Physical properties of a quasi-two-dimensional square lattice antiferromagnet Ba$_2$FeSi$_2$O$_7$

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ABSTRACT

We report the magnetization ($\chi$, $M$), specific heat ($C_P$), and neutron powder diffraction results on a quasi-two-dimensional $S = 2$ square lattice antiferromagnet $\text{Ba}_2\text{FeSi}_2\text{O}_7$ consisting of $\text{FeO}_4$ tetragons with a large compressive distortion (27%). Despite of the quasi-two-dimensional lattice structure, both $\chi$ and $C_P$ present three dimensional magnetic long-range order below the Néel temperature $T_N = 5.2$ K. Neutron diffraction data shows a collinear $Q_m = (1,0,0.5)$ antiferromagnetic (AFM) structure with the in-plane ordered magnetic moment suppressed by 26% below $T_N$. Both the AFM structure and the suppressed moments are well explained by the Monte Carlo simulation with a large single-ion $ab$-plane anisotropy $D = 1.4$ meV and a rather small in-plane Heisenberg exchange $J_{\text{intra}} = 0.15$ meV. The characteristic two dimensional spin fluctuations can be recognized in the magnetic entropy release and diffuse scattering above $T_N$. This new quasi-2D magnetic system also displays unusual non-monotonic dependence of the $T_N$ as a function of magnetic field $H$.

I. INTRODUCTION

Two-dimensional (2D) Heisenberg antiferromagnets have been intensively studied both in theory and in experiment to exploring exotic low-dimensional magnetic behaviors. Mermin-Wagner theorem states that no long range magnetic order can be stablized at finite temperature in the 2D Heisenberg magnetic system due to strong spin fluctuations [1]. However, lattice topology and strong magnetic anisotropy are predicted to be able to realize a 2D Heisenberg antiferromagnet [2] as in 2D-Ising and 2D-XY spin systems [3-7] under an external magnetic field. On the other hand, three-dimensional long-range magnetic ordering have often been observed in many layered magnetic materials [8-10] because of the quasi-2D nature with minimal but non-vanishing interlayer magnetic coupling [11, 12].

The Melilite family of compounds $\text{A}_2\text{MB}_2\text{O}_7$ ($A = \text{Ca}, \text{Sr}, \text{Ba}, M = \text{divalent } 3d$ transition metals, $B = \text{Si, Ge}$) are interesting examples of quasi-2D square lattice Heisenberg antiferromagnetic systems.
The $d$-$p$ metal-ligand hybridization induces distinct magnetoelectricity [13], directional dichroism involving spin wave/optical excitations [14], magnetochiral effect [15], and longitudinal magnon mode associated with electromagnon [16, 17]. Most studies have been performed on Meililite compounds with half-integer spin quantum numbers, $M = \text{Mn} (5/2)$, $\text{Co} (3/2)$, $\text{Cu}(1/2)$ in last decades. Meanwhile, the studies on the compounds with an integer spin number such as $M = \text{Ni}^{2+} (S = 1)$ or $\text{Fe}^{2+} (S = 2)$ have rarely been carried out due to lack of reliable crystal quality samples, and only a few ones have been reported recently; a theoretical work on Jahn-Teller distortion driven ferroelectricity in $\text{Ba}_2\text{NiGe}_2\text{O}_7$ [18] and a THz experimental one on spin-orbital excitations in $\text{Sr}_2\text{FeSi}_2\text{O}_7$ [19]. Especially, the Fe ($S = 2$) based compounds present strongly compressed FeO$_4$ tetrahedrons along the $c$-axis suggesting intriguing magnetic properties governed by a non-trivial magnetic gap [19-22].

Here we present physical properties of a new quasi-2D square lattice integer spin ($S = 2$) antiferromagnet $\text{Ba}_2\text{FeSi}_2\text{O}_7$. As shown in Fig. 1(a), this compound is crystallized in the $P\bar{4}2_1m$ tetragonal melilite-type structure with the lattice constants $a = 8.3261 \, \text{Å}$, $c = 5.3401 \, \text{Å}$ at room temperature [23]. The system is composed of FeO$_4$ tetrahedrons connected via SiO$_4$ polyhedra and the FeSi$_2$O$_7$ layers are separated by Ba layer, forming a quasi 2D square-lattice structure. The magnetic coupling is dominated by the intra-layer Heisenberg interaction ($J_{\text{intra}}$) through the neighboring $\text{Fe}^{2+}$-$\text{O}^2-$-$\text{O}^2-$-$\text{Fe}^{2+}$ exchange path and the layered structure contributes minimal inter-plane interaction ($J_{\text{inter}}$), resulting in a quasi-2D magnetic system. Noticeably, the FeO$_4$ tetrahedron is compressed as large as 27% along the $c$-axis with respect to the perfect tetrahedron. Such a large compression splits both the triplet $t_{2g}$ and doublet $e_g$ orbital states and make the unquenched orbital angular momentum considerable, which is responsible for noticeable single-ion anisotropy ($D$) [20, 21]. Considering that $D \sim 1.1 \, \text{meV}$ was estimated in $\text{Ba}_2\text{CoGe}_2\text{O}_7$ with 13% compression of the CoO$_4$ tetrahedron [16, 24, 25], the $D$ value is expected to be somewhat enhanced in $\text{Ba}_2\text{FeSi}_2\text{O}_7$ with 27% compression of the FeO$_4$ tetrahedron.

In this article, we report the physical properties of a new quasi-2D magnetic material $\text{Ba}_2\text{FeSi}_2\text{O}_7$...
using magnetization, specific heat, and neutron powder diffraction measurements. The results manifest an AFM ordering below the Néel temperature ($T_N = 5.2$ K) with large easy plane magnetic anisotropy. From Monte Carlo simulation, we estimate $J_{\text{intra}}/D \sim 0.1$. Specific heat measurement reveals a Schottky anomaly arising from thermal population of the low-lying excited spin-orbital states. Neutron diffraction measurements reveals that the short-range spin correlations appears below 20 K and that antiferromagnetic structure is characterized by a staggered magnetic moment of 2.95 $\mu_B$, which is considerably smaller than the moment (4 $\mu_B$) expected from $S = 2$. The field dependent measurements exhibit a unusual non-monotonic behavior of $T_N(H)$ as a function of the $H$-field, indicating that a quasi-2D square lattice magnet of Ba$_2$FeSi$_2$O$_7$ is a novel easy-planar integer spin system.

FIG. 1. (a) The crystal structure of Ba$_2$FeSi$_2$O$_7$ obtained from the Rietveld refinement of the structural model against the neutron diffraction data. Thick black arrows indicate nearest neighbor Heisenberg exchange interaction within $ab$-plane ($J_{\text{intra}}$) and between adjacent inter-planes ($J_{\text{inter}}$). (b) A single layer of FeSi$_2$O$_7$ projected in $ab$-plane. The exchange path between Fe$^{2+}$ spins is through two oxygen ligands.

II. METHODS

To obtain single crystals of Ba$_2$FeSi$_2$O$_7$, we prepared a polycrystalline of Ba$_2$FeSi$_2$O$_7$ as a precursor
using the solid-state reaction. Stoichiometric mixture of BaCO$_3$, Fe$_2$O$_3$, and SiO$_2$ were thoroughly ground, pelletized, and heated at 1050°C with intermediate sintering. X-ray and neutron powder diffraction measurements on the polycrystalline samples identified dominant phase of Ba$_2$FeSi$_2$O$_7$ (96.5%) with minor Ba$_2$SiO$_4$ (2.6%) and SiO$_2$ (0.9%) (see Fig. 6). The polycrystalline samples were prepared as feed rods, and single crystal of Ba$_2$FeSi$_2$O$_7$ was grown using floating zone melting method under reducing gas atmosphere. Growth direction was perpendicular to c-axis and size of the as-grown crystals was about 8 mm in diameter and 60 mm in length. The powder XRD pattern on crushed crystals presents a single phase of Ba$_2$FeSi$_2$O$_7$, as described in Appendix A.

Temperature ($T$) and magnetic field ($H$) dependence of dc-magnetization and specific heat measurements on a Ba$_2$FeSi$_2$O$_7$ crystal were performed by using a vibrating sample magnetometry (VSM) option and a standard calorimetric relaxation technique equipped in a physical property measurement system (PPMS) of Quantum Design DynaCool-9 T. The magnetization results were compared with classical Monte Carlo simulations to estimate the energy scale of the interactions in Ba$_2$FeSi$_2$O$_7$. For the calculation, a square lattice with size of 16 × 16 × 6 with periodic boundary conditions was employed.

Neutron powder diffraction measurements were carried out by using the BT-1 High-Resolution Powder Diffractometer (HRPD) at NIST Center for Neutron Research (NCNR), USA. A 2.9 g of polycrystalline sample was loaded into a vanadium can and cooled using flow type cryostat. Constant wavelength $\lambda = 2.0772$ Å of neutron beam was collimated using Ge (311)-60° monochromator. Diffraction data were collected at temperatures, 1.7, 3, 8, 10, 20, and 30 K. The refinement was carried out by the Rietveld methods using the FULLPROF program [26], and software SARA$h$ was used for representational analysis to determine symmetry-allowed magnetic structures [27].

### III. EXPERIMENTAL RESULTS
A. Magnetic properties

Figure 2(a) shows the temperature dependence of magnetic susceptibility ($\chi = M/H$) for a Ba$_2$FeSi$_2$O$_7$ single crystal with magnetic field parallel ($H||ab$) and perpendicular ($H||c$) to the $ab$-plane. The magnetic susceptibility exhibits strongly anisotropic easy-planer spin behavior over a broad temperature range. The $ab$-plane is magnetic easy-plane and $c$-axis is hard axis. At low temperatures, $\chi(T)$ for both field directions exhibit peaks around $T \sim 8$ K, indicating the onset of the short-range magnetic order with the 2D spin fluctuations. The AFM long-range ordering temperature is determined to be $T_N = 5.2$ K from the first derivative of the in-plane magnetic susceptibility ($d\chi/dT$), which exhibits the sharp anomaly (see the inset in Fig. 2(a)).

![Figure 2](image-url)
the data from 100 K to 300 K.

The inverse magnetic susceptibilities in Fig. 2(b) show linear behaviors above 100 K, in which the susceptibility can be described by the Curie-Weiss formula, \( \chi(T) = \chi_0 + C/(T - \Theta_{CW}) \), where \( C \) and \( \Theta_{CW} \) are the Curie constant and the Curie-Weiss temperature, respectively. \( \chi_0 \) is the diamagnetic background susceptibility. The fitting to the experimental magnetic susceptibility in the temperature range from 100 K to 300 K gives an effective magnetic moment \( \mu_{\text{eff}}[ab] = 5.56(1) \mu_B \), \( \mu_{\text{eff}}[c] = 4.84(1) \mu_B \) and Curie-Weiss temperatures \( \Theta_{CW}[ab] = -7.4(2) \) K, \( \Theta_{CW}[c] = -23.7(2) \) K, respectively. The out-of-plane moment is comparable to the spin only value of \( S = 2 \) (\( \mu_{\text{eff}} \sim 4.9 \mu_B \) for \( g = 2 \)) while the in-plane one \( \mu_{\text{eff}}[ab] \) is considerably larger than the value. It implies that an unquenched angular momentum is present and makes anisotropic contribution to the magnetic moment [21], in consistent with the observed anisotropic behavior of \( \chi \) even up to room temperature. The obtained Curie-Weiss temperature larger than \( T_N \) (\( \Theta_{CW}[c] > 4T_N \)) is attributed to the spin fluctuation involving spin-spin interaction with a strong 2D character.

Figure 3 (a) presents isothermal magnetization \( M(H) \) as a function of magnetic field \( H \) up to 9 T for \( H|\parallel ab \parallel (110) \) and \( H|\parallel c \parallel (001) \) at \( T = 1.8 \) K. \( M(H) \) shows large anisotropy for \( H|\parallel ab \parallel \) and \( H|\parallel c \parallel \) reflecting the strong easy-planer spin, but both \( M_{ab}(H) \equiv M(H|\parallel ab \parallel) \) and \( M_c(H) \equiv M(H|\parallel c \parallel) \) almost linearly increase as \( H \) increases. Interestingly, the slope in \( M_{ab}(H) \) changes considerably around \( \mu_0 H \sim 0.3 \) T (\( \mu_0 H_{ab1} \)) and \( \sim 7.4 \) T (\( \mu_0 H_{ab2} \)). As shown in Fig. 3(b), these anomalies become more noticeable in its derivative \( dM_{ab}/dH \) while those disappear at 6.5 K (> \( T_N \)), indicating that there exist two field-induced transitions below \( T_N \). On the other hand, \( M_c \) monotonically increases with \( H \)-field up to 9 T without any noticeable anomaly representing the field induced transition.

The low field transition at \( H_{ab1} \) can be attributed to a spin-flop-like transition aligning two AFM domains. At \( H = 0 \) field, there exist equally populated two AFM domains; the AFM ordered spins along in-plane easy-axis (110) in one and (1-10) in the other (AFM-I). At \( H \) increases across \( H_{ab1} \), the spin axes of both domains align to be perpendicular to the \( H \)-direction in the \( ab \)-plane (AFM-II). A similar transition was also observed in \( \text{Ba}_2\text{CoGe}_2\text{O}_7 \) [25]. We note that \( H_{ab1} \) shows a minimal azimuthal angle
dependence in the plane, indicating that the in-plane magnetic anisotropy is minimal. $H_{ab1}$ exhibits almost no temperature dependence below $T_N$ (not shown here) and disappears above $T_N$. On the other hand, the high field transition enhances $M_{ab}$ across $H_{ab2}$, and the enhanced magnetic moment $\Delta M_{ab}(T) = M_{ab}(T) - M_{ab}(6.5\text{ K})$ is estimated to be $\sim 0.15\ \mu\text{B/Fe}^{2+}$ at $T = 1.8\text{ K}$. To trace the anomalies, we measured $M_{ab}(H)$ at different temperatures below $T_N$. The inset shows $dM_{ab}/dH$ as a function of $H$ at various temperatures below $T_N$. As temperature increases, the $dM/dH$ peak feature becomes weaker and $H_{ab2}$ shifts to lower fields. The peak disappears above $T_N$, indicating this transition is also relevant to the AFM phase.

FIG. 3. (a) Magnetic field ($H$) dependence of magnetization ($M$) curve along $H||ab$ (orange and blue symbols for $T = 1.8\text{ K}$ and 6.5 K, respectively) and $H||c$ (olive symbol, $T = 1.8\text{ K}$). The dotted lines are the results of classical Monte Carlo simulations with $J_{\text{ intra}} = 0.15\text{ meV}, J_{\text{ inter}} = 0.0025\text{ meV}$ and $D = 1.4\text{ meV}$ (for detailed information about calculation, see the section IV.). (b) First derivative of magnetization curve ($dM/dH$) as a function of magnetic field along $H||ab$ measured at 1.8 K (orange symbol) and 6.5 K (blue symbol). Two vertical arrows indicate positions of two critical magnetic fields ($\mu_0H_{ab1} \sim 0.3\text{ T, } \mu_0H_{ab2} \sim 7.4\text{ T}$) showing $H$ induced weak and sharp peak of $dM/dH$ at $T = 1.8\text{ K}$, respectively. The inset in (b) shows
$dM/dH$ as a function of magnetic field along $H_{||ab}$ measured at various temperatures below $T_N$.

FIG. 4. (a) Temperature ($T$) dependence of dc magnetic susceptibility ($\chi = M/H$) and (b) first derivative of magnetic susceptibility ($d\chi/dT$) as a function of temperature ($T$) for applied magnetic fields along $H_{||ab}$. In (b), the dotted guide line is used to indicate $T_N$ as a function of $H$ obtained from the peak position in $d\chi/dT$. For clarity, each $d\chi/dT$ curve is vertically shifted by 0.006 emu mol$^{-1}$ Oe$^{-1}$ K$^{-1}$.

Figures 4 (a) shows $\chi(T)$ as a function of temperature $T$ measured at various $H_{||ab}$ fields up to $\mu_0H = 7.5$ T. $\chi(T)$ below $T_N$ suddenly changes between 0.2 T and 0.5 T due to the spin-flop-like transition across $\mu_0H_{ab1} \sim 0.3$ T observed $M_{ab}$ ($dM_{ab}/dH$). As presented in Fig. 4(b), the derivatives $d\chi/dT$ clearly exhibit peak features representing the AFM transition up to $\mu_0H = 7.2$ T ($< \mu_0H_{ab2}$) and enable us to determine $T_N(H)$ at a given $H_{||ab}$ field. Interestingly, $T_N(H)$ shows a non-monotonic field dependent behavior. $T_N(H)$ slightly increases, as $H$ increases up to $\mu_0H \sim 2$ T, and then it decreases for further increasing $H$ up to 7.2 T. At $\mu_0H = 7.5$ T ($> \mu_0H_{ab2}$), the $d\chi/dT$ peak feature becomes completely suppressed with saturation in $\chi(T)$. 
**B. Specific heat**

Figure 5(a) shows total specific heat \( (C_P) \) of Ba\(_2\)FeSi\(_2\)O\(_7\) at \( H = 0 \). Lattice contribution \( (C_L) \) was estimated using Debye-Einstein model, where \( C_L(T) \) is defined by \([28, 29]\),

\[
C_L(T) = m \left[ 9Rx_D^3 \int_0^{x_D} \frac{x^4 e^x}{(e^x - 1)^2} \, dx \right] + \sum_{i=1}^{s-1} n_i \left[ 3R \frac{x_{E_i}^2 e^{x_{E_i}}}{(e^{x_{E_i}} - 1)^2} \right]
\]  

The first term represents the Debye specific heat for the acoustic phonon modes and the second term represent the Einstein specific heat for optic phonon modes. \( x_D \) and \( x_{E_i} \) are defined as \( x_D = \Theta_D/T \) and \( x_{E_i} = \Theta_{E_i}/T \) where \( \Theta_D \) and \( \Theta_{E_i} \) are the Debye temperature and the Einstein temperatures, respectively. The constant \( m \) and \( n_i \) are the number of degrees of freedom for each contribution and \( R \) is the molar gas constant. We performed fitting Eq. (1) to the experimental data in the temperature range from 70 K to 250 K, which yields \( \Theta_D \sim 237 \text{ K} \ (m = 4.8), \Theta_{E1} \sim 554 \text{ K} \ (n_1 = 4.3) \) and \( \Theta_{E2} \sim 1345 \text{ K} \ (n_2 = 2.9) \) with \( m + n_1 + n_2 = 12 \) (total number of atoms in the formula unit). Based on these fitting parameters, the extracted \( C_L \) is displayed in Fig. 5(a). Magnetic specific heat \( (C_M) \) shown in Fig. 5(b) was obtained by subtracting the lattice contribution from the total specific heat, i.e. \( C_M = C_P - C_L \). \( C_M \) displays a sharp \( \lambda \)-anomaly at \( T_N = 5.2 \text{ K} \), which coincides with \( T_N \) determined from the magnetic susceptibility. Above \( T_N \), \( C_M \) exhibits a broad peak around \( T_{SO} \sim 8 \text{ K} \), which represents the short-range ordering in the quasi 2D spin system where the long-range order is suppressed by the low-dimensionality \([2]\).

The magnetic entropy, \( \Delta S_M(T) \), was calculated by using \( \Delta S_M(T) = \int_0^T \Delta C_M(T)/TdT \). \( \Delta S_M \) at \( T = 50 \text{ K} \) is obtained to be 12.74 J mol\(^{-1}\) K\(^{-1}\) that corresponds to 95% of \( R\ln(2S + 1) = R\ln5 \), the total entropy of \( S = 2 \). We note that only about 20% of the total entropy is released at \( T_N \) and additional entropy involving the short range order is released by above the transition temperature \( (T_{SO} \sim 8 \text{ K}) \). Interestingly, the entropy \( R\ln(3) \sim 9.13 \text{ J mol}^{-1} \text{ K}^{-1} \) corresponding to the degree of freedom for \( S = 1 \) releases up to around 18 K, where the short-range ordering peak diminishes. Above this temperature, a Schottky-like broad peak is visible in \( C_M \) around \( T_{Broad} \sim 23 \text{ K} \) and the entropy gradually releases
remaining the spin degree of freedom for $S = 2$ until even above 50 K.

FIG. 5. (a) Total specific heat ($C_T$). Open circle and red line display the measured total specific heat ($C_T$) and calculated lattice contribution of specific heat ($C_L$), respectively. Inset magnifies the specific heat below 30 K in semi-logarithmic scale. The vertical arrow indicates the magnetic transition temperature ($T_N = 5.2$ K). (b) Magnetic specific heat ($C_M$) and magnetic entropy gain ($\Delta S_M$) as a function of temperature ($T$). Above $T_N$, $C_M$ shows two broad peaks centered at $T_{SO} \sim 8$ K and $T_{Broad} \sim 23$ K, associated with short-range spin correlations and a Schottky anomaly from the excitation between the levels given by single-ion state, respectively. Two gray horizontal dashed lines show $R\ln(2S + 1)$ with spin state $S = 1$ ($R\ln 3$) and $S = 2$ ($R\ln 5$), respectively. Inset represents the level structure of the lowest-energy $d_{z^2}$ orbital for Fe$^{2+}$ ion in the tetrahedral crystal field ligand ($T_d$) with a tetragonal compression ($\delta z$) and further splitting energy level of the spin states ($S$) by the 2nd order spin-orbit coupling (SOC) [19, 20]. The red dashed curve indicates the calculated Schottky anomaly for the transition between $S = |\pm 2\rangle$ and $S = |\pm 1\rangle$ states with gap, $\Delta = 3D = 3*1.4$ meV = 4.2 meV where $D$ is referred from the Monte Carlo calculations (see the text).

C. Powder neutron diffraction
To study the AFM spin structure below $T_N$, we have carried out zero field ($H = 0$) neutron powder diffraction (NPD) measurements on $\text{Ba}_2\text{FeSi}_2\text{O}_7$. Figure 6 shows the NPD patterns at 30 K ($> T_N$) and 1.7 K ($< T_N$). The crystal and magnetic structures were determined from the Rietveld refinement fitting by using FULLPROF [26]. The refined crystallographic parameters are tabulated in Table I ($T = 30$ K) and II ($T = 1.7$ K). Both the $T = 30$ K and $T = 1.7$ K diffraction patterns for the nuclear Bragg peaks are well described by the tetragonal space group, $P\bar{4}2_11m$ (SG: 113), and the Bragg peak profiles exhibit only small variations across $T_N$, evidencing that the AFM transition does not accompany any considerable structural transition. Comparing low $Q$-region ($0.5 \text{ Å}^{-1} \leq Q \leq 2.0 \text{ Å}^{-1}$) neutron diffraction patterns at $T = 1.7$ K and 30 K as shown in the inset, we identify the magnetic Bragg reflections at $Q = (1,0,1/2)$ and $(2,1,1/2)$ below $T_N$, indicating a characteristic vector of $\bm{Q}_m = (1,0,1/2)$.

FIG. 6. Neutron powder diffraction patterns for $\text{Ba}_2\text{FeSi}_2\text{O}_7$ at (a) $T = 30$ K ($> T_N$) and (b) 1.7 K ($< T_N$). Open circles and the red solid line represent the experimental data and the Rietveld refinement fitting line, respectively. At both temperatures, Bragg peaks from $\text{SiO}_2$ and $\text{Ba}_2\text{SiO}_4$ (non-magnetic secondary phases) are visible in the sample, and the Rietveld refinement quantifies the phase fractions of 0.9% and 2.6%, respectively. In (b), the structural and magnetic Bragg reflections are presented by upper (green) and low (violet) ticks, respectively. The inset shows an expanded view of the low-$Q$ region data and miller indexed
magnetic peaks are indicated by arrows. The asterisk marks two peaks from an unknown impurity phase.

### TABLE I. Crystallographic parameters with space group \( P\overline{4}2_1m \) (SG:113) from Rietveld refinements on the diffraction data at \( T = 30 \) K. Lattice constants \( a = b = 8.3193(8) \, \text{Å}, \ c = 5.3348(5) \, \text{Å}, \) and \( \alpha = \beta = \gamma = 90^\circ \). \( R_{wp} = 6.75\% \).

| atom | site | \( x \)     | \( y \)     | \( z \)     | \( B \)   |
|------|------|-------------|-------------|-------------|----------|
| Ba   | 4e   | 0.1648(3)   | 0.6648(3)   | 0.5090(6)   | 0.05(12) |
| Fe   | 2a   | 0           | 0           | 0           | 0.05(4)  |
| Si   | 4e   | 0.3627(3)   | 0.8627(3)   | 0.9610(7)   | 0.12(12) |
| O1   | 2c   | 0           | 0.5         | 0.1371(8)   | 0.36(8)  |
| O2   | 8f   | 0.3649(3)   | 0.8649(3)   | 0.2627(5)   | 0.17(6)  |
| O3   | 4e   | 0.0764(3)   | 0.1990(2)   | 0.1712(4)   | 0.15(5)  |

### TABLE II. Crystallographic parameters with space group \( P\overline{4}2_1m \) (SG:113) from Rietveld refinements on the diffraction data at \( T = 1.7 \) K. Lattice constants \( a = b = 8.3194(2) \, \text{Å}, \ c = 5.3336(5) \, \text{Å}, \) and \( \alpha = \beta = \gamma = 90^\circ \). \( R_{wp} = 7.14\% \).

| atom | site | \( x \)     | \( y \)     | \( z \)     | \( B \)   |
|------|------|-------------|-------------|-------------|----------|
| Ba   | 4e   | 0.1644(3)   | 0.6644(3)   | 0.5098(7)   | 0.08(10) |
| Fe   | 2a   | 0           | 0           | 0           | 0.20(5)  |
| Si   | 4e   | 0.3645(3)   | 0.8645(3)   | 0.9609(7)   | 0.11(8)  |
| O1   | 2c   | 0           | 0.5         | 0.1383(8)   | 0.54(9)  |
| O2   | 8f   | 0.3651(3)   | 0.8651(2)   | 0.2642(5)   | 0.07(6)  |
| O3   | 4e   | 0.0769(3)   | 0.1984(2)   | 0.1694(5)   | 0.32(5)  |
FIG. 7. (a), (b) The magnetic structure of \( \text{Ba}_2\text{FeSi}_2\text{O}_7 \). The structure has collinear spin alignment of Fe spins with \( \mathbf{Q}_m = (1,0,1/2) (= 0.95 \text{ Å}^{-1}) \). (c) Magnetic peak intensity at \( Q = 0.95 \text{ Å}^{-1} \) as a function of temperature (black closed circles). The red solid line is a guide to eye, and \( T_N = 5.2 \text{ K} \) is indicated by a vertical arrow. Near constant intensity above \( T_N \) reflects the structural contribution at \( Q \). (d) Neutron powder diffraction patterns at temperatures as indicated in the figure.

Representation analysis was used to determine symmetry-allowed magnetic structures. Irreducible representations \( \Gamma_{\text{mag}} = 1\Gamma_{11} + 1\Gamma_{12} + 2\Gamma_{25} \) are compatible with the \( P\bar{4}2_1m \) symmetry with two Fe sites at \((0,0,0)\) and \((1/2,1/2,0)\). The basis vectors of \( 2\Gamma_{25} \) describe all of magnetic Bragg peaks with a collinear antiferromagnetic spin structure as depicted in Fig. 7(a) and (b). The in-plane collinear AFM spin alignment indicates that the nearest neighbor spin-spin interaction is governed by the Heisenberg \( J_{\text{intra}} \) through \( \text{Fe}^{2+}-\text{O}^{2-}-\text{O}^{2-}-\text{Fe}^{2+} \) exchange path in the plane (see Fig. 1). The ordered magnetic moment of \( \text{Fe}^{2+} \) ion is determined to be 2.95 \( \mu_B \), which is only 74\% of the full moment of \( \text{Fe}^{2+} \) spin \( (S = 2) \).
Figure 7(c) shows evolution of the magnetic peak intensity at $Q_m = (1,0,1/2)$ ($Q = 0.95 \text{ Å}^{-1}$) with temperature. Figure 7(d) presents NPD $Q$-scans at different temperatures from 3 K to 30 K. The sharp and intense magnetic Bragg peak, which is present at $Q = Q_m = 0.95 \text{ Å}^{-1}$ in the 3 K scan, mostly diminishes at 8 K and becomes negligible at higher temperatures. Besides the remnant of the sharp magnetic peak, an additional broad peak feature is observable around $Q = 0.8 \text{ Å}^{-1}$ (marked with a black arrow) in the 8 K scan. This feature gradually fades out and shifts to low $Q$ upon heating, and then finally disappears at 30 K, well above $T_N$. This $Q$-dependent diffusive scattering is attributed to short range spin-spin correlations, which were also observed in the magnetic specific heat $C_M (T)$ as a broad peak feature around $T_{SO} \sim 8$ K (see Fig. 5). Presence of the diffusive scattering feature reflects strong spin fluctuations in the low dimensional quasi-2D magnetic system.

**IV. DISCUSSION**

We observe multiple magnetic transitions with temperature and in-plane magnetic fields ($H||ab$) in the magnetization and specific heat measurements. Those transitions can be summarized with a phase diagram in an $H$-$T$ space as shown in Fig. 8. The phase boundaries are defined by the peak positions determined from $d\chi/dT$, $dM/dH$, and $C_M$. At a zero field, the system is in the AFM-I phase with two types of AFM domains below $T_N$, and transits to the paramagnetic phase (PM) upon heating across $T_N$.

On the other hand, as $H$ increases across $\mu_0 H_{ab1} \sim 0.3$ T well below $T_N$, the AFM-I phase transits to the AFM-II phase with a single type of AFM domains. The AFM ordered spins, which lie to be nearly perpendicular to the $H$-direction, slightly cant toward the $H$-direction and result in a finite $M$, i.e. a composition of AFM and ferromagnetic (FM) components (field induced canted AFM). As the $H$-field further increases, the AFM component decreases and finally disappears. The AFM-II phase transits to the spin polarized (SP) phase across $H_{ab2}$ with a certain gain of $\Delta M$. $\mu_0 H_{ab2} \sim 7.4$ T determined from $M(H,T)$ at 1.8 K decreases as $T$ increases (see Fig. 3). $H_{ab2}(T)$ nearly coincides with $T_N(H)$ from $\chi(H,T)$ (see Fig. 4) up to $T \sim 4$ K. Upon further heating, $H_{ab2}(T)$ somewhat deviates from $T_N(H)$ and finally
disappears at $T \sim 5$ K (or $\mu_0 H < \sim 4$ T), implying that the SP phase crosses over to the PM phase.

We note that $T_N = 5.2$ K at $H = 0$ increases up to 2 T and then decreases above 2 T as $H$ increases.

This non-monotonic behavior of $T_N(H)$ was also observed in other quasi-two dimensional spin systems with very weak inter-layer exchange coupling ($J_{\text{inter}}$) [9, 10]. At a low magnetic field, the $S^z$ spin fluctuation becomes suppressed and the spin correlation within the $ab$-plane becomes effectively enhanced to increases $T_N$. At a high field, the spin canting effect prevails to reduce $T_N$ as usual. Appearance of the non-monotonic $T_N(H)$ manifests that Ba$_2$FeSi$_2$O$_7$ is a spin system with strong 2D character. It is also consistent with remarkable short-range spin correlation above $T_N$ observed in specific heat and neutron diffraction results.

![Magnetic phase diagram of the Ba$_2$FeSi$_2$O$_7$ with applied magnetic field $H||ab$. Blue and green symbols present $T_N$ determined from the magnetic susceptibility and specific heat measurements, respectively. Orange symbols represent critical magnetic fields ($H_{ab1}$, $H_{ab2}$) determined from the magnetization measurements. AFM-I, AFM-II, SP, and PM denote antiferromagnetic (two types of AFM domains), field induced canted antiferromagnetic, spin-polarized, and paramagnetic phases, respectively.](image)

To quantify energy scales of the exchange interactions and single-ion anisotropy, we performed the Monte Carlo simulations to calculate the magnetic properties. The calculated $\chi(T)$ and $M(H)$ are
compared with the corresponding experimental ones in Fig. 2 and Fig. 3, respectively. For the simulation, we constructed a simple spin Hamiltonian consisting only with Heisenberg exchange interactions, a single-ion anisotropy, and a Zeeman term for $S = 2$ as follows;

$$\mathcal{H} = J_{\text{intra}} \sum_{<i,j>1} S_i \cdot S_j + J_{\text{inter}} \sum_{<i,j>2} S_i \cdot S_j + D \sum_i (S_i^z)^2 - \mu_B \sum_i S_i \cdot \mathbf{g} \cdot \mathbf{B},$$

where $<i, j>1$ and $<i, j>2$ denote the in-plane and inter-plan nearest neighbors, respectively. The direction of $z$ is parallel to the $c$-axis (see Fig. 1(a)). Although it is not possible to uniquely determine values of the exchange parameters, we could quantify $J_{\text{intra}} = 0.15$ meV, $J_{\text{inter}} = J_{\text{intra}}/60$, and $D = 1.4$ meV, $g_{ab} = 2.6$ and $g_c = 2.3$, which fairly well reproduce $T_N$, high temperature $\chi(T)$ above 50 K (Fig. 2(a)), and the magnetic anisotropy $M(H)$ (Fig. 3(a)), $\chi(T)$ below 50 K deviates from the Curie Weiss formula. We ascribe this deviation to thermal depopulation of the high energy spin states split by the strong single-ion anisotropy, which our classical Monte Carlo simulations do not account for.

Together with tetragonal compression of FeO$_4$ tetrahedrons along the $z$-direction in Ba$_2$FeSi$_2$O$_7$, the spin-orbit coupling (SOC) splits the $S = 2$ state with $(2S + 1)$-fold degeneracy into one singlet ground state ($S^z = 0$) and two doublet excited states ($S^z = |\pm 1>$ and $S^z = |\pm 2>$) with finite gaps of $D$ and $3D$, respectively (see inset in Fig. 5(b)) [19-21]. Hence these low-lying ground/excited spin states are governed by thermal populations in the temperature range of $4D$ ($5.6$ meV $\sim$ 70 K) energy scale. The residual broad peak around 23 K in the magnetic specific heat is considered to be associated with the thermal populations of $S^z = |\pm 1>$ and $S^z = |\pm 2>$ states. The Schottky anomaly for the gap $\Delta = 3D$ with $D = 1.4$ meV from the Monte Carlo simulation (red dashed line in Fig. 5(b)) reproduces the peak position and width of the observed broad peak, which is consistent with $D$ value obtained from the recent inelastic neutron scattering analysis [22]. Thermal populations of the two excited states ($S^z = |\pm 1>$ and $S^z = |\pm 2>$) were also similarly observed in the THz absorption data of a sister compound Sr$_2$FeSi$_2$O$_7$ (denoted by $\beta$-mode absorption) [19]. It is worth to note that magnetic susceptibility along $c$-direction deviates from the Curie-Weiss formula below 70 K, which is consistent with the temperature of the onset of the Schottky anomaly peak. The deviations in $\chi_c$ and the Schottky peak evidence the presence
of a single-ion anisotropy in \( \text{Ba}_2\text{FeSi}_2\text{O}_7 \).

V. CONCLUSION

In summary, we have studied the effects of the large single ion anisotropy \( (D) \) on the physical properties in the new \( S = 2 \) quasi-2D square lattice antiferromagnet \( \text{Ba}_2\text{FeSi}_2\text{O}_7 \) with \( M, \chi, C_M, \) and NPD measurements. The spin states gapped with \( D \) and their thermal populations are responsible for the remarkable 2D spin fluctuations such as Schottky anomaly and short-range magnetic ordering with strong release of the magnetic entropy gain. On the other hand, below \( T_N = 5.2 \) K, \( M \) and \( \chi \) exhibits large easy plane type anisotropy behaviors, and the NPD data yields a significantly reduced magnetic ordered moment. For integer spin systems with a large easy-plane type single-ion anisotropy, the paramagnetic ground state with the finite gaps is possibly realized by the local \( S^z = 0 \) state favoring quantum disordered state, \( \text{Ba}_2\text{FeSi}_2\text{O}_7 \) is suspected to be near the quantum critical point on AFM long range order side in the presence of \( J = 0.15 \) meV with \( J/D \sim 0.1 \) (for the effective \( S = 1 \) scheme, \( 3J/D \sim 0.3 \) [30]). In this case, Higgs modes like the longitudinal magnon in the low-energy spin excitation spectra are possibly observable in the inelastic neutron scattering or Raman spectroscopy [22, 31-33]. The presented magnetic results and the constructed magnetic phase diagram suggest that \( \text{Ba}_2\text{FeSi}_2\text{O}_7 \) is an important example of the \( S = 2 \) quasi-2D square lattice Heisenberg antiferromagnet with a strong easy-plane anisotropy, providing a suitable playground to test ideas of intriguing low dimensional quantum magnetism.

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Appendix A: X-ray diffraction data for crushed single crystals

FIG. S1. X-ray powder diffraction pattern from crushed single crystals of Ba$_2$FeSi$_2$O$_7$ collected at $T = 300$ K. Open circles represent experimental data and solid line in red indicates a fitted line from Rietveld refinement using FULLPROF [26]. The blue solid line indicates the difference between experimental data and the fitted line. Green tick marker indicates the location of Bragg reflections for Ba$_2$FeSi$_2$O$_7$ phase. Crushed single crystals shows single phase of Ba$_2$FeSi$_2$O$_7$ but noticeable preferred crystallographic orientations are observed.

TABLE SI. Crystallographic information with space group $P\overline{4}2_12_1$ (SG:113) from Rietveld refinements on the diffraction data at $T = 300$ K. Lattice constants $a = b = 8.3261(2)$ Å, $c = 5.3402(1)$ Å, and $a = \beta = \gamma = 90'$. $R_{wp} = 20.2\%$.

| atom | site | $x$     | $y$     | $z$       | B     |
|------|------|---------|---------|-----------|-------|
| Ba   | 4e   | 0.1693(1)| 0.6693(1)| 0.5098(4)| 1.33(2)|
| Fe   | 2a   | 0       | 0       | 0         | 0.60(9)|
| Si   | 4e   | 0.3689(5)| 0.8689(5)| 0.9665(13)| 1.17(16)|
| O1   | 2c   | 0       | 0.5     | 0.1182(30)| 0.35(44)|
| O2   | 8f   | 0.3452(15)| 0.8452(15)| 0.2767(19)| 1.85(34)|
| O3   | 4e   | 0.0738(12)| 0.1996(11)| 0.1722(11)| 0.51(22)|

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