Two-stage spin-flop transitions in \( S = 1/2 \) antiferromagnetic spin chain BaCu\(_2\)Si\(_2\)O\(_7\)

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Two-stage spin-flop transitions are observed in the quasi-one-dimensional antiferromagnet, BaCu\(_2\)Si\(_2\)O\(_7\). A magnetic field applied along the easy axis induces a spin-flop transition at 2.0 T followed by a second transition at 4.9 T. The magnetic susceptibility indicates the presence of Dzyaloshinskii-Moriya (DM) antisymmetric interactions between the intrachain neighboring spins. We discuss a possible mechanism whereby the geometrical competition between DM and interchain interactions, as discussed for the two-dimensional antiferromagnet La\(_2\)CuO\(_4\), causes the two-stage spin-flop transitions.

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

The magnetic long-range order (LRO) of a low-dimensional \( S = 1/2 \) antiferromagnet (AF) is qualitatively different from that observed in a conventional three-dimensional (3D) AF. The absence of LRO in a purely one-dimensional (1D) \( S = 1/2 \) Heisenberg AF at any temperature and a two-dimensional (2D) one at \( T > 0 \) K was proved several decades ago. Weak but finite interactions between chains (1D) or planes (2D) are thus indispensable for achieving the magnetically ordered state at a finite temperature. In such weakly coupled chain or plane systems, the magnitude of Dzyaloshinskii-Moriya (DM) antisymmetric interactions, if they exist, can be comparable to that of interchain or interplane interactions, and as a result, DM interactions cause several behaviors different from those of conventional 3D AF. For example, the field-induced gap in magnetic excitation has been investigated for 1D Cu benzoate with respect to the effective staggered field induced by DM interactions. In this letter, we report exotic two-stage spin-flop transitions in the quasi-1D spin system BaCu\(_2\)Si\(_2\)O\(_7\), which are probably due to the competition between DM and interchain interactions. The magnetic properties of BaCu\(_2\)M\(_2\)O\(_7\) (\( M = \text{Si and Ge} \)) have been studied recently, and it was found that the DM interactions play a central role in the weak-ferromagnetic order of BaCu\(_2\)Ge\(_2\)O\(_7\). Since BaCu\(_2\)Si\(_2\)O\(_7\) is isomorphic to BaCu\(_2\)Ge\(_2\)O\(_7\), we expect the presence of DM interactions in BaCu\(_2\)Si\(_2\)O\(_7\) also. The results are discussed in comparison with the complicated spin-flop nature of La\(_2\)CuO\(_4\), a parent compound of high-\( T_c \) cuprates, where the symmetric interplane interactions and the antisymmetric intraplane DM interactions give rise to a complex spin rotation under magnetic fields.

A single-crystal sample was prepared by a floating-zone (FZ) method as previously reported. The crystal was cut into a rectangle with dimensions of 1\( \times \)2\( \times \)1 mm\(^3\) \((a \times b \times c)\). The orientations of all the surfaces were confirmed by x-ray Laue backscattering. Since the diffraction patterns from the \( ab \) and \( bc \) planes are difficult to distinguish, we checked the orientation also using an \( \omega-2\theta \) x-ray diffractometer. Temperature and magnetic-field dependences of the magnetization \( M_i(T, H) \), \( i = a, b, \) and \( c \) and susceptibility \( \chi_i(T, H) = \frac{M_i(T, H)}{H} \) were measured using a commercial SQUID magnetometer (MPMS-7) up to \( H = 7 \) T, with which we can control the temperature and magnetic field to within \( \pm 0.01 \) K and \( \pm 1 \) Oe of the set values, respectively.

First we show the previously reported low-field susceptibility data \( (H = 0.1 \) T\) in Fig. 1(a). The high-temperature behavior obeys the theoretical Bonner-Fisher curve, indicating paramagnetic behavior of the uniform 1D \( S = 1/2 \) Heisenberg AF chain. The AF transition occurs at \( T_N = 9.2 \) K, below which the susceptibilities show anisotropic behavior. \( \chi_c(T, 0.1 \) T\) shows a large decrease below \( T_N \) while \( \chi_a(T, 0.1 \) T\) and \( \chi_b(T, 0.1 \) T\) roughly keep the values at \( T_N \) down to 2 K. This indicates that the \( c \) axis is the principal easy axis, as confirmed by neutron diffraction. The large residual susceptibility \( \chi_c(2.0 \) K, 0.1 T\) should also be noted. The absence of divergent behavior toward \( T = 0 \) K indicates that this residual \( \chi_c \) is not the response of free spins due to impurities and/or crystal imperfections, but rather is intrinsic to the spin susceptibility of the BaCu\(_2\)Si\(_2\)O\(_7\) system. Moreover, the anisotropy is also observed above \( T_N \). Two characteristic features are found in this region. On the one hand, \( \chi_a \) is larger than \( \chi_b \) and \( \chi_c \) at room temperature, which can be attributed to the difference in \( g \) values roughly determined from the oxygen coordination around Cu\(^{2+} \) ions. In the vicinity of \( T_N \), on the other hand, the deviation from the Bonner-Fisher curve becomes notable only in \( \chi_b \) and \( \chi_c \), while \( \chi_a \) retains the Bonner-Fisher-like behavior even close to \( T_N \). This upward deviation suggests the appearance of an additional contribution to the magnetization only along the \( bc \) plane.

What characterizes this compound is a peculiar field dependence of \( \chi_a(T, H) \) below \( T_N \). As is shown in Fig. 1(b), \( \chi_c \) traces three different curves at \( H = 0.1, 3.0, \)
and 6.0 T. Since the 0.1 T field is well below the first spin-flop field, as will be mentioned later, \( \chi_c(T, 0.1 \text{T}) \) represents the zero-field susceptibility. \( \chi_c(T, 6.0 \text{T}) \) shows behavior similar to that of conventional AF in the spin-flop phase, where \( \chi_c(T) \) maintains almost the same value as that at \( T_N \). In contrast, \( \chi_c(T, 3.0 \text{T}) \) is notable in that it follows neither \( \chi_c(T, 0.1 \text{T}) \) nor \( \chi_c(T, 6.0 \text{T}) \). It decreases smoothly toward \( T = 0 \text{K} \), but not as fast as \( \chi_c(T, 0.1 \text{T}) \). \( T_N \) is almost unchanged and no indication of another transition is found. Thus we conclude that the three sets of data are intrinsic to BaCu$_2$Si$_2$O$_7$.

The existence of the three phases is more clearly seen in the field dependence of \( M_c(T,H) \), as shown in Fig. 2(a). \( M_c(9.2 \text{K} (= T_N), H) \) has an almost linear relationship with the magnetic field up to \( H = 7.0 \text{T} \). The data at 8.5 K, which is slightly lower than at \( T_N \), shows a steep magnetization jump at \( H = 2.0 \text{T} \), and broad increase from \( H = 5.0 \text{T} \) to 5.3 T. Both transitions become clearer in \( M_c(5.0 \text{K}, H) \). The magnetization shows a discontinuous jump at \( H_{c1} = 2.0 \text{T} \) and \( H_{c2} = 4.9 \text{T} \). Consequently, it becomes evident that the \( \chi_c \)'s shown in Fig. 2(b) represent the susceptibilities of these three regions. The phase diagram obtained from the magnetization and the susceptibility is shown in Fig. 2(b). The low-temperature ordered state is separated into three phases; for convenience, we call the lower-, middle-, and higher-field phases AF, SF1, and SF2, respectively. The phase boundaries between AF and SF1 and between SF1 and SF2 are almost temperature independent. We also confirmed that the spin-flop transition is absent when the field is applied along the \( a \)- and \( b \)-axis directions (only \( \chi_b(5.0 \text{K}, H) \) is shown in Fig. 2(a)). Thus, we can eliminate the possibility of the mixture of misaligned domains being responsible for one of the two transitions.

The presence of three phases is not expected in a conventional AF. To construct a proper model in order to explain these two-stage spin-flop transitions, we consider the following three results. First, the \( c \)-axis is the principal easy axis at \( H = 0 \text{T} \), as was determined by neutron diffraction [14]. Second, \( \chi_b \) and \( \chi_c \) are enhanced in the vicinity of \( T_N \). Such behavior is characteristic of the AF transition with spin canting, as was observed in La$_2$CuO$_4$ [11] and Bi$_2$Sr$_2$CoO$_{6.25}$ [12]. In the present case, the canted moments are confined to the \( bc \) plane and probably originate from the DM interactions. Third, \( \chi_c(T, 6.0 \text{T}) \) is almost unchanged below \( T_N \). Such a weak temperature dependence is usually observed in a conventional spin-flop phase, where spins are almost perpendicular to the applied field with slight canting toward the field direction. In a conventional AF without strong anisotropy, however, the susceptibility above \( T_N \) exhibits a normal paramagnetic behavior (Curie-Weiss law for 3D and Bonner-Fisher curve for 1D), so that the particular enhancement of susceptibility is absent. Thus the presence of additional susceptibility at 6.0 T below \( T_N \) implies that spins are more canted toward the \( c \)-direction than expected for only an axial field. The most probable source of this canting is DM interactions.

DM interactions often occur in a spin system with low crystallographic symmetry. Dzyaloshinskii first pointed out that an asymmetric superexchange interactions such as \( \mathbf{D} \cdot \mathbf{S}_i \times \mathbf{S}_j \) is allowed in several antiferromagnets [13]. Later Moriya gave a microscopic basis for the interactions [14]. For the particular case of BaCu$_2$Si$_2$O$_7$, the intra-chain Cu-O-Cu bond actually has a local symmetry (no inversion, but a mirror plane including two Cu$^{2+}$ and one O$^{2-}$ ion) that allows DM interactions at this bond. Note that DM interactions are perturbative to the main superexchange interaction. Thus it is sufficient to consider DM interactions only between the intrachain neighboring Cu$^{2+}$ ions.

Let us now construct a model structure, taking DM interactions into account. By considering the local symmetry of the intrachain Cu-O-Cu bond, we can estimate Dzyaloshinskii vectors as real-space vectors \( \mathbf{D}_i = D((-1)^i0.86, (-1)^i0.51, 0.07) \). The magnitude of the \( c \)-component is one order lower than those of the \( a \) and \( b \)-components, so that it can be safely ignored. We also assume the presence of an easy-axis anisotropy along the \( c \)-axis as is suggested by \( \chi_c(T, 0.1 \text{T}) \). Then the spin arrangement at \( H = 0 \text{T} \) is obtained as shown in Fig. 3(a) under the experimentally determined inter-chain interactions: \( J = 24.1 \text{meV (AF)}, J_a = -0.460 \text{meV (ferromagnetic)}, J_b = 0.200 \text{meV (AF)}, \) and \( 2J_{110} = 0.152 \text{meV (AF)} \). Spin canting and accompanying weak ferromagnetic moment per chain are present, but such weak ferromagnetic moments are mutually compensated between the \( a \)-axis neighboring chains. Therefore, this model is consistent with the observation of no spontaneous magnetization. Whenever we discuss the effect of DM interactions, we should also pay attention to the effect of additional pseudo-dipole interactions accompanying DM interactions [15]. However, the effect of this term (so-called KSEA interactions) is to erase the anisotropy, and under the presence of easy-axis anisotropy along the \( c \)-axis, it does not change the spin configurations shown in Fig. 3(a). The effect of this term will also be discussed later.

In a conventional spin-flop theory, only symmetric spin-spin interactions are taken into account, and therefore, the competition between Zeeman energy and anisotropy energy determines the spin-flop field \( H_c \). On the other hand, DM interactions are \( antisymmetric \), so that they can compete with symmetric interchain interactions under a certain geometry of the spin arrangement. This idea was first proposed by Thio \textit{et al.} to explain the anomalous spin-flop behavior of La$_2$CuO$_4$ [9]. They discussed the magnetic behavior of La$_2$CuO$_4$ with respect to a staggered moment and a ferromagnetic moment defined as a difference and a sum of two neighboring spins belonging to different sublattices. When DM interactions are sufficiently strong, the spin-flop transition
occurs in such a way that the weak-ferromagnetic moments (initially perpendicular to the field) rotate toward the field direction, and as a result, one does not observe the discontinuous magnetization jump at the critical field that is observed in a conventional AF. The rotation direction (clockwise or counterclockwise) depends on the direction of \(D\) vectors. Thus, if the initial direction of the weak ferromagnetic moments alternate with every layer of \(\text{La}_2\text{CuO}_4\), the rotation directions also alternate \(\pm\). Within this rotation process, a competition between DM and interchain interactions can occur.

To demonstrate such a competition, we further simplify our spin system as follows. First, we ignore the effects of \(J_b\) and \(J_{110}\) and take only \(J_a\) into account, because \(J_a\) is the largest among the interchain interactions. Next, we consider the \(a\)-axis component of \(D\) vectors (\(D_a\)) only, because \(D_a\) must be responsible for the observed \(bc\)-plane anisotropy. Then we can focus our discussion on four particular spins (black arrows) shown in Fig. 3(b), in which white arrows represent \(D_a\). Note that these spin chains are coupled with ferromagnetic \(J_a\). The signs of \(D_a\) alternate along the \(a\) axis, which means that the initial directions of the weak ferromagnetic moments also alternate along the \(a\)-axis. When we consider a single chain with alternating \(D_a\), as shown in Fig. 3(c), magnetic field applied along the \(c\) axis causes one spin-flop transition at \(H_c\). Below the spin-flop field, the weak ferromagnetic moment rotates with increasing field up to \(H_a\), which corresponds to each spin also rotating in the same direction.

Now let us take the effect of \(a\)-axis neighboring chains into account. If the effect of \(J_a\) is far smaller than that of DM interactions, spins may behave in the same way as in the case of a single chain. Figure 3(d) shows a schematic of the behavior; again we will obtain only one spin-flop field. If the magnitude of \(J_a\) becomes comparable to that of \(D_a\), however, the situation differs. Because of the alternating \(D_a\), the rotation direction of the weak ferromagnetic moment (and thus each spin) is opposite to that of the \(a\)-axis neighboring chains. In Fig. 3(d), \(a\)-axis neighboring spins are almost antiparallel at \(H = H_c\); this is unfavorable for large \(J_a\). Such an effect seems to be negligible at \(H \approx 0\) T and \(H \gg H_c\), because in both situations, spins are approximately parallel to each other along the \(a\)-axis. Therefore, a new phase can appear only around \(H_c\). The presence of the SF1 phase suggests that the effect of \(J_a\) is comparable to that of \(D_a\) in \(\text{BaCu}_2\text{Si}_2\text{O}_7\). In this phase, the \(a\)-axis neighboring spins must be parallel to each other. There are two possible configurations according to the crystal symmetry: one is that the spins are pointed approximately in the \(a\) direction, and the other is that they are pointed approximately in the \(b\) direction. However, the latter seems to be unfavorable, considering the effect of KSEA interactions \(\pm\) which effectively add an easy-axis anisotropy along the direction parallel to \(D_a\). This means that spins tend to point in the \(a\) direction, and thus the former case is favored. As a result, we propose a spin configuration of the intermediate SF1 phase, as schematically illustrated in Fig. 3(e). By increasing magnetic field, spins start to rotate within the \(bc\) plane (AF) up to \(H_{c1}\), switch to the \(ac\) plane (SF1), and then return to the \(bc\) plane (SF2) at \(H_{c2}\). This concept is consistent with the appearance of additional spin canting in the SF2 phase; the alternating \(D_a\) can produce additional spin canting toward the field direction in every chain. Such complex spin-flop transitions cannot be observed in a spin system with only symmetric spin-spin interactions, and we believe that they are possible only when the symmetric and antisymmetric interactions coexist with comparable magnitude.

For further quantitative discussion, we should consider the effects of \(J_b\), \(J_{110}\), and the \(b\) component of \(D\). We intentionally ignore the possibility that spins continuously change their directions from the \(ac\) to the \(bc\) plane. This corresponds to assuming the existence of some unknown potential barrier between these two configurations. However, a recent neutron diffraction study of \(\text{BaCu}_2\text{Si}_2\text{O}_7\) in a magnetic field revealed a sudden change of the spin directions, which is consistent with the proposed model \(\pm\). The detailed quantitative analysis will be reported in the future.

In summary, we have observed a new type of spin-flop transition, where the low dimensionality and accompanying antisymmetric interaction cooperatively induce characteristic spin-flop transitions. The study of DM interactions is still one of the hot topics of low-dimensional quantum antiferromagnets, particularly from a theoretical viewpoint \(\pm\), and we believe that this compound will be a well-defined basic material with which to study the weakly coupled \(S = 1/2\) spin chain system with the DM interaction.

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FIG. 2. (a) Field dependence of the magnetization along the c axis at T = 5.0, 8.5, and 9.2 K. At T = 5.0 K, spin-flop transitions are observed at H = 2.0 and 4.9 T. The b-axis magnetization shows no anomaly. (b) Phase diagram around T_N. Open and filled circles are the boundaries obtained from \( \chi - T \) and \( M - H \) measurements, respectively. Solid and dotted lines are guides for the eye.

FIG. 1. (a) Magnetic susceptibilities along the three principal axes around the Néel temperature measured at \( H = 0.1 \) T. The data were taken from Ref. [5]. (b) Low-temperature c-axis susceptibilities measured with three different fields. \( T_N \) is almost unchanged with applied field.
FIG. 3. (a) Expected spin arrangement at $H = 0$ T under the effect of DM + KSEA interactions. (b) Four spins on the $a$-axis neighboring chains at $H = 0$ T. (c) Spin configurations of a single chain with DM interactions with the field applied along the $c$ axis. (d) Spin-flop process expected when $J_a$ is negligibly small. Spins are confined within the $bc$ plane, and a spin-flop transition occurs only at $H_c$. (e) Possible two-stage spin-flop transitions. Spins are confined to the $bc$ plane in the AF and SF2 phases, while they turn to the $ac$ plane in the SF1 phase.