Non-magnetic ion site disorder effects on the quantum magnetism of a spin-1/2 equilateral triangular lattice antiferromagnet

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Abstract
With the motivation to study how non-magnetic ion site disorder affects the quantum magnetism of Ba3CoSb2O9, a spin-1/2 equilateral triangular lattice antiferromagnet, we performed DC and AC susceptibility, specific heat, elastic and inelastic neutron scattering measurements on single crystalline samples of Ba2.87Sr0.13CoSb2O9 with Sr doping on non-magnetic Ba2+ ion sites. The results show that Ba2.87Sr0.13CoSb2O9 exhibits (i) a two-step magnetic transition at 2.7 K and 3.3 K, respectively; (ii) a possible canted 120 degree spin structure at zero field with reduced ordered moment as 1.24 μB/Co; (iii) a series of spin state transitions for both H || ab-plane and H || c-axis. For H || ab-plane, the magnetization plateau feature related to the up–up–down phase is significantly suppressed; (iv) an inelastic neutron scattering spectrum with only one gapped mode at zero field, which splits to one gapless and one gapped mode at 9 T. All these features are distinctly different from those observed for the parent compound Ba3CoSb2O9, which demonstrates that the non-magnetic ion site disorder (the Sr doping) plays a complex role on the magnetic properties beyond the conventionally expected randomization of the exchange interactions. We propose the additional effects including the enhancement of quantum spin fluctuations and introduction of a possible spatial anisotropy through the local structural distortions.

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(Some figures may appear in colour only in the online journal)

1. Introduction

Quantum magnets are the focus of modern condensed matter physics research, since they not only provide unique opportunities to explore quantum many-body physics but also have potential applications in advanced technologies such as spintronics and quantum computers. More attention has recently been paid to their disorder effects, since materials inevitably have defects and/or random disorder. Compared to the disorder on magnetic ion sites which usually destroys the magnetic interactions and leads to glassy or paramagnetic states, the disorder on non-magnetic ion sites remains more intriguing and illusive. How such kind of disorder affects the magnetism on the chemically ordered magnetic sublattice is a challenging question with limited knowledge so far.

A good example of non-magnetic ion site disorder is the heavily studied YbMgGaO₄ (YMGO). In YMGO, the Yb³⁺ ions with effective spin-1/2 form a geometrically frustrated triangular layer [1, 2], between these layers the site mixture of Mg²⁺/Ga³⁺ ions cause the intrinsic disorder of the non-magnetic ion sites. Earlier studies on YMGO show that: its inelastic neutron scattering (INS) spectrum has a continuum mode [3–6], the specific heat behaves as \( C_p \sim T^{6/7} \) [1], its muon spin relaxation rate exhibits a temperature-independent plateau [7], and its DC susceptibility saturates below 0.1 ~ 0.2 K [8]. All of which suggest that YMGO has a gapless quantum spin liquid (QSL) state. More recently, the reports including no residual \( \kappa_0/T \) term on the thermal conductivity observed [9] and the frequency dependent AC susceptibility peak [10], suggest a glassy ground state in YMGO which could be due to the Mg²⁺/Ga³⁺ site disorder [2, 11]. Several theoretical models which include this site disorder effect have been proposed for YMGO: highly anisotropic nearest-neighbor interactions [12], the random singlet (RS) state [13, 14], randomness-induced QSL state [15], the mimicry of a spin liquid [16, 17], and randomness induced spin-liquid-like phase in \( J_1-J_2 \) model [18–24]. Of these, the RS state and randomness-induced QSL have also been applied to other quantum magnets with disorder [25–43]. However, a most recent study on high quality YMGO single crystals reveals a residual \( \kappa_0/T \) term and series of quantum spin state transitions at the zero temperature limit. This suggests the survival of itinerant excitations and quantum spin state transitions in YMGO [44].

The controversial magnetic ground state of YMGO reflects the complex role that the disorder on the non-magnetic ion sites plays in quantum magnets. To better understand this role, more studies on quantum magnets with such kind of disorder is highly desirable. While searching for ideal quantum magnets to incorporate non-magnetic ion site disorder, \( \text{Ba}_3\text{CoSb}_2\text{O}_9 \) (BCSO) caught our attention. \( \text{Ba}_3\text{CoSb}_2\text{O}_9 \) (BCSO) is a rare example of an equilateral triangular lattice antiferromagnet (TLAF) with effective spin-1/2 (for Co²⁺ ions) and easy plane anisotropy. Its exotic quantum magnetism has been well documented. First, the theoretical studies have proposed that in a spin-1/2 TLAF, the quantum spin fluctuations stabilize a novel up–up–down (UUD) phase while approaching zero temperature with the applied field parallel to either easy plane or easy axis [45, 46]. The UUD phase exhibits itself as a magnetization plateau within a certain magnetic field regime and with one-third of the saturation moment (1/3\( \text{Ms} \)). Experimentally, such an UUD phase has been reported for BCSO [47–52].

Detailed studies further reveal a series of quantum spin state transitions (QSSTs) in BCSO. With increasing field along the \( ab \) plane, its 120 degree spin structure at zero field is followed by a canted 120 degree spin structure, the UUD phase, a coplanar phase (the V phase), and another coplanar phase (the \( V' \) phase) before entering the fully polarized state [53–59]. While for \( H \parallel c \)-axis, the 120 degree spin structure will be followed by an umbrella spin structure, and the V phase. Second, several abnormal features about its spin dynamics have been experimentally studied by the INS experiments [60–64] and theoretically investigated [65–67], including the quantum renormalization of excitation energies, a rotonlike minimum at the \( M \) point, and the intense continuum mode extending to a high energy.

Another fact is that the triple perovskite structure for BCSO is very flexible on its chemical composition. For example, one can replace Ba³⁺ ions with Sr²⁺ or Ca²⁺ ions [68, 69], or replace Sb⁵⁺ ions with Nb⁵⁺ or Ta⁵⁺ ions [70–72] while keeping the Co-triangular lattice. In fact, \( \text{Ba}_3\text{CoNb}_2\text{O}_9 \) [70] exhibits a two-step ordering process at 1.36 K and 1.10 K with

| Crystal system | Hexagonal |
|---------------|-----------|
| F.W. (g/mol)  | 851.74    |
| Space group; Z| \( P6_3/mmm; 2 \) |
| \( a \) (Å)    | 5.847(3)  |
| \( c \) (Å)    | 14.507(6) |
| \( V \) (Å³)  | 429.5(4)  |
| Extinction coefficient | 0.000 44(7) |
| \( \theta \) range (deg) | 2.808–34.487 |
| No. reflections: \( R_{int} \) | 8552; 0.0254 |
| No. independent reflections | 394 |
| No. parameters | 24 |
| \( R_1 \); \( \omega R_2 \) (\( I < 2 \sigma(I) \)) | 0.0104; 0.0190 |
| Goodness of fit | 1.199 |
| Diffraction peak and hole (e⁻/Å³) | 0.804; –0.800 |
Table 2. Atomic coordinates and equivalent isotropic displacement parameters of Sr-BCSO system. $U_{eq}$ is defined as one-third of the trace of the orthogonalized $U_{ij}$ tensor ($\text{Å}^2$)

| Atom     | Site | Occ. | $x$  | $y$  | $z$  | $U_{eq}$  |
|----------|------|------|------|------|------|------------|
| Ba/Sr1   | 2b   | 0.952(5)/0.048 | 0    | 0    | 0.25 | 0.009(1)   |
| Ba/Sr2   | 4f   | 0.955(4)/0.045 | 1/3  | 2/3  | 0.01011(1) |
| Sb       | 4f   | 1    | 1/3  | 2/3  | 0.65183(2) | 0.0066(1) |
| Co       | 2a   | 1    | 0    | 0    | 0    | 0.0057(1)  |
| O1       | 6h   | 1    | 0.5189(2) | 0.0378(2) | 0.25 | 0.0094(4)  |
| O2       | 12k  | 1    | 0.8299(2) | 0.6597(3) | 0.0848(1) | 0.0150(3)  |

easy axis anisotropy and also exhibits the QSSTs. Unfortunately, so far, no single crystalline form of Ba$_3$CoNb$_2$O$_9$ has been prepared, which limits its studies.

These two features, exotic quantum magnetism and flexible chemical composition, make BCSO an ideal system to incorporate the non-magnetic ion site disorder and thereafter study its effects on quantum magnetism. In this paper, we successfully grew single crystals of Ba$_{2.87}$Sr$_{0.13}$CoSb$_2$O$_9$ to introduce the disorder (the mixture of Ba/Sr ions) on the non-magnetic Ba$^{2+}$ ion sites and studied its magnetic properties by performing DC and AC susceptibility, specific heat, elastic and inelastic neutron scattering measurements. By comparing the obtained results to those of the parent compound BCSO, we learned that such disorder on the non-magnetic ion sites significantly tunes the magnetic ground state, phase diagram, and spin dynamics of this spin-1/2 equilateral TLAF.

2. Experimental

Single crystalline Sr-doped Ba$_3$CoSb$_2$O$_9$ (Sr-BCSO) was synthesized by the floating-zone method. The feed and seed rods for the crystal growth were made by solid state reaction. The appropriate amount of BaCO$_3$, SrCO$_3$, CoCO$_3$ and Sb$_2$O$_3$ were ground together, pressed into a 6 mm-diameter 10 cm-long rod under 40 MPa hydrostatic pressure, and annealed in air at 1300 °C for 20 h. The single crystal growth was carried out in a 10%O$_2$/90%Ar forming gas with a 0.4 MPa in an IR-heated image furnace equipped with two halogen lamps. The crystal growth rate is 30 mm/hour. The Laue back diffraction technique is used to align the single crystal sample in specific orientation for measurements. The single crystal x-ray diffraction measurement was performed in Bruker D8 Quest Eco diffractometer with Mo radiation ($\lambda$ = 0.71073 Å), which is equipped with photon II detector. The crystal structure, especially the atomic mixture and disorders, were refined using SHELXTL package with full matrix least-squares on $F^2$ model [73].

The DC magnetic susceptibility measurements were performed using a vibrating sample magnetometer option in a commercial physical property measurement system (PPMS, Quantum Design). The specific heat data was also obtained using a PPMS. The polarization measurement up to 35 T was measured with a vibrating sample magnetometer (VSM) at the National High Magnetic Field Laboratory (NHMFL), Tallahassee. Another magnetization measurement up to 40 T using compensated induction coil with sample-in/sample-out background subtraction was performed at the NHMFL, Los Alamos. The single crystal neutron diffraction measurements were performed at the High Flux Isotope Reactor (HFIR) of the Oak Ridge National Laboratory (ORNL). The zero field measurements were carried out at 300 mK with the wavelength of $\lambda = 1.5424$ Å in the Oxford cryogen-free Heliox VT refrigerator at the single crystal diffraclometer DEMAND [74]. HB3A and at 1.5 K with the wavelength of $\lambda = 4.2636$ Å in the orange cryostat on the Cold Neutron Triple-Axis Spectrometer, CIX. The measurements under magnetic field were conducted at 1.5 K with the wavelength of $\lambda = 2.3779$ Å in an 8 T vertical asymmetric field cryomagnet on the Fixed-Incident-Energy Triple-Axis Spectrometer, HB1A. The diffraction patterns were analyzed by the Rietveld refinement program FullProf. The magnetic structure compatible with the lattice symmetry was obtained by SARAH software. The INS measurements under zero field were performed at 300 mK on the disk chopper spectrometer with the He-3 dipper insert in the NIST Center for Neutron Research (NCNR). The INS measurements under applied magnetic field were conducted at 1.6 K in an 11 T magnet on the multi axis crystal spectrometer (MACS) in NCNR [75].

3. Results

3.1. Crystal and magnetic structure

The refinement of the single crystal x-ray data confirms that the composition for the as-grown crystal is Ba$_{2.87}$Sr$_{0.13}$CoSb$_2$O$_9$. It has a hexagonal structure with the space group $P6_3/mmc$ and lattice parameters $a = 5.847(3)$ Å and $c = 14.507(6)$ Å. The detailed refinement and crystallographic information is listed
in tables 1 and 2. The results show ∼ 4% Sr mixed on Ba site. Moreover, no atomic vacancies were observed on Co, Sb and O sites. As shown in figure 1(a), in this structure, each Co\(^{2+}\) ion is surrounded by six O\(^{2-}\) ions, forming a CoO\(_6\) octahedron. The layers of the triangular lattice of CoO\(_6\) octahedra in the \(ab\) plane are separated by two face-shared SbO\(_6\) octahedra. The intralayer and interlayer distances between the Co\(^{2+}\) ions are 5.847(3) Å and 7.253(5) Å, respectively, which results in a quasi-2D triangular lattice system.

Elastic neutron scattering measurements under zero and varying applied magnetic fields were performed to probe the magnetic structure of Sr-BCSO. As shown in figure 2(a), the temperature dependence of the intensity for a magnetic peak \([1/3 1/3 1]\) measured at zero field shows a rapid increase below \(T_{N1} = 2.8\) K, which indicates a magnetic ordering. Moreover, a set of magnetic peaks indexed by propagation vector \([1/3 1/3 1]\) were collected in a single crystal neutron scattering measurement. As shown in figure 2(b), the data can be fitted by a 120 degree spin structure in the \(ab\) plane. The refined magnetic moment is \(1.24(7)\) \(\mu_B/\text{Co}\).

The field dependence of the intensities for the \([1/3 1/3 1]\) and \([1/3 1/3 2]\) peaks measured at 1.5 K are shown in figures 3(a) and (b), respectively. For the \([1/3 1/3 1]\) peak, its intensity is basically a constant from 0 T to 6 T, and then shows a drastic drop around \(\mu_0 H_{a1} = 6\) T. For the \([1/3 1/3 2]\) peak, its intensity increases with increasing field but with a slope change around 6 T. These features suggest there is a spin state transition around \(H_{a1}\).

### 3.2. DC and AC magnetic susceptibility

The temperature dependence of the DC magnetic susceptibility, \(\chi(T)\), under magnetic fields is shown in figure 4. As \(H \parallel ab\)-plane is increased (figures 4(a)–(c)), \(\chi(T)\) shows several features. (i) A broad peak appears around 6 K with \(\mu_0 H < 5\) T; (ii) a peak appears around 3 K at \(\mu_0 H = 5\) T, which is labeled as \(T_{N1}\) and shifts to lower temperatures with increasing field; (iii) in addition to the peak at \(T_{N1}\), at \(\mu_0 H = 7\) T the data shows that \(\chi(T)\) increases rapidly below 5 K. Here we use the peak position of its second-order derivative (figure 4(c)) to represent this feature, labeled as \(T_{N2}\). With increasing field, \(T_{N2}\) shifts to higher temperatures between 7 T ≤ \(\mu_0 H ≤ 11\) T; (iv) with \(\mu_0 H ≥ 12\) T, the feature at \(T_{N2}\) involves to be a peak again (figure 4(b)).
Figure 4. The temperature dependence of the DC susceptibility under different magnetic fields with $H \parallel ab$-plane (a) and (b) and $H \parallel c$-axis (d) and (e) for Sr-BCSO. The second-order derivative of the $\chi$–$T$ curves under high magnetic fields for $H \parallel ab$-plane (c) and $H \parallel c$-axis (f).

Figure 5. The dc magnetization (black line) and its derivative (red line) measured at 1.5 K with $H \parallel ab$-plane (a) and $H \parallel c$-axis (b). The dashed line represents the Van Vleck paramagnetic background.

For $H \parallel c$-axis, the peak at $T_{N1}$ is not as strong as that for $H \parallel ab$-plane and appears when $\mu_0 H \geq 7$ T (figure 4(d)). The feature at $T_{N2}$ also appears when $\mu_0 H > 11$ T (figures 4(e) and (f)). Compared to the $H \parallel ab$-plane case, for the $H \parallel c$-axis, both features appear at a higher magnetic field.

As shown in figure 5, the DC magnetization, $M(H)$, measured at 1.5 K by using a VSM shows a weak plateau feature...
Figure 7. The temperature dependence of the specific heat measured with $H \parallel ab$-plane (a) and $H \parallel c$-axis (b).

For $H \parallel ab$-plane while only a slope change for $H \parallel c$-axis. Accordingly, the derivative $dM/dH$ for $H \parallel ab$-plane shows a peak-valley-peak feature with two critical fields $\mu_0 H_{a1} = 7.5$ T and $\mu_0 H_{a2} = 16.4$ T. Meanwhile, the derivative for $H \parallel c$-axis only shows one peak at $\mu_0 H_{c1} = 8.7$ T. The saturation field is around 33 T for both directions. The saturation moments are $1.8 \mu_B$ and $1.9 \mu_B$ for $H \parallel ab$-plane and $H \parallel c$-axis, respectively. For $H \parallel ab$-plane, the DC magnetization was also measured at 0.7 K by using a compensated induction coil with sample-in/sample-out background subtraction (not shown here), which shows similar behavior to the 1.5 K data.

Since the field dependent AC magnetic susceptibility, $\chi'(H)$, is basically equivalent to $dM/dH$, we measured $\chi'(H)$ at 50 mK to double check the critical fields. As shown in figure 6, two critical fields at $\mu_0 H_{a1} = 8.1$ T and $\mu_0 H_{a2} = 16.0$ T for $H \parallel ab$-plane and one at $\mu_0 H_{c1} = 9.8$ T for $H \parallel c$-axis were observed. This is consistent with the DC $M(H)$ results. Since the $\chi'(H)$ signal is too high on the coil background, it appears less pronounced than $dM/dH$ in figure 5.

3.3. Specific heat

Figure 7 shows the temperature dependence of the specific heat, $C_p$, measured at different fields. At zero field, $C_p$ shows two sharp peaks at $T_{N1} = 2.7$ K and $T_{N2} = 3.3$ K, respectively, which indicates a two-step magnetic ordering. The $T_{N1}$ value is consistent with the ones determined by the neutron diffraction and $\chi(T)$ data. With increasing field $H \parallel ab$-plane, these two peaks at $T_{N1}$ and $T_{N2}$ become less pronounced while their positions remain almost unchanged. The peak at $T_{N1}$ disappears around 6.5 T while the peak at $T_{N2}$ disappears around 8 T. At around 7 T, another broad peak start to appear, labeled as $T_{N3}$ (figure 7(a)). This peak becomes stronger and shifts to higher temperatures with increasing field. For $H \parallel c$-axis (figure 7(b)), the peak at $T_{N1}$ becomes weaker with increasing field and is unrecognizable around 8 T. Meanwhile, the peak at $T_{N2}$ does not change obviously. Apparently, the evolution of $C_p$ under field is quite different between the $H \parallel ab$-plane and $H \parallel c$-axis cases.

3.4. Magnetic phase diagrams

Magnetic phase diagrams for $H \parallel ab$-plane and $H \parallel c$-axis were constructed by using the critical temperatures and fields obtained above, as shown in figure 8. Besides the high temperature paramagnetic phase and high field fully polarized phase, the $H \parallel ab$-plane phase diagram includes three phases while the $H \parallel c$-axis one has two phases.

3.5. Inelastic neutron scattering spectra

The INS spectra of Sr-BCSO were measured at zero field and 9 T in the $ab$ plane, which allows us to study the spin dynamics in phase I and II in figure 8(a). Figures 9(a) and (b) show the INS spectra dispersion up to $\sim 2.5$ meV along the $[111]$ and $[1\over2 1\over2 1\over2]$ directions at zero field, respectively. While the intralayer dispersion is sharp and the interlayer dispersion
Figure 9. The zero field INS spectra along the [H H 1] (a) and [1/3 1/3 L] (b) directions, which were measured at 300 mK using the wavelength $\lambda = 5$ Å; for (c) and (d), the zero field INS spectra were measured at 300 mK using the wavelength $\lambda = 3.5$ Å. The INS spectra measured at 1.6 K with $H \parallel ab$-plane and $\mu_0 H = 9$ T along [H H 1] (e) and [1/3 1/3 L] (f) directions.

Figure 10. (a) The energy cut at [1/3 1/3 1] as the function of magnetic field with $H \parallel ab$-plane. Comparison of the energy cut between Sr-BCSO and BCSO at the [1/3 1/3 1] position at zero field (b) and applied field (c), which is 9 T for Sr-BCSO and 11.5 T for BCSO.

is quite broad, both of them only show one gapped mode. The energy cut at the zone center of [1/3 1/3 1] plotted in figure 10(b) shows no intensity near zero energy but a broad peak around 0.5 meV, which further confirms that there is only one gapped mode with the gap around 0.5 meV for the INS spectra. Another noteworthy feature is that there is no intensity at the $M$ point for the intralayer dispersion. Figures 9(c) and (d) show the INS spectra up to 5 meV along the two directions, both of them show no obvious intensity at energy above 1.5 meV.

The spectra under 9 T are shown in figures 9(e) and (f) for the two directions, respectively. It is obvious that there are two modes with broad dispersion along the H direction but two flat modes along the L direction. The energy cut at [1/3 1/3 1] plotted in figure 10(c) further confirms that one mode is gapless and the other mode is gapped, with a gap at around 2.5 meV. The more detailed field scan of the cut at [1/3 1/3 1] is shown in figure 10(a). It shows that with increasing field, the gapped mode at zero field splits into two modes, one of which decreases to zero at fields above 6 T while the other mode increases.

4. Discussions

To learn the effects of non-magnetic ion site disorder, we compare several aspects of the observed magnetic properties of Sr-BCSO to those of the parent compound BCSO.

(i) Anisotropy. The anomaly at $T_{N1}$ for $\chi(T)$ measured at low fields such as 5 T and the magnetization plateau feature are only observed for $H \parallel ab$-plane in Sr-BCSO. Both features are similar to those of BCSO, which indicates that the Sr-BCSO has the same anisotropy, the easy-plane anisotropy, as BCSO.

(ii) Magnetic ground state. The magnetic ground state for Sr-BCSO is a two-step transition with a weak ferromagnetic moment, or a possible canted 120 degree spin structure, as evidenced by the appearance of the [1/3 1/3 0] and [1/3 1/3 2] magnetic peaks at zero field. This is different from that of BCSO, which is a one step transition with a 120 degree spin structure showing no ferromagnetic moment [49, 50, 63].
In BCSO, the [1/3 1/3 0] and [1/3 1/3 2] magnetic peaks only appear under applied fields. The room temperature single crystal diffraction measurement confirms that Sr-BCSO is isostructural to BCSO with an equilateral $\text{CoO}_6$ triangular layer. The low temperature single crystal neutron diffraction measurements further show no evidence of structural distortion below the magnetic ordering temperatures for Sr-BCSO. Moreover, as argued in (i), both samples have the same easy-plane anisotropy. Therefore, it is surprising to see that the Sr-doping can lead to such a different magnetic ground state in Sr-BCSO.

One possible scenario is that the Sr doping can cause local structural distortion of the CoO$_6$ octahedra and therefore introduce a spatial anisotropy into the system. This spatial anisotropy, on top of the easy-plane anisotropy, can lead to a two-step transition with canted spins. For example, Ba$_2$NiNb$_2$O$_9$ has an equilateral triangular lattice for spin-1 Ni$^{2+}$ ions and orders at 4.9 K with a 120 degree spin structure in the $ab$ plane [68]. By replacing Ba$^{2+}$ ion with Ca$^{2+}$ ion with smaller ionic size, a structural distortion is introduced into the system and therefore Ca$_3$NiNb$_2$O$_9$ now has a isosceles triangular lattice for Ni$^{2+}$ ions. One consequence is that Ca$_3$NiNb$_2$O$_9$ orders with a two-step transition at 4.2 K and 4.8 K [68]. Future studies on the local structure of Sr-BCSO is desirable to exam this possibility and better understand its magnetic ground state.

(iii) **Ordering temperature and ordered moment.** The ordering temperature of Sr-BCSO is around $3.3 \, \text{K}$, which is $13\%$ reduction of the ordering temperature, $3.8 \, \text{K}$, for BCSO. From the structural view, Sr-BCSO should have higher ordering temperature due to its shorter Co–Co intralayer distance than the Sr doping leads to a smaller lattice parameter $a$, which is $5.847$ Å. For BCSO, it is $5.856$ Å. Therefore, this lower ordering temperature could be related to the randomization of exchange interactions due to the Ba/Sr mixture. Meanwhile, the ordered moment for Sr-BCSO is around $1.24 \mu_B$/Co, which is smaller than the $1.5 \mu_B$/Co of BCSO. For BCSO, we also performed single crystal neutron diffraction measurements and obtained this ordered moment through refinement by using a 120 degree spin structure (the data is not shown here). In fact, both of these ordered moments are smaller than the saturation moment around $1.8 \sim 2 \mu_B$/Co. In a spin-1/2 triangular lattice antiferromagnet, the reduced ordered moment could be due to the quantum spin fluctuations. Therefore, the even smaller ordered moment of Sr-BCSO indicates that the Sr-doping enhances such kind of spin fluctuations. This enhancement could be another factor for the reduced ordering temperature.

(iv) **Field induced spin state transitions.** For $H \parallel ab$-plane, it is noted that the magnetization at $H_{a1}$ and $H_{a2}$ for Sr-BCSO is $0.5 \mu_B$ and $1.1 \mu_B$, respectively, which is around 1/3, and $\sqrt{3}/3$ of the saturation value ($1.8 \mu_B$, figure 5(a)). For BCSO, with increasing field along the $ab$ plane, its 120 degree spin structure at zero field is followed by a canted 120 degree spin structure, the UUD phase, a coplanar 2:1 canted phase ($V$ phase) with one spin in the 120 degree spin structure rotated to be parallel with another spin, which gives $\sqrt{3}/3M_s$; and another coplanar phase ($V'$ phase) before entering the fully polarized state [47–50, 53–59]. Therefore, here we tend to assign the phases I, II, and III for $H \parallel ab$-plane of Sr-BCSO as the cantled 120 degree spin structure, the UUD phase, and the V phase. For Sr-BCSO, no $V'$ phase was observed. It is obvious that the magnetization plateau feature in Sr-BCSO is much weaker than that of BCSO, which could be due to the Sr-doping disorder effect. In another triangular lattice antiferromagnet Rb$_{1-x}$K$_x$(MoO$_4$)$_2$, the disorder introduced by the K-doping also weakens the magnetization plateau feature related to the UUD phase [76].

As learned from BCSO, while for $H \parallel c$-axis, its 120 degree spin structure will be followed by an umbrella spin structure and a V phase. However, for Sr-BCSO, the magnetic ground state is the canted 120 degree spin structure, which also should be the spin structure for phase I in its $H \parallel c$-axis phase diagram. Therefore, it is difficult to make the analogy between the $H \parallel c$-axis phase diagrams for Sr-BCSO and BCSO. The nature of the phase II for Sr-BCSO needs future studies to clarify.

(v) **Spin dynamics.** The observed INS spectra of Sr-BCSO have several differences from those of BCSO. (a) At zero field, only one gapped mode for Sr-BCSO but two modes (one gapless mode and one gapped mode with gap around $6 \sim 7 \, \text{meV}$) for BCSO [61–64]; (b) under field in the UUD phase, two modes for Sr-BCSO but three modes for BCSO [60]. The comparison of the energy cut at the [1/3 1/3 1] position (figures 10(b) and (c)) further highlights these two differences. It is noticed that the two modes at low energy in the UUD phase for BCSO (the data measured at $11.25 \, \text{T}$) may merge into each other in the UUD phase for Sr-BCSO (the data measured $9 \, \text{T}$), as shown in figure 10(c); (c) no intensity at $M$ point for Sr-BCSO but a flat mode and a rotonlike minimum at $M$ point for BCSO [61–64]; (d) no intensity above 1.5 $\mu_e$V for Sr-BCSO but a columnar continuum extending to at least 6 $\mu_e$V for BCSO [61–64].

For BCSO, the modes at zero field correspond to the gapless Goldstone mode associated with rotation of the spins in the $ab$ plane and an out-of-plane mode that is gapped in the presence of an easy-plane anisotropy, respectively. The rotonlike minimum at $M$ point has been related to a magnon decay [63], but is under debate [64]. The origin for the continuum at high energy is not clear so far. As we proposed above, the Sr-doping possibly introduces local spatial anisotropy to account for its two-step magnetic ordering. This spatial anisotropy will break the rotational symmetry of the spins in the $ab$ plane. Whether such kind of effect will lead to the disappearance of the gapless mode, or furthermore, the disappearance of the intensity at $M$ point and the continuum, needs future theoretical studies to clarify.

In summary, the Sr-doping on the non-magnetic Ba$^{2+}$ ion sites in BCSO affects its magnetic properties profoundly, including the reduction of the ordering temperature and suppression of the magnetization plateau through the randomization of exchange interactions, the reduction of the ordered moment by enhancing quantum spin fluctuations, and the modification of the magnetic ground states, phase diagrams, and spin dynamics by possibly introducing extra spatial anisotropy through local structural distortion. This study serves as a good example for demonstrating that disorder on non-magnetic ion
sites play a complex role on quantum magnetism beyond the expected disruption of the exchange interactions. In fact, such kind of disorder can be treated as an perturbation to efficiently tune the magnetic properties of quantum magnets.

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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References

[1] Li Y et al 2015 Sci. Rep. 5 16419
[2] Li Y, Chen G, Tong W, Pi L, Liu J, Yang Z, Wang X and Zhang Q 2015 Phys. Rev. Lett. 115 167203
[3] Paddison J A, Daum M, Dun Z, Ehlers G, Liu Y, Stone M B, Zhou H and Mourigal M 2017 Nat. Phys. 13 117
[4] Shen Y et al 2016 Nature 540 559
[5] Li Y, Adroja D, Voneshen D, Bewley R I, Zhang Q, Tsirlin A A and Gegenwart P 2017 Nat. Commun. 8 15814
[6] Shen Y et al 2018 Nat. Commun. 9 4138
[7] Li Y, Adroja D, Biswas P K, Baker P J, Zhang Q, Liu J, Tsirlin A A, Gegenwart P and Zhang Q 2016 Phys. Rev. Lett. 117 097201
[8] Li Y, Bachus S, Liu B, Radelytskiy I, Bertin A, Schneidewind A, Tokiwa Y, Tsirlin A A and Gegenwart P 2019 Phys. Rev. Lett. 122 137201
[9] Xu Y, Zhang J, Li Y, Yu Y, Hong X, Zhang Q and Li S 2016 Phys. Rev. Lett. 117 267202
[10] Ma Z et al 2018 Phys. Rev. Lett. 120 087201
[11] Li Y, Adroja D, Bewley R I, Voneshen D, Tsirlin A A, Gegenwart P and Zhang Q 2017 Phys. Rev. Lett. 118 107202
[12] Luo Q, Hu S, Xi B, Zhao J and Wang X 2017 Phys. Rev. B 95 165110
[13] Kimchi I, Nahum A and Senthil T 2018 Phys. Rev. X 8 031028
[14] Parker E and Balents L 2018 Phys. Rev. B 97 184413
[15] Kawamura H and Uematsu K 2019 J. Phys.: Condens. Matter. 31 504003
[16] Zhu Z, Maksimov P, White S R and Chernyshev A 2017 Phys. Rev. Lett. 119 157201
[17] Zhu Z, Maksimov P, White S R and Chernyshev A 2018 Phys. Rev. Lett. 120 207203
[18] Wu H-Q, Gong S-S and Sheng D 2019 Phys. Rev. B 99 085141
[19] Kaneko R, Morita S and Imada M 2014 J. Phys. Soc. Japan 83 093707
[20] Li P H, Bishop R F and Campbell C E 2015 Phys. Rev. B 91 014426
[21] Zhu Z and White S R 2015 Phys. Rev. B 92 041105
[22] Hu W-J, Gong S-S, Zhu W and Sheng D 2015 Phys. Rev. B 92 140403
[23] Iqbal Y, Hu W-J, Thomale R, Poilblanc D and Becca F 2016 Phys. Rev. B 93 144411
[24] Saadatmand S and McCulloch I 2016 Phys. Rev. B 94 121111
[25] Kimchi I, Shekhtel J P, McQueen T M and Lee P A 2018 Nat. Commun. 9 4367
[26] Volkov P A, Won C-J, Gorbunov D, Kim J, Ye M, Kim H-S, Pidkrye J, Cheong S-W and Blumberg G 2020 Phys. Rev. B 101 020406
[27] Kundu S et al 2020 Phys. Rev. Lett. 125 117206
[28] Song P et al 2021 arXiv:2103.05820
[29] Syzranov S and Ramirez A 2021 arXiv:2105.08070
[30] Liu L, Shao H, Lin Y-C, Guo W and Sandvik A W 2018 Phys. Rev. X 8 041040
[31] Hong W et al 2021 Phys. Rev. Lett. 126 037201
[32] Baek S-H, Yeo H W, Do S-H, Choi K-Y, Janssen L, Vojta M and Büchner B 2020 Phys. Rev. B 102 094407
[33] Do S-H et al 2020 Phys. Rev. Lett. 124 047204
[34] Huang Y et al 2021 arXiv:2105.14749
[35] Hu X et al 2021 Phys. Rev. Lett. 127 017201
[36] Ren H-D, Xiong T-Y, Wu H-Q, Sheng D and Gong S-S 2020 arXiv:2004.02128
[37] Gomez S et al 2021 Phys. Rev. B 103 214419
[38] Shimokawa T, Watanabe K and Kawamura H 2015 Phys. Rev. B 92 134407
[39] Kawamura H, Watanabe K and Shimokawa T 2014 J. Phys. Soc. Japan 83 103704
[40] Watanabe K, Kawamura H, Nakano H and Sakai T 2014 J. Phys. Soc. Japan 83 034714
[41] Uematsu K and Kawamura H 2017 J. Phys. Soc. Japan 86 044704
[42] Uematsu K and Kawamura H 2018 Phys. Rev. B 98 134427
[43] Uematsu K and Kawamura H 2019 Phys. Rev. Lett. 123 087201
[44] Rao X et al 2021 Nat. Commun. 12 4949
[45] Miyashita S 1986 J. Phys. Soc. Japan 55 3605
[46] Chubukov A and Golosov D 1991 J. Phys.: Condens. Matter. 3 69
[47] Shirata Y, Tanaka H, Matsuo A and Kindo K 2012 Phys. Rev. Lett. 108 057205
[48] Susuki T, Kurita N, Tanaka T, Nojiri H, Matsuo A, Kindo K and Tanaka H 2013 Phys. Rev. Lett. 110 267201
[49] Sera A, Kousaka Y, Akimitsu J, Sera M, Kawamata T, Koike Y and Inoue K 2016 Phys. Rev. B 94 214408
[50] Zhou H et al 2012 Phys. Rev. Lett. 109 267206
[51] Li M, Zelenskiy A, Quilliam J, Dun Z, Zhou H, Plumer M and Quirion G 2019 Phys. Rev. B 99 094408
[52] Quirion G, Lapointe-Major M, Poirier M, Quilliam J, Dun Z and Zhou H 2015 Phys. Rev. B 92 014414
[53] Gekht R S and Bondarenko I N 1997 J. Exp. Theor. Phys. 84 345
[54] Chen R, Ju H, Jiang H-C, Starykh O A and Balents L 2013 Phys. Rev. B 87 165123
[55] Starykh O A, Jin W and Chubukov A V 2014 Phys. Rev. Lett. 113 087204
[56] Yamamoto D, Marmorini G and Danshita I 2014 Phys. Rev. Lett. 112 127203
[57] Koutroulakis G, Zhou T, Kamiya Y, Thompson J, Zhou H, Batista C and Brown S 2015 Phys. Rev. B 91 024410
[58] Yamamoto D, Marmorini G and Danshita I 2015 Phys. Rev. Lett. 114 027201
[59] Liu X, Prokhnenko O, Yamamoto D, Bartkowiak M, Kurita N and Tanaka H 2019 Phys. Rev. B 100 094436
[60] Kamiya Y et al 2018 Nat. Commun. 9 3110
[61] Ito S, Kurita N, Tanaka H, Ohira-Kawamura S, Nakajima K, Itoh S, Kuwahara K and Kakurai K 2017 Nat. Commun. 8 235
[62] Verresen R, Moessner R and Pollmann F 2019 Nat. Phys. 15 750
[63] Ma J et al 2016 Phys. Rev. Lett. 116 087201
[64] Macdougal D, Williams S, Prabhakaran D, Bewley R I, Voneshen D J and Coldea R 2020 Phys. Rev. B 102 064421
[65] MouriRial M, Fuhrman W, Chernyshev A and Zhitomirsky M 2013 Phys. Rev. B 88 094407
[66] GhioIldi E A, Mezio A, Manuel L O, Singh R, Oitmaa J and Trumper A E 2015 Phys. Rev. B 91 134423
[67] Maksimov P, Zhitomirsky M and Chernyshev A 2016 Phys. Rev. B 94 140407
[68] Lu Z, Ge L, Wang G, Russina M, Günther G, dela Cruz C, Sinclair R, Zhou H and Ma J 2018 Phys. Rev. B 98 094412
[69] Primo-Martín V and Jansen M 2001 J. Solid State Chem. 157 76
[70] Lee M, Hwang J, Choi E, Ma J, Cruz C D, Zhu M, Ke X, Dun Z and Zhou H 2014 Phys. Rev. B 89 104420
[71] Lee M, Choi E, Ma J, Sinclair R, Cruz C D and Zhou H 2017 Mater. Res. Bull. 88 308
[72] Yokota K, Kurita N and Tanaka H 2014 Phys. Rev. B 90 014403
[73] Sheldrick G M 2015 Acta Crystallogr. C 71 3
[74] Cao H et al 2019 Crystals 9 5
[75] Rodriguez J et al 2008 Meas. Sci. Technol. 19 034023
[76] Smirnov A, Soldatov T, Petrenko O, Takata A, Kida T, Hagiwara M, Shapiro A Y and Zhitomirsky M 2017 Phys. Rev. Lett. 119 047204