Weak ferromagnetism of quasi-one-dimensional $S = 1/2$ antiferromagnet $\text{BaCu}_2\text{Ge}_2\text{O}_7$

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Abstract

Weak ferromagnetism of quasi-one-dimensional $S = 1/2$ antiferromagnet $\text{BaCu}_2\text{Ge}_2\text{O}_7$ is studied by the magnetization measurement. The spontaneous magnetization appears along the $b$ axis below 8.8 K. The local symmetry between the intra-chain nearest neighbor spins allows the presence of Dzyaloshinskii-Moriya interaction, and the only possible spatial configuration of the weak ferromagnetic moment per spin uniquely determines the sign of the inter-chain interaction. A weak $a$-axis magnetic field can change the direction of the magnetization to the $a$-axis direction, which shows that the spin chain forms a weakly coupled weak-ferromagnetic chain system.

75.10.Jm, 75.25.+z, 75.40.Cx, 75.50.Ee

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One-dimensional (1D) quantum antiferromagnet (AF) is of particular interest in both theory and experiment of quantum magnetism. It is widely accepted that a pure 1D S=1/2 antiferromagnet has no long-range order at $T = 0$ K. On the other hand, almost all the actual spin-chain systems show magnetic three-dimensional long-range order (3D-LRO) at their ground states due to a finite inter-chain interaction. While in general there are many kinds of magnetic 3D-LRO states, the transition to a normal 3D AF-LRO state has been studied mostly. One remarkable exception is a weak ferromagnetic transition that was recently found in 1D compound Sr$_{0.73}$CuO$_2$. However, this compound cannot be treated as a uniform spin-chain system but rather is well explained as an alternating-chain system. In this paper, we report weak ferromagnetism (WF) of a uniform $S = 1/2$ spin chain in BaCu$_2$Ge$_2$O$_7$, which is isomorphous to antiferromagnet BaCu$_2$Si$_2$O$_7$. In BaCu$_2$Ge$_2$O$_7$, intra-chain Dzyaloshinskii-Moriya (DM) interaction and inter-chain Heisenberg interaction cooperatively add a spontaneous magnetization in contrast to AF BaCu$_2$Si$_2$O$_7$.

The single-crystal sample of BaCu$_2$Ge$_2$O$_7$ was grown by a floating-zone method, and was cut into a rectangular shape ($a \times b \times c = 1.7 \times 1.6 \times 3.1$ mm$^3$). Since the $a$- and the $c$-axis lengths are almost the same, particular attention was paid to determine the crystal orientation by x-ray diffraction. We took the diffraction at randomly selected three different points at every surface, and found no trace of a twinned structure. However, the possibility of inclusion of misoriented grains inside the crystal was not eliminated. Magnetization measurement was carried out with a commercial SQUID magnetometer (MPMS, Quantum Design) in the field range from 0 to 5 T. We also measured transverse magnetization with this system.

Figure 1 shows the magnetic susceptibility measured at $H = 1000$ Oe. A broad peak is observed around 300 K, and the data can be fitted with a calculation by Bonner and Fisher (BF), which indicates that the system is well described as an 1D Heisenberg AF. $\chi_b$ and $\chi_c$ are well fitted assuming different $g$ values, and $J = 540$ K is obtained as an intra-chain coupling showing a good agreement with that for the polycrystalline sample. As the temperature decreases to the WF transition temperature at $T_N = 8.8$ K, deviation
from the BF curves becomes significant. Below $T_N$, spontaneous magnetization appears as shown in the inset of Fig. 1. The magnetization along the $b$ axis ($M_b$) shows a typical evolution for ferromagnetic transition and is saturated at approximately $9 \times 10^{-2}$ emu/g for $T \to 0$, which corresponds only to 0.42% of what we may observe when all the $S = 1/2$ spins on Cu$^{2+}$ site are aligned toward the same direction. Thus we eliminate the possibility of normal ferromagnetic transition. Ferrimagnetism is impossible, because BaCu$_2$Ge$_2$O$_7$ has no magnetic ions other than Cu$^{2+}$ that occupies an equivalent site. Since the sample is highly insulating, itinerant or band ferromagnetism is impossible.

To see the anisotropic magnetization, the field dependence of magnetization was measured at the WF state. Figure 2 shows low-field magnetization along three principal axes. A characteristic steep increase of the magnetization is found along the $a$ and $c$ axes up to $H = 280$ Oe ($H_c$). $M_a$ reaches more than $1.6 \times 10^{-1}$ emu/g, while $M_b$ remains approximately $9 \times 10^{-2}$ emu/g. Once magnetic field exceeds $H_c$, the slopes become similar to one another as shown in the inset of Fig. 2. The magnetization continues to increase along all the axes, which is a typical behavior of WF-LRO state. We did not observe a spin-flop anomaly in this field region, which indicates the lack of a strong easy-axis anisotropy in this system.

Let us first discuss the crystal structure to reveal this WF-LRO state. BaCu$_2$Ge$_2$O$_7$ has a structure isomorphous to BaCu$_2$Si$_2$O$_7$ (see Fig. 1 of Ref. 4) with slightly longer lattice parameters: $a = 7.028$ Å, $b = 13.403$ Å, and $c = 7.044$ Å. Two neighboring Cu$^{2+}$ ions are connected by one O$^{2-}$ ion and they form a chain along the $c$ axis. However, the bond of Cu-O-Cu is not straight as shown in Fig. 3(a). The angle of $\angle$ Cu-O-Cu ($135^\circ$) is larger than that of BaCu$_2$Si$_2$O$_7$ ($124^\circ$), which is consistent with the larger intra-chain interaction. Two mechanisms of WF are known up to now: one is a single-ion anisotropy for NiF$_2$ and the other is a DM antisymmetric interaction for $\alpha$-Fe$_2$O$_3$, where the antisymmetric exchange interaction $D \cdot [S_i \times S_{i+1}]$ gives spin canting. There cannot be a single-ion anisotropy in BaCu$_2$Ge$_2$O$_7$, because a magnetic moment in BaCu$_2$Ge$_2$O$_7$ is attributed to a $S = 1/2$ spin on Cu$^{2+}$ ions. Then it necessarily follows that the DM interaction is the origin of WF in this compound. The local symmetry of nearest neighbor (nn) Cu$^{2+}$ ions is actually low enough.
to allow the DM interaction. According to the rule given by Moriya, the Dzyaloshinskii vectors $D_i$ at bond $i$ are approximately defined as schematically drawn in Fig. (a). The positions of only two neighboring Cu$^{2+}$ ions and one intermediate O$^{2-}$ ion are taken into account. According to the room-temperature structural data, $D_i$ is written as $D_i = D((-1)^i0.8332, (-1)^i0.5462, 0.0860)$. Here, the components perpendicular and parallel to the chain have different effects on the spin order; the former ($D_i^\perp = (-1)^iD(0.8332, 0.5462, 0)$) changes its sign from one bond to the next, while the latter ($D_i^\parallel = D(0, 0, 0.0860)$) keeps its sign along the chain. For the rest of the paper we shall ignore the effect of $D_i^\parallel$ and simply consider only $D_i^\perp$ from the following two reasons: 1) the magnitude of $D_i^\parallel$ is far smaller than that of $D_i^\perp$, and 2) $D_i^\parallel$ will stabilize a spiral order that is against the experimental observation.

We must know the arrangement of D vectors in the whole magnetic unit cell, because the bulk spontaneous magnetization is closely related to how D vectors are distributed. It is noted that D vectors and spin operators are both an axial vector when we consider the symmetry operations. For the $a$-axis directions, one chain is transformed to the neighboring one by the successive operations of a) reflection in the ac plane and b) rotation around the axis located at the middle of two adjacent Cu$^{2+}$ ions along the [101] direction and parallel to the $b$ axis. Through these operations, the $a$ component of $D_i^\perp$ changes its sign twice, the $b$ component is unchanged, and the order of the concerning spin operators are exchanged. As a result, $D_i^\perp$ at the $a$-axis neighboring bonds points an opposite direction. We can also transform a chain to the $b$-axis neighboring one by the operation of reflection in the $ac$ plane and following parallel shift to the $b$ direction. This process changes the sign of the $a$ component only. In this way we determined all the D vectors in the magnetic unit cell as shown in Fig. (b).

Next we discuss how these D vectors tilt spins to create the $b$-axis spontaneous magnetization. For this purpose, we must determine the principal direction of the spins. The crystal symmetry is high enough that it must be along the $a$, $b$, or $c$ direction. If we take only DM interaction into account, the fact that D vectors are not collinear along the $b$ direc-
tion can differentiate the three cases because there is a finite inter-chain interaction along the $b$ axis. However, the recent theoretical studies proved that DM interaction is always accompanied by an additional term quadratic to $D$, which recovers $O(3)$ symmetry of the spin-spin interaction. This term is called as KSEA interaction, and has been established also experimentally. Therefore we cannot predict the principal spin direction from DM and KSEA interactions even in the presence of inter-chain interaction.

On the other hand, experimental results indicates that the principal spin direction is along the $c$ axis. This is explained as follows; 1) Each chain must have weak ferromagnetic moment along the $b$ direction, while $D_\perp$ has the $a$ and $b$ components, 2) if the principal direction is along the $a$ or $b$ direction, spins are canted only toward the $c$ direction and we will have no $b$-axis magnetization, 3) only when the principal direction is along the $c$ axis, we will observe weak ferromagnetic moment along both the $a$ and $b$ directions. Thus, we safely concluded that the $c$ axis is the easy-axis direction in the actual system. Under this condition, spins on a single chain are confined in the plane perpendicular to D vectors (we shall call it as easy plane for convenience) as shown in Fig. (c). It is convenient to define the WF moment per chain as the sum of the two sub-lattice magnetizations: $M_{WF,k} = (M_{1,k} + M_{2,k})/2$, where $M_{i,k}$ denotes the magnetic moment at the $i$-th sub-lattice in the $k$-th chain. Obviously the direction of the weak ferromagnetic moment is parallel to the easy-plane and simultaneously perpendicular to the $c$ axis. Once we obtain the direction of $M_{WF,k}$ on each spin chain, the spatial configuration of $M_{WF,k}$ determines the bulk magnetization. Relative directions of $M_{WF,k}$ between the neighboring chain depend on the inter-chain interaction. In Fig. (d), four different cases according to the signs of $J_a$ and $J_b$ are schematically drawn. Among the four cases, a spontaneous magnetization along the $b$ axis is realized only when $J_a > 0$ and $J_b > 0$, and therefore BaCu$_2$Ge$_2$O$_7$ is considered to be the case. Consequently, the spin configurations in the magnetic unit cell os determined as shown in Fig. (e).

So far, we have assumed that the DM interaction is the dominant perturbation to the spin system and the inter-chain interaction gives only a secondary effect. This assumption is probably valid by the following discussion. The magnitude of DM interaction can be
estimated from the magnetization data. Using the angle between the easy plane and the ac plane being 57.3°, the canting angle of each spin from the c-axis direction is estimated as \( \theta = 0.95° \). Then the coarse relation, \( \tan 2\theta \cong D/J \), gives \( D \) as 18 K. On the other hand, we can also estimate the inter-chain interaction as an averaged value according to the chain mean-field theory: \( J = 540 \) K and \( T_N = 8.8 \) K give the averaged inter-chain interaction as \( |J^\perp| = 2.9 \) K, which is sufficiently smaller than \( D \). Of course, the direct estimation of \( J_a \) and \( J_b \) is necessary for further quantitative discussion, but \( |D| \gg |J_a| \) and \( |D| \gg |J_b| \) are probably valid in BaCu\(_2\)Ge\(_2\)O\(_7\). The above discussion means that BaCu\(_2\)Ge\(_2\)O\(_7\) is a good system to study the magnetism of weak-ferromagnetic spin chains that are weakly coupled with each other, and the sign of the inter-chain interaction can easily change the magnetic ground state demonstrated as the difference between BaCu\(_2\)Ge\(_2\)O\(_7\) and BaCu\(_2\)Si\(_2\)O\(_7\).

Finally we discuss the low-field anisotropic magnetization of BaCu\(_2\)Ge\(_2\)O\(_7\) upon this model structure. \( M_a \) steeply increases up to \( H_c \) first and suddenly changes its slope. This is qualitatively explained by the rotation of WF moment as schematically shown in Fig. 4 (a). When the field is applied parallel to the \( a \) axis, \( M_{WF,1} \) and \( M_{WF,2} \) hold their directions, while \( M_{WF,3} \) and \( M_{WF,4} \) are rotated almost by 180°, which can produce a large magnetization along the \( a \) axis. We consider that the spins on the chains 3 and 4 are cooperatively rotated without changing their relative angle so much, because both \( J_b \) and the Zeeman energy are too weak to change the relative angle of the spins against the dominant DM interaction. After this rotation has been finished at 280 Oe, large magnetization appears along the \( a \) axis, and simultaneously net magnetization along the \( b \) axis should disappear. In order to confirm this rotation, we carried out the transverse magnetization measurement, and found that the \( b \)-axis magnetization is actually suppressed with increasing field along the \( a \) axis as shown in Fig. 4 (b). Since the geometry of the pick-up coil for our transverse magnetization measurement was the second differential type, finite \( M_b \) gives an even-function response to the direct signal. Actually we got such a signal around 0 Oe, and observed the evolution of \( M_b \). However, as the field approach 280 Oe, the direct signal changes its shape and finally turns to an odd-function response, which means that the \( M_a \) induced by the field dominates.
the response of the pick-up coil. $M_b$ is now negligibly small, and we conclude that the spin structure shown in Fig. 4(b) is realized. Such spin rotation is one of the characteristics of weakly-coupled spin chain, where DM interaction roughly keeps WF moment per chain, while the direction of WF moment is determined as a result of the competition between Zeeman energy and inter-chain coupling.

The difference of the magnetic ground states in BaCu$_2$Ge$_2$O$_7$ and BaCu$_2$Si$_2$O$_7$ provides us useful spin system to study the effect of randomness in the inter-chain interaction. Both compounds are the end materials of the solid-solution system of BaCu$_2$(Ge$_{1-x}$Si$_x$)$_2$O$_7$. The mixture of Ge and Si will introduce randomness to the sign of the inter-chain coupling along the $a$ axis. This randomness reduces the evolution of 3D long-range order as is reported in a polycrystalline samples by Yamada and Hiroi.

To summarize, we discovered the weak-ferromagnetic state in the 1D Heisenberg antiferromagnet BaCu$_2$Ge$_2$O$_7$, which is to our knowledge the first uniform $S = 1/2$ spin chain system that shows weak-ferromagnetic long-rang order. The Dzyaloshinskii-Moriya interaction adds a weak-ferromagnetic moment to each spin chain, and the relatively weak inter-chain interaction allows us to treat this system as weakly-coupled weak-ferromagnetic chains. The spin rotation by weak external field becomes possible by the combination of weak ferromagnetic moment per each spin and relatively weak inter-chain interaction, which is expected only in such a weakly coupled 1D spin system.

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FIGURES

FIG. 1. Magnetic susceptibilities along the three principal axes measured at 1000 Oe. The solid and dashed lines show the calculation by Bonner and Fisher with $J = 540$ K as a fitting parameter assuming a different $g$ values. Inset: Low-temperature magnetization along the three principal axes measured at $H = 10$ Oe.

FIG. 2. Field dependence of the magnetization along the principal axes below 1000 Oe at $T = 5$ K. At $H = 0$ Oe, spontaneous magnetization appears along the $b$ axis, while the magnetization along the $a$ axis becomes the largest above 180 Oe and has a kink at 280 Oe. Inset: Field dependence of the magnetization up to 5 T at the same temperature.

FIG. 3. (a) Single Cu-O chain, and $\mathbf{D}$ vectors between the nn Cu$^{2+}$ ions deduced from the local symmetry. (b) 3D schematic arrangement of $\mathbf{D}_\perp$’s in the magnetic unit cell. All the vector products are calculated from left to right as indicated by the arrow. See details in the text. (c) Model of spin canting on the easy plane. The WF moment per spin chain is defined as $\mathbf{M}_{WF,k} = (\mathbf{M}_{1,k} + \mathbf{M}_{2,k})/2$. (d) Spatial configuration of $\mathbf{M}_{WF,k}$ for $[J_a > 0, J_b > 0]$, $[J_a < 0, J_b > 0]$, $[J_a > 0, J_b < 0]$, and $[J_a < 0, J_b < 0]$. (e) 3D spin arrangements of BaCu$_2$Ge$_2$O$_7$.

FIG. 4. (a) Schematic picture of spin rotation by the $a$-axis field. $\mathbf{M}_{WF,k}$ is indicated by an arrow. (b) Transverse magnetization measurement. Magnetic field is applied along the $a$ axis and the magnetization along the $b$ axis is measured. The inset shows a direct response of the pick-up coil.
Bonner-Fisher (g=1.95)  
Bonner-Fisher (g=2.35)
Magnetization (10^1 emu/g) vs. Magnetic Field (Oe)

- H || a
- H || b
- H || c
\( H_a = 0 \) \quad \text{and} \quad \left \{ \begin{array}{l} H_a = 280 \text{ Oe} \\ M_{WF,1} \quad M_{WF,2} \\ M_{WF,3} \quad M_{WF,4} \\ M_{WF,5} \quad M_{WF,6} \end{array} \right. 

(a) 

(b) 

\( H \parallel a \)

\( M_b (10^2 \text{ emu/g}) \)

Magnetic Field (Oe)