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MAGNETIC ORDERING OF QUASI 2D ANTIFERROMAGNET $Cu(HCOO)_2 4D_2O$ IN A MAGNETIC FIELD

Y. Ajiro, T. Goto*, M. Matsuura**, N. Terata*** and Y. Endoh****

Faculty of Science, Kyoto University, Kyoto, Japan
*College of Liberal Arts, Kyoto University
**Faculty of Engineering Science, Osaka University
***College of Education, Akita University
****Faculty of Science, Tohoku University

A magnetic field effect on the magnetic phase transition of a quasi two dimensional Heisenberg S=1/2 antiferromagnet $Cu(HCOO)_2 4D_2O$ is studied by means of NMR and neutron diffraction. An antiferromagnetic order evidently exists under an external field well above the ordering temperature at zero field T_N. The dynamic behaviour of the spins shows a definite anomaly at a certain temperature which is appreciably higher than T_N and increases largely as a function of the field intensity. These results are explained in terms of the field induced magnetic ordering through a coupling between the applied uniform field and the staggered magnetization which is predicted for a crystallographic two-sublattice system.

1. Introduction

$Cu(HCOO)_2 4H_2O$ has a definite layer structure with alternating sheets of copperformates and of water molecules parallel to the (001) plane and exhibits a quasi two dimensional, nearly Heisenberg S=1/2 antiferromagnet. An each magnetic layer of copperformate forms a crystallographic two-sublattice system, owing to non-equivalency of the g-factors of Cu^{2+} ions at (000) and (1/2 1/2 0) sites. For such a system, it has been discussed [1,2,3] that an antiferromagnetic staggered magnetization can be induced by a uniform magnetic field. This means, quite equivalently, that an external field can produce simultaneously a staggered magnetic field in the system. The effect has an important significance, since the concept of a staggered field has been long recognized only as fictious theoretical one in the sence that such a field can not be applied at all by any experimental procedures.

Here, we are interested in the influence of the applied field on the phase transition of this salt. More explicitly, does the applied field destroy the phase transition or not? As the staggered field couples directly to the antiferromagnetic order parameter, we think that the above mentioned effect may affect strongly on the magnetic ordering of the salt. In our view, the study offers a rare oppotunity to investigate the staggered field effect on the magnetic behaviors of S=1/2 two dimensional Heisenberg antiferromagnet whose ordering character remains still unresolved. Experiments were made in the D_2O substituted salt, $Cu(HCOO)_2 4D_2O$ which is Physically equivalent to $Cu(HCOO)_2 4H_2O$.

2. Induced Antiferromagnetic Order above T_N

As early as 1970, we firstly noticed [4] that an anomalous lineshift of the proton NMR in the salt can be explained by considering a field induced antiferromagnetic order well above the three dimensional ordering temperature at zero field, T_N = 16.8 K. More recently, we have established from NMR [5] and neutron diffraction [6] studies that the phenomenon is interpreted in terms of the effect mentioned above.

Figure 1 shows the angular dependence of the lineshift of proton NMR at 20.4 K and 6.3 kG. The magnitude of the shift is surprisingly larger than the usual paramagnetic lineshift caused by the uniform magnetization in the paramagnetic state and is roughly 1/2 of the lineshift observed in the antiferromagnetic state at 4.2 K well below T_N. However, the shift is proportional to the field intensity at low field, indicating that it comes from the field induced magnetization, anyhow. The solid curves in Fig. 1 are the calculated dipolar lineshift from the induced staggered magnetization whose magnitude is nearly half of the fully ordered state. We see a good agreement with the experimental result both in amplitude and in phase angle. While, the dotted curves calculated from the measured uniform magnetization are in quite disagreement with the data. Of particular interest is the large magnitude of the induced staggered magnetization. The fact is explained by a highly developed antiferromagnetic spin correlations in the two dimensional lattice.

Neutron diffraction gives a more direct evidence for the existence of the field induced antiferromagnetic state above T_N. In the presence of an external field, we found a significant magnetic contribution only to the (h 0 l) reflections with odd h and even l, which increases proportionally to the square of the field intensity with tendency of saturated behavior at high field, as shown in Fig. 2 for 20.5 K. The location of these magnetic reflections in the reciplocal lattice evidently shows that the induced magnetic state is of a two-sublattice antiferromagnetic structure with ferromagnetic stacking along the c-axis.

Now, we are in a position that we look more closely at the nature of the phase transition in the applied field. Fig. 3 shows the temperature dependence of diffraction intensity of the (100) reflection at various field intensities for H// b-axis, from which we see the temperature variation of the antiferromagnetic sublattice magnetization. Also included is the temperature variation of the (103) reflection at H=0, definitely showing a spontaneous order state of a four sublattice antiferromagnetic structure with antiferromagnetic stacking along the c-axis below T_N, in contrast with the field induced order state above T_N. It has been discussed by some authors [4,7,8] that the four-sublattice state changes into a two-sublattice one below T_N by applying an external field in the bc-plane. As shown in the insert of Fig. 3, the fact is evidenced by the field dependence of the intensities of (103) and (100) reflections which are the typical representatives for the four- and two-sublattice state, respectively.

Turning back to the temperature region above T_N, we note, in particular, that the intensity of the (100) reflection gradually decreases as temperature increases, without any abrupt change in intensity across T_N. It is clear that the two-sublattice antiferromagnetic order persists above T_N in the presence of magnetic field.

3. Magnetic Phase Transition

Thus, an interesting question for us is what happens to the boundary between the induced antiferromagnetic state and a paramagnetic state. Figure 4 shows the temperature dependence of the relaxation rate of proton NMR at 5 and 7.5 kG. It shows a definite peak, at a certain temperature $T_t(H)$ appreciably higher than T_N, depending on the field intensity. The fact strongly suggests that the dynamic behavior of the spins changes at the boundary. ESR [9,10] also shows anomalous broadening of the linewidth as well as a large shift of the resonance field of paramagnetic and antiferromagnetic lines at a temperature above T_N.

The transition temperature $T_t(H)$, which manifests itself as an anomalous peak of T_1^{-1} does not coincide with an inflection point in the staggered magnetization vs temperature curve, but does with the temperature of zero magnetization estimated from a smooth linear extrapolation. Refering to this fact, we estimated further the transition temperatures $T_t(H)$ at H = 10 kG and at H = 30 kG from Fig. 3. $T_t(H)$ thus obtained are shown in Fig. 5. We see a large increase of $T_t(H)$ when the external field is applied.

It is of interest to inquire the field dependence of $T_t(H)$, especially at the strong field limit. For the purpose, we tried to plot the data in various functional forms and found that the data are well fitted by the relation

$$T_t(H) = T_N[1 + \exp(-a/H)], \qquad (1)$$

with $T_N = 16.8$ K and $a = 6.6\ 10^3$ G, as shown in Fig. 6 and solid curve in Fig.5. Thus, in the strong field limit or at $T \to \infty$, we have $T_t(\infty) = 33.6$ K, which is very close to $T_C = 34.2$ K ($T_C = 1.14|J|/k$) for the $S = 1/2$ two-dimensional Ising spin system. It may suggest that the spin system for the present case behaves like an Ising system in the strong magnetic field.

4. Summary

Based on the experimental evidence from the NMR and neutron diffraction studies that an external field induces an antiferromagnetic order above T_N, we showed an existence of the phase boundary between this induced antiferromagnetic state and the paramagnetic state. There exists an anomaly in the fluctuating part of the spins at the boundary. The field induced antiferromagnetic order above T_N is essentially due to the characteristic of the spin system on a two dimensional lattice with non-equivalent g-factors. The transition temperature rather strongly increases with increasing field. The fact may be a direct consequence of the coupling between the applied uniform field and the staggered magnetization. A further investigation is in proceeding.

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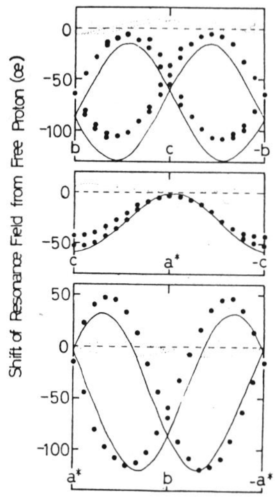


Fig.(1)

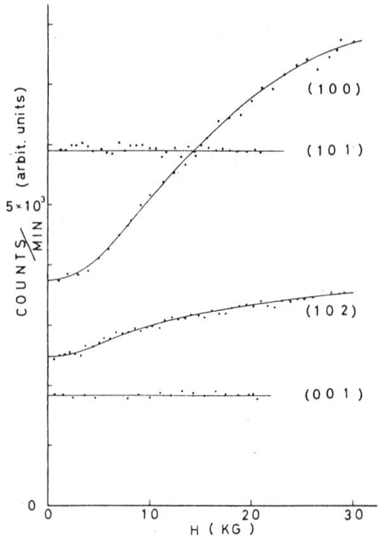


Fig.(2)

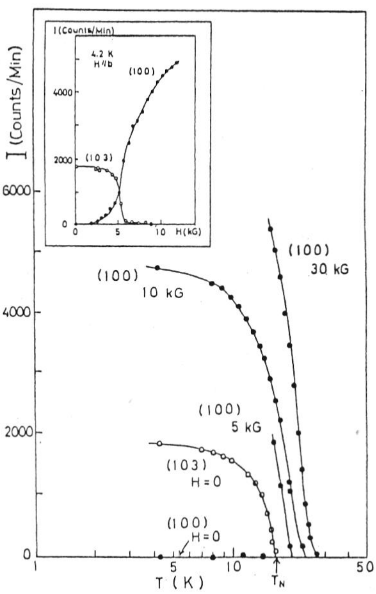
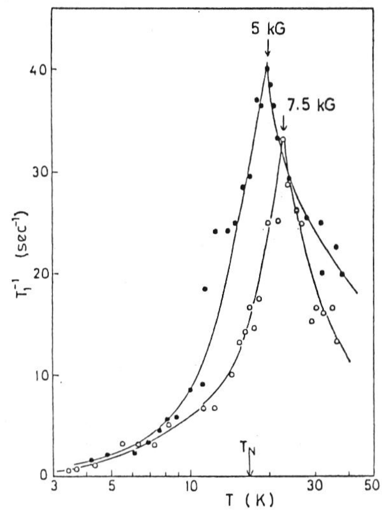


Fig.(3)



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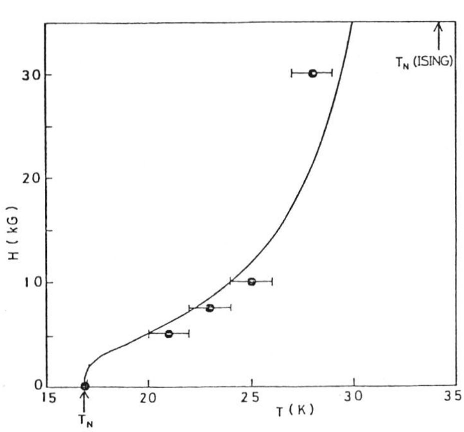

Fig.(5)

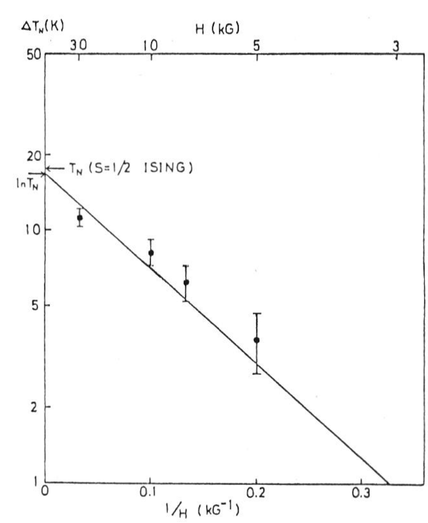

Fig.(6)