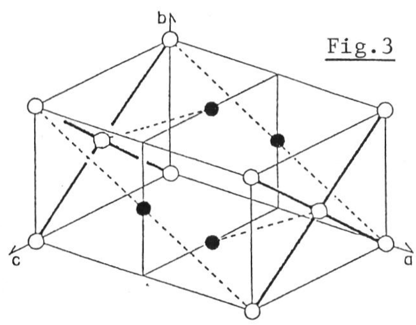


Fig.3

○ M^{2+} on A plane ● M^{2+} on B plane

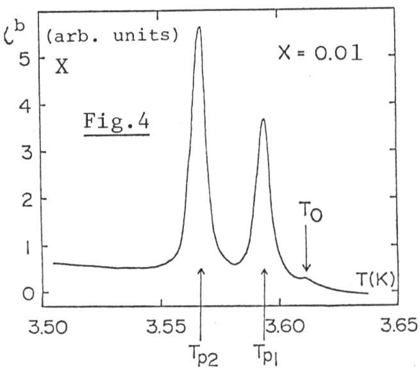
— COOH bond on A plane (J_{AA})

---- COOH bond between A and B planes (J_{AB})

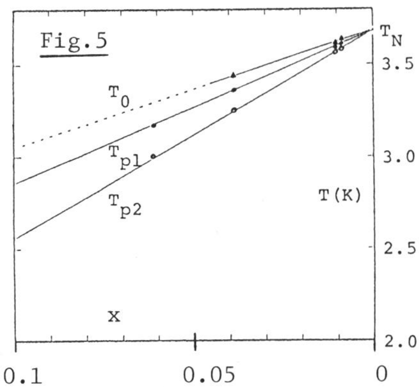
As shown in Fig.3, MnF2H is a heterogeneous system consisting of two kinds of subsystems (A and B subsystems). Half Mn ions in A subsystem are coupled strongly in each (100) A plane and the other half Mn ions in B subsystem are sandwiched between the A planes. A very weak coupling exists between an intermediate Mn ion in (200) B plane and a Mn ion in the adjacent A planes. Such a weakly coupled model of two different subsystems has explained the magnetic and thermal properties very well in the whole temperature region above and below T_N [4]. The remarkable λ-type anomaly of heat capacity at T_N, which is not expected for simple quasi 2D systems, could be well explained, too [4]. So we suggest that it may be a characteristic of such a heterogeneous magnetic system and cirtainly be caused by the cooperative actions of two subsystems.

3. Successive Transitions in $Mn_{1-x}Zn_xF2H$

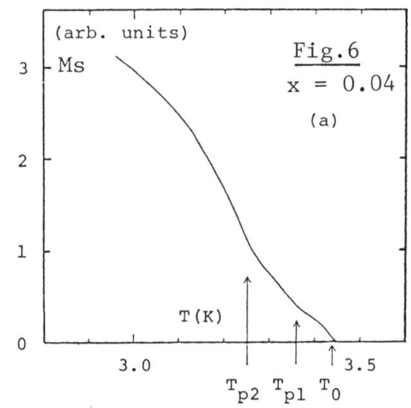
Figure 4 is the temperature dependence of X for the sample of x = 0.01 measured in almost zero fields ($H_0 < 3$ mOe, $H_1 \sim 5$ mOe). Three different peaks of X appear at T_0, T_{p1} ($<T_0$) and T_{p2} ($<T_{p1}$), respectively, instead of a sharp single anomaly at T_N in the pure system (see Fig.1(a)). Correspondingly, Ms decreases in three steps and disappears around T_0 as temperature increases. These facts suggest three successive phase transitions in the dilute system. These temperatures change systematecally with Zn concentration x and tend to T_N when $x \rightarrow 0$

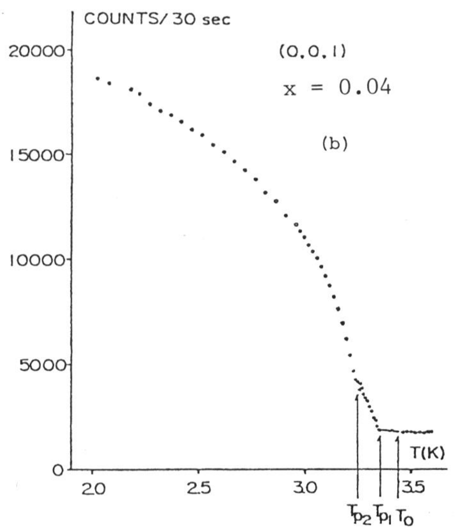


as shown in Fig.5. An example of Ms - T curve for x = 0.04 is given in Fig.6(a). Figure 6(b) is the temperature dependence of the (001) Bragg point reflection intensity I_p in neutron diffraction for the sample with the same concentration. The intensity does not grow at T_0 but at T_{p1}. These results shows that the 3D order occurs at T_{p1} and that the intermediate state between T_0 and T_{p1} is a 2D ordered state. The detailed discussion on the state is given elsewhere including the growing feature of the Bragg ridge along the (100) direction which shows the 2D correlation in each antiferromagnetic plane.[5].



The summary of the discussion is as follows. The first transition temperature T_0 is that from the paramagnetic into a kind of 2D ordered state. It may be an ordered state with a local order character named as a "regional long range order" (R-LRO) [6], in which each plane is divided into many ordered sub-area with intermediate sizes. The R-LRO state [6] is not strictly long range ordered state in the statistical mechanical sense because the correlation length is limited in each sub-area and not extended to infinity.





The second transition at T_{p1} is that from the 2D R-LRO into a 3D ordered state. It may be noteworthy that the 3D order parameter I_p begin to grow almost linearly from T_{p1} as seen in Fig.6(b). It is qualitatively different from the growing feature of Ms for the pure system (see Fig.1(b)) and for other regular systems below the transition temperature where I_p follows the exponential law with the critical index 2β.

Recent proton NMR experiment showed that the phase below T_{p2} is quite similar to the ordered state of the pure system below T_N [7]. So, the transition at T_{p2} is that from the intermediate 3D into final unified long range ordered state over the whole system. The NMR experiment also suggest that the Mn ions in B subsystem may remain paramagnetic above T_{p2} at least partially. Therefore the 3D ordered state between T_{p1} and T_{p2} is not perfectly long range ordered one. At many places, inter plane mis-match seems to occur in the system, which might be concerned with the slow growth rate of I_p below T_{p1}.

4. Summary

From the experimental results mentioned above, the successive phase transition at T_0 and at T_{p1} in the dilute salt may be understood as a possible hierarchic nature of ordering in a quasi 2D random system as follows. Below T_0, a long range order is established in a microscopic scale within each A plane. In the intermediate scale, however, the ordered sub-areas still behave paramagnetically as a whole subarea and the Mn ions in B subsystem remains perfectly paramagnetic. Below T_{p1}, a 3D order is established in the intermediate scale, among the ordered subareas. In the ordered state, however, many inter plane mismatchs would exist everywhere in the system. The Mn ions in B subsystem still remain paramagnetic at least partially. Below T_{p2}, the perfect long range order over the whole system is established including both A and B subsystems.

In the pure MnF2H, the characteristic critical phenomena which is apparently inconsistent with the scaling law and universality may suggest another hierarchic nature of ordering from 2D to 3D natures.

Such hierarchic natures of ordering, we think, should be attributed to the cooperative actions between the two different subsystems in the present heterogeneous quasi 2D system. Further investigation is in progress.

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