Progress of Theoretical Physics, Vol. 52, No. 2, August 1974

Theoretical Investigation of Magnetization Process in $CoCl_2 \cdot 2H_2O$

Takehiko OGUCHI

Department of Physics, Tokyo Institute of Technology
Oh-okayama, Meguro-ku, Tokyo

(Received January 31, 1974)

It is theoretically shown that the magnetization of $CoCl_2 \cdot 2H_2O$ in antiferromagnetic state has a jump at well-known transition H_{c1} and it becomes regular ferrimagnetic state, by the three-spin-flip process and the exchange process, when the magnetic field is increased very slowly. Another jump in magnetization curve is shown theoretically to occur at well-known transition H_{c2}.

§ 1. Introduction

In a previous paper[1] we investigated the magnetization process in $CoCl_2 \cdot 2H_2O$ by the computer simulation in which only one spin was allowed to flip at a time. We found new two transitions at $H_c' = 2|J_1| - |J_2|$ and $H_c'' = 2|J_1|$ as well as the well-known transition[2)~5)] at $H_{c2} = 2|J_1| + |J_2|$, where J_1 and J_2 are exchange integrals usually defined in $CoCl_2 \cdot 2H_2O$. However, another well-known transition at $H_{c1} = 2|J_1| - 2|J_2|$ was never found in the computer simulation. Here and henceforth, for convenience, the magnetic moment of spin is taken to be unity, and the magnetic moment and spin are assumed to point to the same direction.

In this paper we take account of the three-spin-flip process in which three spins such as $\downarrow\uparrow\downarrow$ flip to $\uparrow\downarrow\uparrow$ simultaneously. This process is caused by the coherent combination of the interaction proportional to S_i^+ (one-spin-flip process) from heat reservoir, and the transverse exchange interaction $J_\perp(S_j^+S_k^- + S_j^-S_k^+)$ between spins, provided that the gain of Zeeman energy between states before and after spin flipping would overcome the loss of exchange energy. We also take account of the process in which two spins such as $\uparrow\downarrow$ flip to $\downarrow\uparrow$ simultaneously, provided that the exchange energy would not change by spin flipping (of course the Zeeman energy does not change). In this process the location of the $+$ spin moves without any change of the total magnetization. The exchange process is caused by the transverse exchange interaction.

As will be shown in the next section, by the three-spin-flip process the magnetization in the antiferromagnetic spin configuration jumps to $M_s/4$ at the field H_{c1} which is lower than H_c', where M_s is the saturation magnetization. Then by the combination of the exchange process and three-spin-flip process, the magnetization is increased to $M_s/3$ at H_{c1} in agreement with the almost static experimental results.[2),3)]

§ 2. Linear chain model

It is known[6)] that spin-spin interactions in $CoCl_2 \cdot 2H_2O$ can be expressed by a linear chain with the nearest and the second nearest neighbor exchange integrals $2J_1$ and J_2, respectively, provided that J_3 is negligibly small. The factor 2 of $2J_1$ is due to the fact that a spin in $CoCl_2 \cdot 2H_2O$ has four J_1 bonds instead of two in a linear chain. In this section we consider the antiferromagnetic linear chain for $CoCl_2 \cdot 2H_2O$. We keep the constant magnetic field to the up direction infinitesimally larger than H_{c1}. Henceforth we denote it by $H_{c1}+0$. The one-spin-flip process cannot occur because all down spins are still stable locally and they would become unstable locally when the field gets to H_c' which is larger than H_{c1}. However, by the three-spin-flip process, $\downarrow\uparrow\downarrow$ spins can flip to $\uparrow\downarrow\uparrow$ at a time, if spin configurations on both sides of them are antiferromagnetic. We call these three flipped spins ($\uparrow\downarrow\uparrow$) a "spin triplet." The appearance of one spin triplet increases the magnetization by 2. Many spin triplets are created randomly in the chain. But $\downarrow\uparrow\downarrow$ spins adjacent to a spin triplet cannot flip at H_{c1}, because H_{c1} is insufficient to overcome the loss of exchange energy. This means two spin triplets keep away by some separation between them. There are three kinds of separation between two spin triplets, which are denoted by X, Y, Z type, respectively as shown in Fig. 1. Let the numbers of X, Y, Z type in the chain be denoted by x, y, z, respectively. We have

$$6x+8y+10z=N=\text{total number of spins},$$

$$2(x+y+z)=M=\text{magnetization}.$$

Since X, Y, Z type occur with the equal probability ($x=y=z$), we obtain $M=M_s/4$ from the above equations.

Next, we consider the exchange process. The $\downarrow\uparrow$ spins surrounded by a square (a) in Fig. 2, in Y type adjacent to the left side of spin triplet can flip

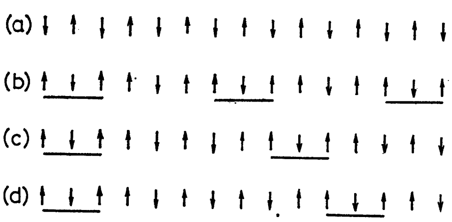

Fig. 1. (a) Antiferromagnetic linear chain, (b) X type, (c) Y type, (d) Z type. Underlines indicate spin triplets.

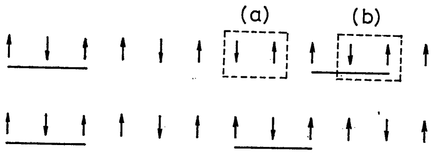

Fig. 2. In Y type spin configuration, after spins $\downarrow\uparrow$ in a square (a) flipped, spins $\downarrow\uparrow$ in (b) flip. Thus the spin configuration will be X type shown in the figure below. Underlines indicate spin triplets.

simultaneously by the exchange process, because the exchange energy and Zeeman energy would not change by spin flipping in this configuration. After two spins in (a) have exchanged, $\downarrow\uparrow$ spins in a square (b) in Fig. 2 can flip by the same reason. As a result, it may be seen that the spin triplet has moved to the left by 2 lattice constants, and therefore Y type changes to X type, and the separation between two spin triplets is narrowed. In the same way, a spin triplet belonging to Z type can move by 4 lattice constants and becomes X type. When a spin triplet has moved to the left and the separation to a spin triplet on the right side becomes 10 lattice constants, $\downarrow\uparrow\downarrow$ spins in the middle of them can flip by the three-spin-flip process. In this way, by the combination of the exchange process and three-spin-flip process, the spin configuration becomes regular ferrimagnetic one such as $\uparrow\uparrow\downarrow\uparrow\uparrow\downarrow\uparrow\uparrow\downarrow\cdots$.

In the ferrimagnetic state, even when the magnetic field is increased from H_{c1}, all spins do not flip until the field gets to H_{c2}. When the field is $H_{c2}+0$, all down spins can simply reverse and the whole spins are up and the magnetization is saturated.

When the magnetic field is decreased and kept at $H_{c2}-0$, some of up spins flip down by the one-spin-flip process, and then by the combination of exchange process and one-spin-flip process, the spin configuration becomes regular ferrimagnetic. When the magnetic field is decreased further and kept at $H_{c1}-0$, the spin configuration becomes regular antiferromagnetic by the combination of three-spin-flip process and exchange process. Thus we have obtained the two-step magnetization curve at H_{c1} and H_{c2} in cases both of increasing and decreasing field.

§ 3. Two-dimensional model

In the regular antiferromagnetic spin array of two-dimensional model, the one-spin-flip process or three-spin-flip process cannot occur until the magnetic field is larger than $2|J_1|-|J_2|$ or $4|J_1|-2|J_2|$, respectively, as shown in Fig. 3. However, spins on the surface of the crystal can flip by the one-spin-flip process in the magnetic field more than $|J_1|-|J_2|$, $|J_1|$, $|J_1|+|J_2|$, respectively, according as the neighboring spins are up or down as shown in Fig. 3. Therefore, if we keep the field at $H_{c1}+0$, at first, all spins on the surface flip up. Once spins on the surface flipped up, it is possible energetically that three spins (a) adjacent to the surface shown in the

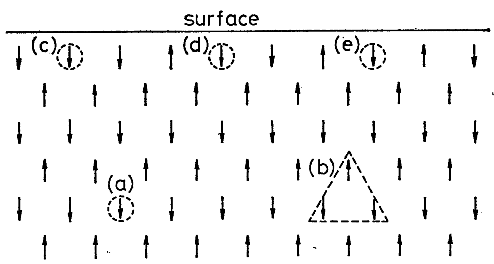

Fig. 3. Intensities of magnetic field necessary to reverse spins in antiferromagnetic state except spins on the surface which are not antiferromagnetic order. (a) $2|J_1|-|J_2|$, (b) $4|J_1|-2|J_2|$, (c) $|J_1|-|J_2|$, (d) $|J_1|$, (e) $|J_1|+|J_2|$.

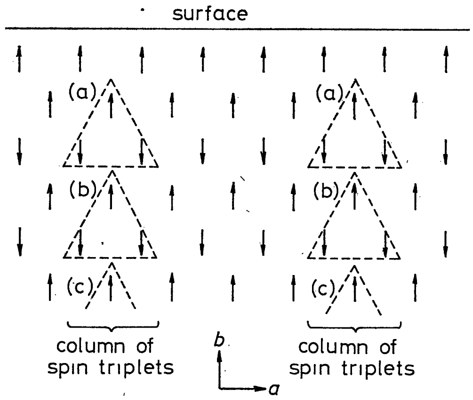

Fig. 4. After three spins in a triangle (a) flipped, three spins in (b) flip, and so on, in the regular antiferromagnetic spin configuration except for spins on the surface which are all up. a and b are the crystalline axes.

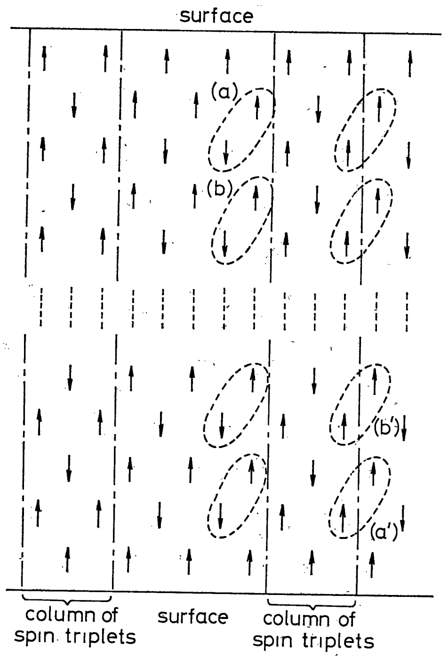

Fig. 5. The exchange process starts from the pair of spins (a) and (a′), respectively. Then it propagates into the interior. The region between two chain lines is a column of spin triplets.

triangle in Fig. 4, flip by the three-spin-flip process. Then three spins (b) below it can flip, and so on like the domino style. Thus spin triplets are developed into the interior from the surface along the $\boldsymbol{b}$ axis. Henceforth we call them a "column of spin triplets." Since the column of spin triplets are created at random from any sites on the surface, we have also X, Y, Z type of separation between columns of spin triplets like the linear chain model. Since these types appear with the equal probability, the magnetization becomes $M_s/4$ in the same way as the linear chain. As is shown in Fig. 5, by the exchange process, $\uparrow\downarrow$ spin pair (a) adjacent to the left side of the column of spin triplets can flip and then spin pair (b) flips and so on. The exchange process can propagate from the top surface into the interior. While $\uparrow\downarrow$ spin pair (a′) on the right side of the column of spin triplets can flip and then spin pair (b′) flips and so on. The exchange process can propagate from the bottom surface into the interior. As a result, the column of spin triplets has moved to the left. When the separation between two columns of spin triplets becomes big enough, new column of spin triplets is created in it. In this way, finally the spin array becomes regular ferrimagnetic and the magnetization becomes $M_s/3$.

When the field gets to $H_{c2}+0$, all down spins simply flip up and the system becomes ferromagnetic.

In the case of decreasing field, when the field is decreased to $H_{c2}-0$, by the combination of one-spin-flip process and exchange process, the spin array becomes regular ferrimagnetic, except spins on the surface, all of which are still pointing to the field direction. Let the field be decreased further, spins do not flip until the field is H_{c1}. When the field gets to $H_{c1}-0$, spin triplets (a) just below the surface in Fig. 6 flip, then spin triplets (b) flip and so on like the domino style, and the spin array becomes regular antiferromagnetic.

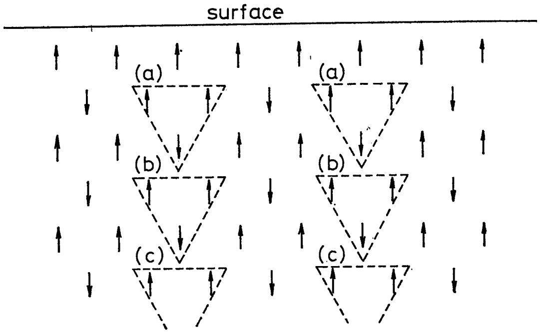

Fig. 6. After spin triplets (a) flipped, spin triplets, (b) flip, and so on, in the regular ferrimagnetic spin configuration except for spins on the surface which are all up.

Thus the magnetization curve has two jumps at H_{c1} and H_{c2} in cases both of increasing and decreasing field.

§ 4. Discussion

We have succeeded in giving the theoretical explanation of the almost static magnetization curve in $CoCl_2 \cdot 2H_2O$ which has two jumps at H_{c1} and H_{c2}, by introducing the three-spin-flip process and exchange process. They are due to the transverse exchange interaction between spins. Although the exchange interactions in $CoCl_2 \cdot 2H_2O$ are Ising like, they have the weak transverse part.[6] The transverse part of exchange interactions in $CoBr_2 \cdot 2H_2O$ is relatively stronger than that in $CoCl_2 \cdot 2H_2O$ so that it can be understood that the two-jump-magnetization curve is more easily observed[7] in $CoBr_2 \cdot 2H_2O$ than $CoCl_2 \cdot 2H_2O$.

Of course the one-spin-flip process happens more easily than the three-spin-flip process when the field is bigger than H_c'. Consequently if the increasing rate of field is fairly rapid, there is no enough time to complete the three-spin-flip process at H_{c1}. In such a case we expect the transitions at H_c' as well as at H_{c1}. This is the reason why Kuramitsu et al.[8] and Motokawa[9] observed peaks of high-frequency susceptibility at H_{c1} and H_c'.

The exchange process itself is reversible so that it may proceed and return back. If it proceeds and then the three-spin-flip process happens, it cannot return back any more. Therefore the exchange process contributes to the magnetization process, although it does not take place efficiently. Therefore when we apply the field and keep it at $H_{c1}+0$ in antiferromagnetic spin array, we anticipate that the magnetization reaches $M_s/4$ quickly, then increases to $M_s/3$ very slowly. This is really observed in the recent computer simulation,[10] and similar results seem to be observed[11] in $FeCl_2 \cdot 2H_2O$.

In the two-dimensional model, the magnetization process starts from the surface's spins which point to the opposite direction to the field. If these spins point to the same direction as the field, spins on the opposite surface would be antiparallel to the field. In such a case the magnetization process would start from the opposite surface. The surface which we have called may be replaced by domain wall or some other defect.

The present theory is very similar to Tinkham's theory.[12] The main difference between his theory and ours is that he did not take account of three-spin-flip process nor exchange process.

Finally we have to mention that real $CoCl_2 \cdot 2H_2O$ is the three-dimensional crystal. A spin in the two-dimensional model actually represents a ferromagnetic chain perpendicular to the paper. In order to flip all spins in a chain, at least a single spin must be reversed at first. This process was discussed in detail in the prominent paper by Tinkham.[12]

The author expresses his sincere thanks to Dr. I. Ono for the valuable discussion.

References

1) I. Ono and T. Oguchi, Phys. Letters **38A** (1972), 39.
2) T. Haseda and H. Kobayashi, J. Phys. Soc. Japan **19** (1964), 765.
3) A. Narath, Phys. Rev. **136** (1964), A766.
4) M. Date and M. Motokawa, Phys. Rev. Letters **16** (1966), 1111; J. Phys. Soc. Japan **24** (1968), 41.
5) J. B. Torrance, Jr. and M. Tinkham, Phys. Rev. **187** (1969), 505.
6) T. Oguchi, J. Phys. Soc. Japan **20** (1965), 2236.
7) T. Haseda, private communication.
8) Y. Kuramitsu, K. Amaya and T. Haseda, J. Phys. Soc. Japan **33** (1972), 83.
9) M. Motokawa, J. Phys. Soc. Japan **35** (1973), 1315.
10) I. Ono, private communication.
11) K. Katsumata, reported at the Meeting of Phys. Soc. Japan in Nov. 1973.
12) M. Tinkham, Phys. Rev. **188** (1969), 967.