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 $\text{BaM}_{\{2\}}\text{Si}_{\{2\}}\text{O}_{\{7\}}$  system ( $M=\text{Cu}, \text{Co}, \text{Mn}$ )

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# Magnetic properties of the low dimensional $\text{BaM}_2\text{Si}_2\text{O}_7$ ( $\text{M} = \text{Cu}, \text{Co}, \text{Mn}$ ) system

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We investigated the magnetic properties of the low dimensional  $\text{BaM}_2\text{Si}_2\text{O}_7$  ( $\text{M} = \text{Cu}, \text{Co}$ , and  $\text{Mn}$ ) system using both experimental measurements and theoretical calculations. Magnetization, specific heat, and single crystal neutron diffraction measurements have been performed on single crystal  $\text{BaMn}_2\text{Si}_2\text{O}_7$ . The spin structure was determined and a magnetic phase diagram with applied field along the  $b$ -axis was constructed, which contains a spin flop transition around 6 T. Magnetization and specific heat measurements confirmed the presence of weak ferromagnetism in  $\text{BaCo}_2\text{Si}_2\text{O}_7$ . Furthermore, we performed local-spin density approximation with on-site Coulomb energy (LSDA+U) calculations for the  $\text{BaM}_2\text{Si}_2\text{O}_7$  ( $\text{M} = \text{Cu}, \text{Co}$ , and  $\text{Mn}$ ) system. Based on the first-principles calculations, the origin of the magnetic differences of the three materials are discussed.

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## I. INTRODUCTION

Unlike traditional one-dimensional (1D) and three-dimensional (3D) magnetic systems, a quasi-1D magnetic material has unique magnetic properties. If the magnetic moment is as small as  $1/2$  or  $1$ , the quantum effect as spin/thermal fluctuation could interfere the ground state and complicate the system: the magnetic order could not form even at 0 K in a purely 1D spin- $1/2$  chain system, while the inter-chain interactions could induce a Neel ordering state as a 3D antiferromagnet<sup>1-4</sup>. As a result, a quasi-1D system with weak coupling between the magnetic chains will exhibit a crossover from 1D magnetic behavior<sup>5-10</sup> at high temperatures to a 3D ordered state at low temperatures. Moreover, the strong spin anisotropy of the system could exhibit rich magnetic phase diagram under applied magnetic field below the ordering temperature. Hence, studying the inter- and intralayer interaction of the quasi-1D system with different momentum is very important and has received considerable attention in the past years.

$\text{BaM}_2\text{Si}_2\text{O}_7$  ( $\text{M} = \text{Cu}, \text{Co}$ , and  $\text{Mn}$ ) with layered structure is an excellent system to study such low-dimensional magnetic behavior. Among of these three compounds,  $\text{BaCu}_2\text{Si}_2\text{O}_7$ , which has a spin  $1/2$  ( $\text{Cu}^{2+}$ ) feature, has been extensively studied. This compound adopts an orthorhombic structure with a space group of  $Pnma$ . The nearest  $\text{Cu}^{2+}$  ions through the  $\text{O}^{2-}$  ions construct a zigzag chain along the  $c$ -axis. Below  $T_N = 9.2$  K, an antiferromagnetic ordered state is formed, in which the magnetic easy axis is the  $c$ -axis<sup>11</sup>. With applied magnetic field along the  $c$ -axis, a two step spin-flop transitions have been reported<sup>12-15</sup>. Moreover, the exchange interactions of the 1D-dimensional magnetic spin chain has been studied by inelastic neutron scattering measurements and theoretical calculations<sup>16-20</sup>.

The replacement of  $\text{Cu}^{2+}$  ions with larger-sized  $\text{Co}^{2+}$  and  $\text{Mn}^{2+}$  ions results in a structural distortion.  $\text{BaCo}_2\text{Si}_2\text{O}_7$

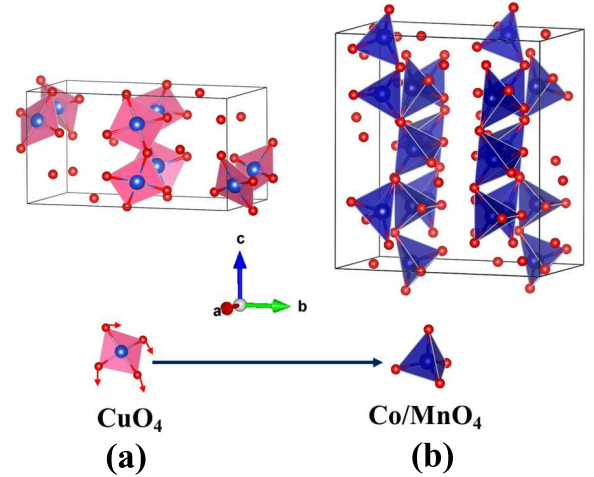


FIG. 1: (color online) a) Schematic crystalline structures for (a)  $\text{BaCu}_2\text{Si}_2\text{O}_7$  and (b)  $\text{BaM}_2\text{Si}_2\text{O}_7$  ( $\text{M} = \text{Mn}$  and  $\text{Co}$ )

and  $\text{BaMn}_2\text{Si}_2\text{O}_7$  have a monoclinic crystal structure with the space group  $C2/c$ <sup>21</sup>. Accordingly, the  $\text{M-O}$  ligands for the  $\text{CuO}_4$  plaquettes in the  $\text{Cu}$  sample now form a  $\text{Co/MnO}_4$  tetrahedron in the  $\text{Co}$  and  $\text{Mn}$  samples<sup>22,23</sup>, as shown in Fig. 1. Previous studies, while limited, suggested a ferromagnetic-like ground state for  $\text{BaCo}_2\text{Si}_2\text{O}_7$  with spin- $3/2$  ( $\text{Co}^{2+}$ )<sup>22,24</sup>. For  $\text{BaMn}_2\text{Si}_2\text{O}_7$ , powder neutron diffraction study demonstrated an antiferromagnetic spin structure along  $c$  axis below  $T_N = 26$  K<sup>25</sup>. Magnetization measurements with an applied field along the  $b$ -axis suggested a spin flop transition at  $B = 6$  T. Taking into account these previous studies, it becomes clear that each of the three compositions in the  $\text{BaM}_2\text{Si}_2\text{O}_7$  system have distinct magnetic properties.

Due to the limited studies on  $\text{BaCo}_2\text{Si}_2\text{O}_7$  and  $\text{BaMn}_2\text{Si}_2\text{O}_7$ , several questions have been left open.

For example, the ground state of  $\text{BaCo}_2\text{Si}_2\text{O}_7$  needs to be confirmed by more detailed investigation. In the case of  $\text{BaMn}_2\text{Si}_2\text{O}_7$ , the magnetic properties and magnetic structure were preliminarily studied using magnetization measurements and powder neutron diffraction in our previous work<sup>25</sup>. Although a spin-flop transition was observed with magnetic field, further studies are necessary to build a complete magnetic phase diagram. Moreover, The spin structure of  $\text{BaMn}_2\text{Si}_2\text{O}_7$  was determined using a polycrystalline sample. As such, an investigation utilizing single crystal neutron diffraction, which usually leads to a more accurate determination of spin structure is deserved. Most importantly, there has been no systematic study on this system to better understand the driving force for the distinct magnetic ground states. In this paper, we (1) performed magnetic properties, specific heat, and single crystal neutron diffraction measurements under applied fields to revisit the spin structure and construct the magnetic phase diagram for single crystalline  $\text{BaMn}_2\text{Si}_2\text{O}_7$ ; (2) studied the physical properties of polycrystalline  $\text{BaCo}_2\text{Si}_2\text{O}_7$  to confirm its magnetic ground state; and (3) performed LSDA + U calculations to systematically study the exchange interactions of the system. Our discussions based on the detailed comparison among the obtained exchange interactions for the system show that the structure distortion and the outer shell electronic configuration are two main reasons for the systematic changes of the magnetic ground states for these three samples.

## II. EXPERIMENTAL

Single crystal  $\text{BaMn}_2\text{Si}_2\text{O}_7$  was grown using an image furnace. The detailed method is described elsewhere.<sup>25</sup>. Polycrystalline  $\text{BaCo}_2\text{Si}_2\text{O}_7$  was synthesized by solid state reactions. Stoichiometric mixtures of  $\text{BaCO}_3$ ,  $\text{CoCO}_3$ , and  $\text{SiO}_2$  were ground and reacted at a temperature of 1100 °C in air for 60 hours with several intermediate grindings. The magnetic susceptibility, magnetization, and heat capacity were measured using a PPMS (physical property measurement system, Quantum Design). The zero field single-crystal neutron diffraction was performed at the HB-3A Four-Circle Diffractometer and high-field neutron diffraction measurements were carried out at the cold neutron triple-axis (CTAX) spectrometer using a 11-Tesla cryomagnet at the High Flux Isotope Reactor, Oak Ridge National Laboratory. A neutron wavelength of 1.005 Å from a bent perfect Si-331 monochromator was used in HB-3A<sup>26</sup>. The neutron diffraction data were refined by the FullProf Suite<sup>27</sup>.

## III. RESULTS

### A. $\text{BaMn}_2\text{Si}_2\text{O}_7$

The temperature dependence of susceptibility,  $\chi$ , under selected magnetic fields for  $\text{BaMn}_2\text{Si}_2\text{O}_7$  is shown in Fig. 2. With an applied field  $H = 0.1$  T along the  $b$ -axis,  $\chi$  shows a broad peak around 30 ~ 40 K, that is followed by a sharp

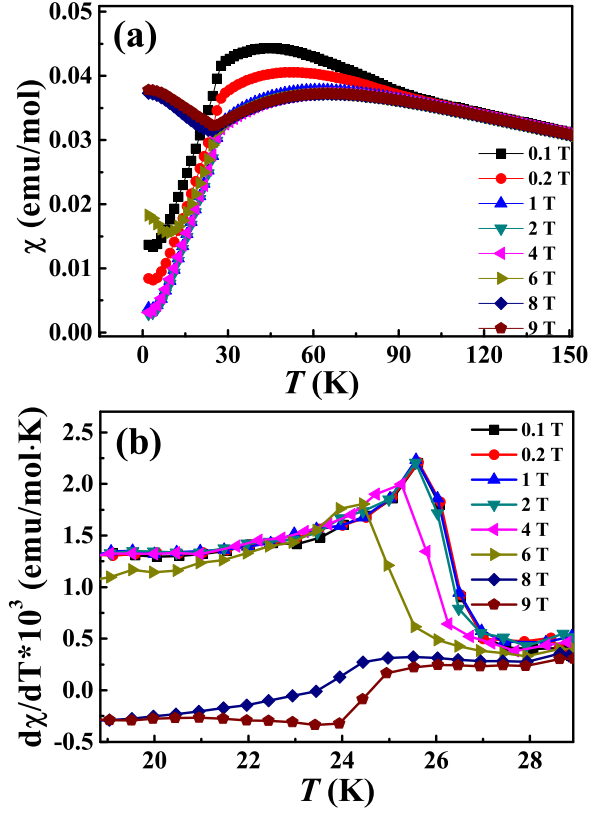


FIG. 2: (color online) (a) The temperature dependence of susceptibility ( $\chi$ ) (b) and its derivative,  $d\chi/dT$  at selected fields for  $\text{BaMn}_2\text{Si}_2\text{O}_7$ . The applied field is along the  $b$ -axis.

decline around 26 K, which suggest that  $\text{BaMn}_2\text{Si}_2\text{O}_7$  undergoes a transition from the 1D Bonner-Fisher model<sup>6,28</sup> (broad peak) to long-range magnetic order (sharp drop). The ordering temperature,  $T_N = 26$  K for 0.1 T, is defined as the peak position of the derivative of  $\chi$ , Fig. 2(b). For  $H \leq 6$  T,  $T_N$  decreases with increasing magnetic field; for  $H \geq 8$  T,  $T_N$  increases with increasing magnetic field, and,  $\chi$  increases with decreasing temperature below  $T_N$ . This distinct behavior between different field regimes suggests either spin reorientation or a spin flop transition induced by an applied field of 6 ~ 8 T.

The field dependence of magnetization,  $M$ , at selected temperatures for  $\text{BaMn}_2\text{Si}_2\text{O}_7$  is shown in Fig. 3. With  $H$  along the  $b$ -axis and temperatures below  $T_N$ ,  $M$  exhibits a sharp slope change around 6 T. Accordingly, the  $dM/dH$  curve (Fig. 3(b)) shows a sharp peak, which defines the critical field,  $H_c$ . At 2 K,  $H_c = 6.0$  T and shifts to higher fields with increasing temperature. As the temperature approaches  $T_N$ , (e.g., 25 K), this increase becomes very weak.

The specific heat for  $\text{BaMn}_2\text{Si}_2\text{O}_7$  is shown in Fig. 4. At zero field, the sharp peak at 26 K, corresponds to the  $T_N$ . For  $H \leq 6$  T along the  $b$ -axis, the peak (or  $T_N$ ) shifts to lower temperature with increasing magnetic field. However, the peak position of the  $H = 9$  T curve is higher than the 8 T curve, which is consistent with the trend of  $T_N$  defined by the

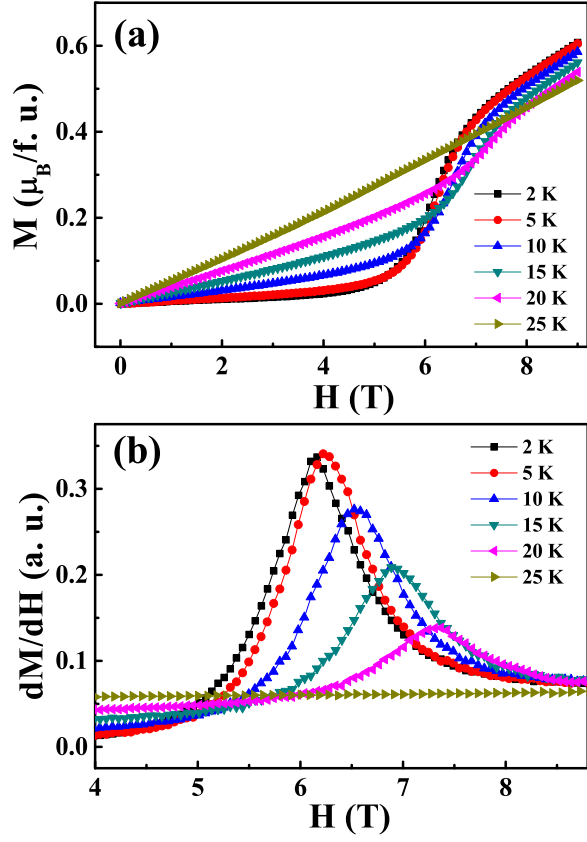


FIG. 3: (color online) (a) The field dependence of magnetization ( $M$ ) and (b) its derivative,  $dM/dH$  at selected temperatures for  $\text{BaMn}_2\text{Si}_2\text{O}_7$ . The applied field is along the  $b$ -axis.

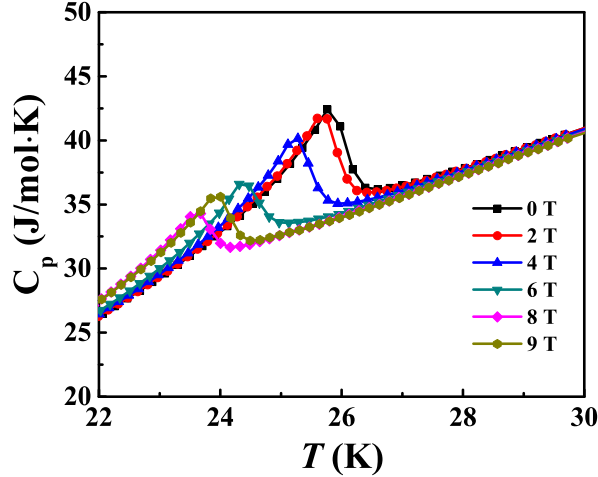


FIG. 4: (color online) The temperature dependence of specific heat around the transitions at selected fields for  $\text{BaMn}_2\text{Si}_2\text{O}_7$ . The applied field is along the  $b$ -axis.

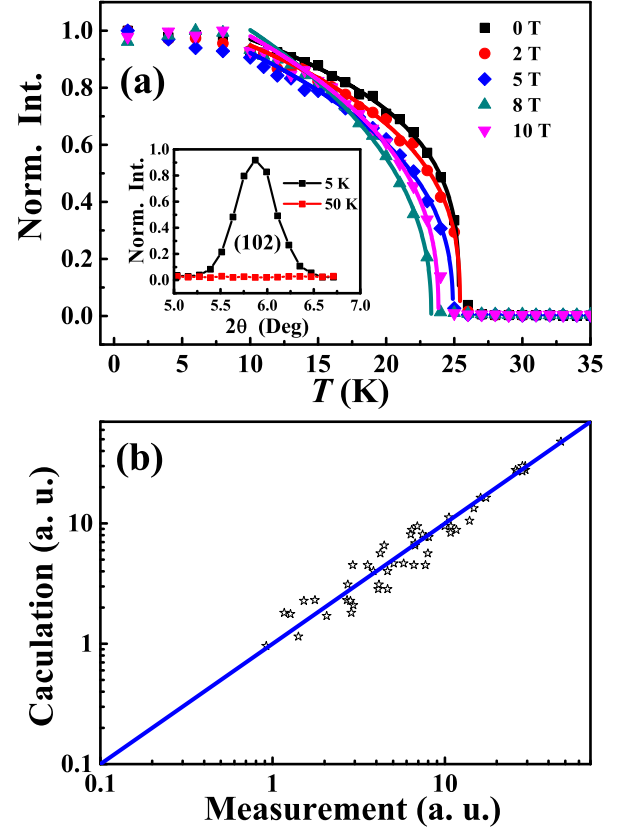


FIG. 5: (color online) (a) The temperature dependence of the normalized intensity for the  $(1\ 0\ 2)$  peak under different magnetic fields. The lines correspond to the power law fits described in the text. Inset: the intensity of the  $(1\ 0\ 2)$  peak at 5 K and 50 K. The field is applied along the  $b$ -axis for  $\text{BaMn}_2\text{Si}_2\text{O}_7$ . (b) The comparison between the observed and calculated  $F^2$  (squared structure factor) for the magnetic reflections.

magnetic susceptibility. Therefore, the susceptibility, magnetization, and specific heat all consistently exhibit a field-induced spin flop transition around 6 T for  $\text{BaMn}_2\text{Si}_2\text{O}_7$ , that is similar to the spin flop transition that has been observed in  $\text{BaCu}_2\text{Si}_2\text{O}_7$ <sup>12</sup>.

To further probe the magnetic properties of  $\text{BaMn}_2\text{Si}_2\text{O}_7$ , single crystal neutron diffraction measurements were performed under selected temperatures and fields. As shown in the inset of Fig. 5(a), there is a peak in intensity for the  $(102)$  plane that appears at 5 K but disappears at 50 K, which represents the antiferromagnetic (AFM) ordering that occurs at lower temperature. The normalized intensities (i.e., the order parameter)—for the  $(102)$  peak under different magnetic fields are shown in Fig. 5. The  $T_N$  shifts to lower temperature with increasing field while  $H \leq 8$  T, and shifts back to a higher temperature for 10 T. The order parameter data can be described by the power law function as

$$I = I_0 (1 - T/T_N)^{2\beta} \quad (1)$$

where  $T_N$  is the ordering temperature,  $I_0$  is the intensity at

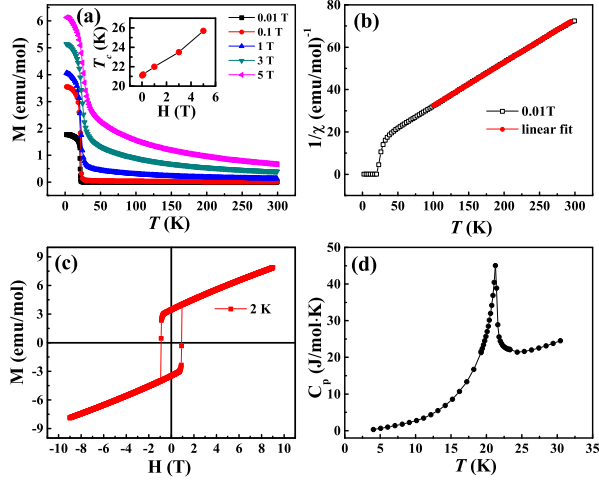


FIG. 6: (color online) All data for  $\text{BaCo}_2\text{Si}_2\text{O}_7$ . (a) The temperature dependence of magnetization under different magnetic fields. (b) The inverse susceptibility measured with  $H = 0.01$  T. The squares are experimental data and the solid line is the linear fit. (c) The hysteresis loop measured at 2 K. (d) The temperature dependence of the specific heat. Inset of (a): the field dependence of  $T_C$ .

base temperature, and  $\beta$  is the order parameter critical exponent. Fitting the data at different magnetic fields (solid lines in Fig. 5(a)) yields values of  $\beta$  ranging from 0.14(8) to 0.21(1), which are slightly smaller than the reported  $\beta = 0.22$  from a polycrystalline sample<sup>25</sup>.

In total, 53 magnetic Bragg peaks were measured. The symmetry analysis and refinement based on these peaks determined a spin structure as plotted in Fig. 7(b). In this spin structure, the magnetic moment is along the  $b$ -axis, and has a magnitude of approximately  $3.9 \mu_B$  at 5 K. The arrangement of the spins along the  $c$ - and  $a$ -axes is antiferromagnetic, whereas it is ferromagnetic along the  $b$ -axis. This spin structure differs from the one reported in the polycrystalline sample study, in which the arrangement of the spin along the  $a$ -axis is ferromagnetic<sup>25</sup>. Due to the average effect of powder samples, it was difficult to accurately determine the spin structure in our previous study that utilized polycrystalline samples. Therefore, the spin structure obtained from this single crystal using neutron diffraction should represent the true ground state magnetic structure. Moreover, the refinement of the nuclear Bragg peaks yields the crystallographic details presented in Table I. There are some small discrepancies between these results and those reported for polycrystalline samples<sup>25</sup>.

### B. $\text{BaCo}_2\text{Si}_2\text{O}_7$

The magnetic properties of polycrystalline  $\text{BaCo}_2\text{Si}_2\text{O}_7$  ( $S=3/2$ ) were also investigated. As shown in Fig. 6(a), the temperature dependence of magnetization exhibits a sharp increase below 21 K with  $H = 0.01$  T. Meanwhile, the specific heat shows a sharp peak at 21 K in Figure 6(d). Both results suggest that a long-range magnetic

TABLE I: Crystallographic information, including selected inter-atomic distances ( $\text{\AA}$ ) and bond angle ( $^\circ$ ) of  $\text{BaMn}_2\text{Si}_2\text{O}_7$  at 5 K.

crystal symmetry	monoclinic
space group	C2/c
a ( $\text{\AA}$ )	7.2937
b ( $\text{\AA}$ )	12.9656
c ( $\text{\AA}$ )	13.9819
$\beta$ ( $^\circ$ )	90.22
V ( $\text{\AA}^3$ )	1327.18
band	atomic coordination
Mn-O	Tetrahedral
Si-O	Tetrahedral
fitted result	Chi2(Intens): 0.782

ordering occurs at 21 K. The transition temperature,  $T_C$ , is defined as the peak position of the derivative of magnetization (not shown here). As shown in the inset of Fig. 6(a),  $T_C$  increases with increasing magnetic field. The hysteresis loop measured at 2 K (Fig. 6(c)) exhibits a square loop that reaches a magnetic moment of  $0.3 \mu_B/\text{Co}$ , which is much smaller than the theoretical value  $3 \mu_B/\text{Co}$ . The temperature- and field-dependence of susceptibility and the magnetic loop suggest a weak ferromagnetic ground state for  $\text{BaCo}_2\text{Si}_2\text{O}_7$ . The linear Curie-Weiss behavior of the inverse susceptibility from 100 to 300 K, as shown in Fig. 6(b), suggests AFM exchange interactions with a Curie temperature  $\Theta_{CW} = -58.5$  K. It is interesting that  $\text{BaCo}_2\text{Si}_2\text{O}_7$  exhibits weak ferromagnetic ordering but has dominant AFM interactions.

### C. LSDA+U calculation

To better understand the exchange interactions in the  $\text{BaM}_2\text{Si}_2\text{O}_7$  ( $M = \text{Cu}, \text{Co}, \text{and Mn}$ ) system, first-principles density-functional theory (DFT)<sup>29,30</sup> calculations have been performed using the LSDA+U method<sup>31</sup> with the Vienna *abinitio* simulation package (VASP)<sup>32</sup>. In this calculation, crystal structures from the references<sup>22,33</sup> were used for the Cu and Co samples, while the crystal structure for the Mn sample was determined from analysis of the single crystal neutron diffraction data in this work. Proper U values,  $U = 5.6$  eV<sup>34</sup> for  $\text{BaCu}_2\text{Si}_2\text{O}_7$ ,  $U = 7$  eV for  $\text{BaMn}_2\text{Si}_2\text{O}_7$ , and  $U = 5$  eV for  $\text{BaCo}_2\text{Si}_2\text{O}_7$ , were selected, so that the calculated crystal structures are consistent with the experimental results<sup>35</sup>.

Using the total energies obtained from these calculations, various collinear magnetic configurations are mapped to the Heisenberg model. Magnetic couplings  $J_i$  are calculated by linear regression<sup>36</sup>. The equations of regression are given by Hamiltonians of different magnetic structures. For the Cu compound, four interactions,  $J_a$ ,  $J_c$ ,  $J_b$ , and  $J_{[110]}$  or  $J_{ab}$  (Fig. 7(a)), have been taken into account. For the Mn and Co compounds, there are three nonequivalent Mn/Co sites due to the lower lattice symmetry. Therefore, the following—six interactions have been considered  $J_c(\text{M1-M3})$ ,  $J_c(\text{M2-M3})$ ,  $J_a(\text{M1-M2})$ ,  $J_a(\text{M3-M3})$ ,  $J_b$  and  $J_{ab}$  (Fig. 7(b)). Equations (2) and (3) are the Hamiltonians of  $M = \text{Cu}$  and  $\text{Co/Mn}$  samples, respectively. In equation (3),  $n = 9$  or  $25$  and is the number of



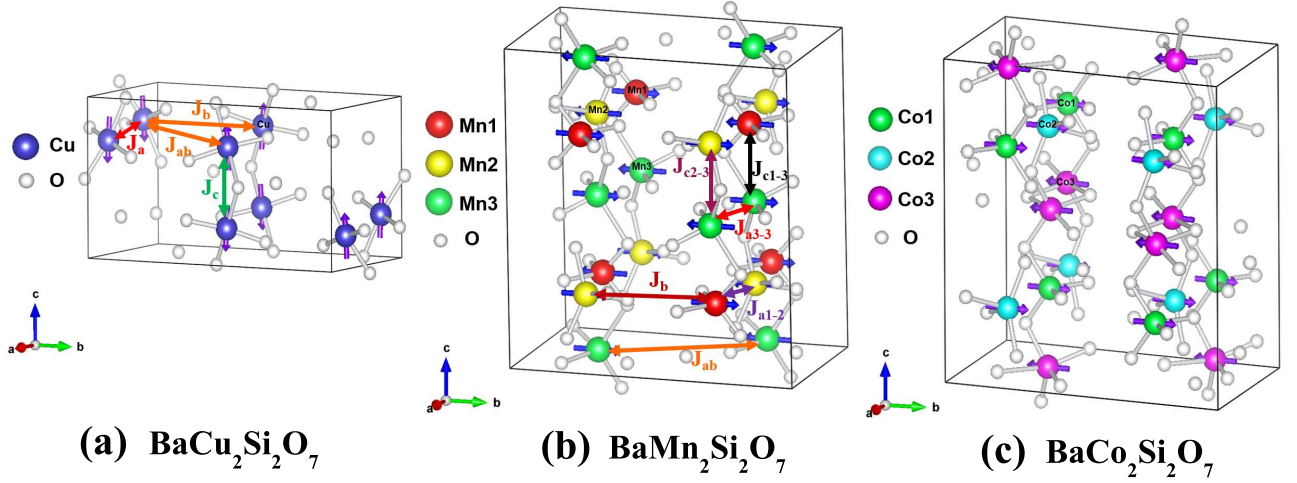


FIG. 7: (color online) The schematic superexchange paths and spin structures for  $\text{BaM}_2\text{Si}_2\text{O}_7$ . The white spheres represent the  $\text{O}^{2-}$  ions. The arrows represent the spins of  $\text{M}^{2+}$  ions.

TABLE II:  $J$  values (in meV) deduced from the LSDA+U calculations. Negative  $J$  represents an AFM interaction and positive  $J$  represents a FM interaction.

	$\text{BaCu}_2\text{Si}_2\text{O}_7$		$\text{BaCo}_2\text{Si}_2\text{O}_7$		$\text{BaMn}_2\text{Si}_2\text{O}_7$	
	LSDA+U	Mean-field <sup>11</sup> and Spin wave <sup>17</sup>	LSDA+U		LSDA+U	
$J_c$	-17.6	-24.1	-0.40 (Co3-Co3)	-0.13 (Mn3-Mn3)	-0.40 (Co1-Co2)	-0.13 (Mn1-Mn2)
$J_b$	0.18	-0.2	0.03	0.0002		
$J_a$	0.27	0.46	0.10 (Co3-Co3)	-0.03 (Mn3-Mn3)	0.10 (Co1-Co2)	-0.04 (Mn1-Mn2)
$J_{ab}$	-0.08	-0.15	0.01	-0.0002		

possible types of superexchange interactions for the Co and Mn-sample, respectively.

$$H_{Cu} = -\left(\frac{1}{4}J_c \sum_{ij \in c} \vec{s}_i \cdot \vec{s}_j + \frac{1}{4}J_b \sum_{ij \in b} \vec{s}_i \cdot \vec{s}_j + \frac{1}{4}J_a \sum_{ij \in a} \vec{s}_i \cdot \vec{s}_j + \frac{1}{4}J_{ab} \sum_{ij \in ab} \vec{s}_i \cdot \vec{s}_j\right) + H_0 \quad (2)$$

$$H_{Co/Mn} = -n\left(\frac{1}{4}J_{c1-3} \sum_{ij \in c1-c3} \vec{s}_i \cdot \vec{s}_j + \frac{1}{4}J_{c2-3} \sum_{ij \in c2-c3} \vec{s}_i \cdot \vec{s}_j + \frac{1}{4}J_b \sum_{ij \in b} \vec{s}_i \cdot \vec{s}_j + \frac{1}{4}J_{a1-2} \sum_{ij \in a1-a2} \vec{s}_i \cdot \vec{s}_j + \frac{1}{4}J_{a3-3} \sum_{ij \in a3-a3} \vec{s}_i \cdot \vec{s}_j + \frac{1}{4}J_{ab} \sum_{ij \in ab} \vec{s}_i \cdot \vec{s}_j\right) + H_0 \quad (3)$$

There are five noteworthy features of the exchange interactions: (i) The dominating interaction for the Cu sample is  $J_c$

= -17.6 meV, which is at least two orders of magnitude larger than the other interactions. Most of the obtained interactions from linear regression are quite comparable to those obtained from the mean field theory calculation<sup>11</sup> and experimental spin wave measurement<sup>17</sup>, as listed in Table II. One deviation lies with  $J_b$ , for which we obtained 0.18 meV and the spin wave simulation led to -0.2 meV. Considering the dominant magnetic couplings in this research, the comparison further validates our calculations. (ii)  $J_c$  for the Cu sample is much larger than for the Mn ( $J_c = -0.13$  meV) and Co ( $J_c = -0.40$  meV) samples. (iii) For the Mn and Co samples,  $J_c$  is not significantly larger than  $J_a$  and they are comparable on energy scale. (iv) The  $J_a = 0.1$  meV for the Co sample show that is FM, but the Mn sample is AFM as -0.03 and -0.04 meV. (v) For all samples, the  $J_b$  and  $J_{ab}$  are the weakest interactions.

#### IV. DISCUSSION

First, we present the magnetic phase diagram for  $\text{BaMn}_2\text{Si}_2\text{O}_7$  with H along the  $b$ -axis, which was constructed by combining the susceptibility, magnetization, heat capacity and neutron diffraction data, as shown in Fig. 8. At zero field, long-range antiferromagnetic ordering forms below  $T_N = 26$  K, which then shifts to lower temperature as the magnetic field increases. Around 6 T, there is a spin flop transition. Because the field applied along the  $b$ -axis induces the spins to flop perpendicular to the  $b$ -axis (i.e., possibly in the  $ac$  plane) and the magnetization continues to increasing linearly between 6 and 9 T, the spin state after the spin flop could be canted state in the  $ac$  plane. The exact nature of the spin state needs to be studied further. It is noteworthy that a spin flop transition also occurs in  $\text{BaCu}_2\text{Si}_2\text{O}_7$  with a smaller critical field of 2 T applied along the  $c$ -axis. As shown in Fig. 7, the spin structure differs from quasi-1D Cu compound to the 2D Mn compound, which induce a different easy axis of the spin flop that depends

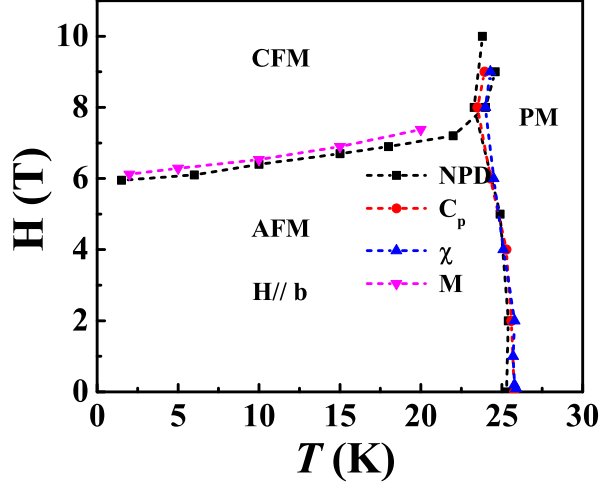


FIG. 8: (color online) Magnetic phase diagram for  $\text{BaMn}_2\text{Si}_2\text{O}_7$ .

on the dimensionality of the sample.

Second, we discuss the magnetic couplings of  $\text{BaM}_2\text{Si}_2\text{O}_7$  in detail. The Crystal and electronic structures of magnetic atoms cause different interactions. We will analyze the magnetic couplings along the  $c$ - and  $a$ -axis in three samples.

In the Cu sample, the interaction between the nearest  $\text{Cu}^{2+}$  is through superexchange  $\text{Cu-O-Cu}$  along the  $c$  axis but super-superexchange through  $\text{Cu-O-Si-O-Cu}$  along the  $a$  axis and  $\text{Cu-O-Si-O-Si-O-Cu}$  along the  $b$  axis. Therefore, its reasonable to see our calculation lead to dominating  $J_c$ , which further confirming that Cu-sample is approaching a one dimensional nature for magnetism.

The fast drop of  $J_c$  from Cu to Mn/Co samples could be related to their different outshell electronic configurations. For  $\text{Cu}^{2+}$  ion with one half-filled orbital, the interaction along  $c$  axis only depends on the superexchange of  $3d_{x^2-y^2}(\text{Cu}^{2+})-\text{p}(\text{O}^{2-})-3d_{x^2-y^2}(\text{Cu}^{2+})$ . For  $\text{Mn}^{2+}$  ion, its five half-filled  $3d$  orbitals split to three high energy  $t_{2g}$  and two low energy  $e_g$  orbitals due to the  $\text{MnO}_4$  tetrahedral site. All five orbitals can involve super-exchange interaction through  $\text{p}(\text{O}^{2-})$  orbitals with orbitals in another  $\text{Mn}^{2+}$  ion, which results to 25 combination of superexchange in Mn compound. Since the bond angles,  $121.9^\circ$  for  $\text{Mn3-O1-Mn2}$  and  $105.22^\circ$  for  $\text{Mn1-O4-Mn3}$  along the  $c$ -axis are between  $90^\circ$  and  $180^\circ$ , each interaction of these 25 combination is determined by the competition between ferromagnetic and anti-ferromagnetic superexchange nature according to GKA rules<sup>38</sup>. Then it is possible that this competition can compensate each other within the possible interactions and lead to a significant decrease of the total  $J_c$  interaction. For Co-sample with isostructure to Mn sample, there are only three half-filled  $3d$  orbitals, which can leads to smaller magnitude of  $J_c$ .

The structural distortion in Mn/Co sample has another consequence: the ratio between the M-M bond length along the  $c$  and  $a$ -axis is smaller than that for Cu-sample. Moreover, the  $J_c$  is reduced in Mn/Co sample, and is comparable to  $J_a$ , hence make the Mn/Co sample approaches two dimensional nature in magnetism. The higher dimension of Mn/Co sam-

ples induce the higher magnetic ordering temperatures than that of Cu compound. Although Mn and Co samples had the isostructure, the magnetic ground states are different, which is AFM and ferrimagnetic-like, respectively. This difference reflected in our calculation demonstrated the different nature of  $J_a$ , which is AFM for Mn but FM for Co compound.  $\text{Co}^{2+}$  ion has no half filled  $e_g$  orbitals involving the interactions while  $\text{Mn}^{2+}$  ion has two half filled  $e_g$  orbitals. Since the interactions involving these  $e_g$  orbitals along the  $a$ -axis favor AFM, the total interactions of Co sample are still under competition between AFM and FM. Furthermore, the reduction of the AFM interaction with the lack of half filled  $e_g$  orbitals can lead to a final FM nature of the total interaction for Co sample. Finally, the spin structure for Co-sample shows FM along the  $a$  and  $b$ -axis AFM along the  $c$ -axis. The calculation assumed the collinear spins, this calculated spin structure of the Co-sample could be slightly different from the experimental result. While its true spin structure needs further neutron measurements to be confirmed, the magnetization measurements on single crystal samples<sup>22</sup> suggested that the spins are canted along the  $c$ -axis with a small angle around  $5^\circ$  and this canting should be the origin for its weak ferromagnetism.

To further elaborate this interesting difference between Mn and Co samples, we looked into the monoxide MnO and CoO samples, which a NaCl structure with the  $\text{M}^{2+}$  ( $\text{M}=\text{Co/Mn}$ ) ion on the  $\text{MO}_6$  octahedral site. The nearest interaction in MnO is AFM<sup>39</sup> while the nearest interaction in CoO is FM<sup>40</sup>. When analyzing MnO and CoO similarly to the analysis of  $\text{BaX}_2\text{Si}_2\text{O}_7$  ( $\text{X}=\text{Co, Mn}$ ) present here, the results are qualitatively the same.

## V. CONCLUSION

In summary, we constructed a magnetic phase diagram and obtained a more accurate antiferromagnetic spin structure for single crystalline  $\text{BaMn}_2\text{Si}_2\text{O}_7$  by performing susceptibility, magnetization, specific heat and single crystal neutron diffraction measurements. We also confirmed the weak ferromagnetism of polycrystalline  $\text{BaCo}_2\text{Si}_2\text{O}_7$ . Finally, in order to systematically understand the different magnetic ground states in the  $\text{BaM}_2\text{Si}_2\text{O}_7$  ( $\text{M}=\text{Cu, Co, and Mn}$ ) system, we performed LSDA+U calculations and extracted the magnetic exchange interactions. Our discussions based on the comparison among the exchange interactions suggest that the different crystal field and the orbital effect on the interaction are the main reasons for the changes of magnetic properties from Cu to Co and to Mn samples.

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