Synthesis and characterization of sodium-iron antimonate Na$_2$FeSbO$_5$: One-dimensional antiferromagnetic chain compound with spin-glass ground state

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ABSTRACT

A new oxide, sodium–iron antimonate Na$_2$FeSbO$_5$, was synthesized and structurally characterized, and its static and dynamic magnetic properties were comprehensively studied both experimentally by dc and ac magnetic susceptibility, magnetization, specific heat, ESR and Mössbauer measurements and theoretically by density functional calculations. The resulting single crystal structure ($a = 15.6991(9)$ Å; $b = 5.3323$ (4) Å; $c = 10.8875(6)$ Å; S.G. $Pbnm$) consists of edge-shared SbO$_6$ octahedral chains, which alternate with vertex-linked, magnetically active FeO$_4$ tetrahedral chains. The $^{57}$Fe Mössbauer spectra confirmed the presence of high spin Fe$^{3+}$ ($3d^5$) ions in distorted tetrahedral oxygen coordination. The magnetic susceptibility and specific heat data show absence of a long-range magnetic ordering in Na$_2$FeSbO$_5$ down to 2 K, but ac magnetic susceptibility unambiguously demonstrates spin-glass-type behavior with unique two-step freezing at $T_{f1} = 80$ K and $T_{f2} = 35$ K. Magnetic hyperfine splitting of $^{57}$Fe Mössbauer spectra was observed below $T^* = 104$ K ($T_{f1} < T^*$). The spectra just below $T^*$ ($T_{f1} < T < T^*$) exhibit a relaxation behavior caused by critical spin fluctuations indicating the existence of short-range correlations. The stochastic model of ionic spin relaxation was used to account for the shape of the Mössbauer spectra below the freezing temperature. A complex slow dynamics is further supported by ESR data revealing two different absorption modes presumably related to ordered and disordered segments of spin chains. The data imply a spin-cluster ground state for Na$_2$FeSbO$_5$.

KEYWORDS: Spin 5/2 chain one-dimensional; Single crystal XRD; ESR; Mössbauer spectroscopy; Density functional calculations
1. INTRODUCTION

The design and optimization of materials for the purpose of identification of new electrodes for Li (Na) batteries is an ongoing challenging area of research. Among many systems that are being investigated, there are quite a few compounds hosting Li$^+$ or Na$^+$ ions in combination with transition metal cations, particularly with Fe or Mn. The notable examples are LiCoO$_2$, LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ belonging to the well-established AMO$_2$ (A = Li, Na; M = transition, post transition element or their combination) family of oxides, together with LiMn$_2$O$_4$ and the olivine-type compounds like LiFePO$_4$. The selection of materials for designing the electrodes is a challenging task that requires the consideration of various factors including the structure, the type and potential of redox metal ions, the composition and morphology, etc. Choosing an appropriate synthetic method plays a key role in the entire process. One specific direction for synthetic exploration, which is actively developing during two last decades, has been the introduction of multiple metal ions (2/3 of M$^{2+}$ ions with 1/3 of M$^{3+}$ ions) replacing M$^{3+}$ ions in AMO$_2$ stoichiometry. The resulting oxides belong to the ordered rocksalt superstructure variants. The various members of this family, in particular Li$_3$M$_2$XO$_6$ (M = Mg, Co, Ni, Cu, Zn; X = Nb, Ta, Sb, Bi)\(^2-\)\(^6\) and Na$_3$M$_2$XO$_6$ (M = Mg, Co, Ni, Cu, Zn; X = Sb, Bi)\(^7-\)\(^10\) excluding those containing niobium and tantalum have edge shared honeycomb ordered layers (M$_2$XO$_6$)\(^3^-\) separated by Li$^+$/Na$^+$ interlayer ions. Additional examples include Li$_4$MTeO$_6$ (M = Co, Ni, Cu, Zn)\(^11-\)\(^13\) and Li$_4$MSbO$_6$ (M = Cr, Fe, Al, Ga, Mn)\(^11,\)\(^14-\)\(^15\) along with Na$_4$FeSbO$_6$\(^16,\)\(^17\) and Na$_3$LiFeSbO$_6$.\(^18\) The latter oxides contain twice less of magnetic ions and as a consequence triangular magnetic sublattice. Out of these oxides, Na$_3$Ni$_2$SbO$_6$ and Li$_4$NiTeO$_6$ have been investigated as potential cathode materials for Na$^-$ion and Li$^+$-ion batteries.\(^19,\)\(^20\) Li$_4$FeSbO$_6$ has been shown to exhibit a complex electrochemical behaviour; the oxidation of iron and oxygen together occurs at 4.2 V during charging with the release of oxygen at higher voltages.\(^15,\)\(^21\)
The honeycomb topology of the magnetic $M^{2+}$ ion lattices found in $Li_3M_2XO_6$ and $Na_3M_2XO_6$ and other related oxides is responsible for the plenty of unusual magnetic phenomena and stabilization of exotic quantum states in this class of materials. For example, a spin-gap behaviour has been reported in $Na_2Cu_2TeO_6$,\textsuperscript{22} $Na_3Cu_2SbO_6$\textsuperscript{23,24} and the presence of fragmented Haldane-like chains in $Li_3Cu_2SbO_6$.\textsuperscript{25} An antiferromagnetic ordering at low temperatures has been observed for $Na_3M_2SbO_6$ ($M = Ni, Co$),\textsuperscript{8,9,26,27} $Na_{3.76}Co_{1.15}TeO_6$,\textsuperscript{28} $Li_3Ni_2SbO_6$,\textsuperscript{26,29,30} $Ag_3Co_2SbO_6$,\textsuperscript{31} and in $A_3Ni_2BiO_6$ ($A = Li, Na$).\textsuperscript{6,10} Other oxides, $Na_4FeSbO_6$, $Na_3LiFeSbO_6$ and $Li_4MSbO_6$, demonstrated the absence of a long range magnetic order.\textsuperscript{14-18} Several other rock-salt based oxides, $Li_4M^{II}TeO_6$ ($M = Co, Ni, Cu, Zn$),\textsuperscript{11-13,15} $Li_4M^{III}SbO_6$ ($M = Al, Cr, Fe$),\textsuperscript{11,15,16} $Li_3(Li_{1.5}Fe_3-(x+1.5)x)TeO_6$ ($0.1 \leq x \leq 1.0$)\textsuperscript{32} and $Li_4M^{III}_{0.5}Te_{1.5}O_6$ ($M = Cr, Mn, Al, Ga$)\textsuperscript{33} have been structurally characterized, but investigations of their magnetic properties are limited at the moment.

Subsolidus phase relations in $Na_2O-Fe_2O_3-Sb_2O_3$ have been studied earlier by Politaev and Nalbandyan,\textsuperscript{16} who briefly reported the formation of $Na_2FeSbO_5$ with (S.G $Pbcn$; $a = 10.8965(13)$ Å; $b = 15.7178(13)$ Å; $c = 5.3253(4)$ Å) based on the indexation of the powder X-ray diffraction (PXRD) pattern. They noted similarity with brownmillerite structure in lattice metrics and coordination of the cations but considerable difference in diffraction intensities. In the present work, we report a successful structure determination of $Na_2FeSbO_5$ using single crystals obtained from sodium sulfate flux. The structure solution substantiated the observed PXRD pattern for the bulk polycrystalline sample of $Na_2FeSbO_5$. The resulting structure confirms the space group (No. 60) and predicted coordination numbers based on the formula volume;\textsuperscript{16} six for Sb and Na and four for Fe. It differs from the brownmillerite structure but still possesses the corner-linked chains of $FeO_4$ tetrahedra along the shortest unit-cell edge. Mixed metal oxides of $Fe^{3+}$ and $Sb^{5+}$ are known to crystallize in different structures such as rutile ($FeSbO_4$),\textsuperscript{34} perovskite ($Ba_2FeSbO_6$)\textsuperscript{35} and pyrochlore ($Pr_2FeSbO_7$, $Nd_{1.8}Fe_{0.2}(FeSb)O_7$)\textsuperscript{36} and to exhibit a spin-glass ground state. In contrast in the crystal
structure of Na₂FeSbO₅, there are edge shared zigzag octahedral (SbO₆) chains linked through corners to tetrahedral (FeO₄) chains formed by vertex oxygen sharing. This type of structure provides the conditions for low-dimensional spin-exchange interactions and frustration in magnetic sublattice. In what follows, we report the synthesis of Na₂FeSbO₅, the characterization of its structure and detailed study of its magnetic properties.

2. EXPERIMENTAL SECTION

2.1. Synthesis

Polycrystalline Na₂FeSbO₅ was prepared by standard solid-state method. A mixture of Na₂CO₃ (Fischer Scientific, 99.9 %), Fe₂O₃ (Sigma Aldrich, ≥ 99.0 %) and Sb₂O₃ (Sigma Aldrich, + 99.9 %) in the ratio of 1:0.5:0.5 was thoroughly ground and heated in an alumina crucible to 700 °C followed by 1000 °C for 12 h with several intermittent grindings. Crystals of Na₂FeSbO₅ were grown using Na₂SO₄ flux. Stoichiometric amounts of Na₂CO₃, Fe₂O₃ and Sb₂O₃ were ground with excess of Na₂SO₄ (5 times by weight) and heated at 1000 °C for 3 h in an alumina crucible. This was followed by slow cooling (1 °C/h) to 950 °C, and then to 900 °C with a rate of 2 °C/h and further down to 800 °C with a rate of 5 °C/h and finally the furnace was cooled to room temperature. Single crystals with light brown colour obtained were washed with hexane and were used for further single crystal X-ray diffraction (XRD) measurements.

2.2. Characterization

Energy Dispersive X-ray (EDX) measurements of solid samples were carried out using JEOL 6610 LV scanning electron microscope. Field emission scanning electron microscopy (FE-SEM) images of the samples were collected using a Carl Zeiss Gemini SEM 500 microscope. Single crystal X-ray diffraction data of freshly grown single crystals were collected using an Oxford Xcalibur NOVA diffractometer with a four circle κ goniometer employing a graphite-
monochromatized Mo Kα (\(\lambda = 0.71073 \text{ Å}\)) radiation at 150 K. The diffraction intensities were corrected for Lorentz and polarization effects. The data were reduced using CrysAlisRED\(^3\) (programs available with the diffractometer), the shape and size of the crystal were determined with the video microscope attached to the diffractometer, and an analytical absorption correction (after Clark and Reid) from the crystal shape was applied.\(^3\) The crystal structure was determined and refined by direct methods using SHELXS-97 incorporated in WINGX suite.\(^{39,40}\) All atoms in the structure were refined using full matrix least-squares methods on \(F^2\).

The EDX analysis of the single crystals obtained from the \(\text{Na}_2\text{SO}_4\) flux and that of the polycrystalline sample confirmed the Na:Fe:Sb atomic ratio of 2:1:1 (Figure S1, Supporting Information). The preliminary experiments in the single crystal X-ray diffractometer resulted in orthorhombic lattice parameters, \(a = 15.6991(9) \text{ Å}\), \(b = 5.3323(4) \text{ Å}\), \(c = 10.8875(6) \text{ Å}\). The systematic absences suggested the \(\text{Pbna}\) space group. The solution using direct methods resulted in locating two antimony, one iron and three sodium atom positions in the asymmetric unit. Subsequent refinement cycles assisted in locating the five oxygen atoms, thus yielding the expected stoichiometry, \(\text{Na}_2\text{FeSbO}_5\). Refinements of the site occupancies did not show significant deviations. The anisotropic displacement parameters were obtained for all the atoms other than the oxygen. The largest residual electronic density peak and hole in the final difference map were +7.85 and -2.915 e/Å\(^3\). The crystallographic data, positional and thermal parameters are summarized in Tables 1-2, with the anisotropic displacement parameters listed in Table S1. The packing diagrams were generated by DIAMOND version 3.\(^{41}\)

PXRD measurements were taken at room temperature on a PANalyticalX’Pert PRO diffractometer equipped with Cu Kα radiation (\(\lambda = 1.5418 \text{ Å}\)). Data were collected in the angular range of \(2\theta = 3 – 70^\circ\) with a scan step width of 0.04° and a scan rate of 4.5 s/step. Using these data, Le Bail fit was carried using the TOPAS 3 software, which estimates the
background using a Chebyshev polynomial function with 5 coefficients, and describes the peak shape by a pseudo-Voigt function.\textsuperscript{42} The zero error, shape parameters, lattice parameters and the profile coefficients were refined to obtain a suitable fit.

Second Harmonic Generation (SHG) measurements on powder samples were performed by the Kurtz powder technique. In this experiment, Q-switched pulses were obtained from a Nd-YAG laser of wavelength 1064 nm with pulse duration of 10 ns and frequency repetition of 10 Hz, which was passed through the sample powder to get maximum SHG efficiency. The sample was ground to a particle size of 63 µm, packed in a micro capillary of uniform bore and then exposed to laser radiation. The second harmonic radiations generated by the randomly oriented micro crystals were focused by a lens and detected by a photomultiplier tube and then converted into electrical signal. The signal amplitude in volts indicated the SHG efficiency of the sample. KDP crystals grounded into identical size (63 µm) were used as the reference material.

Mössbauer (MS) experiments were performed in the temperature range between 17 - 300 K in closed-cycled Janis CCS-850-1 cryostat in transmission geometry with a 900 MBq $\gamma$-source of $^{57}$Co(Rh) mounted on a conventional constant acceleration drive. The radiation source $^{57}$Co(Rh) was kept at room temperature. All isomer shifts refer to the $\alpha$-Fe absorber at 300 K. The experimental Mössbauer spectra were analyzed using the SpectrRelax software package.\textsuperscript{43}

The magnetic measurements were performed by means of a Quantum Design PPMS system using teflon capsule. The temperature dependence of the $dc$ magnetic susceptibility was measured at the magnetic field $B = 0.1, 1$ and 9 T in the temperature range $1.8 - 400$ K. The temperature dependence of the $ac$ magnetic susceptibility was measured at the magnetic field $B = 0.0001$ T in the temperature range between 2 – 300 K while varying the frequency $f$ between $f = 0.5 - 10$ kHz. The isothermal magnetization curves were obtained for magnetic
fields $B \leq 7$ T at $T = 1.8, 2.5, 5, 50, 70, 90, 200$ K after cooling the sample in zero magnetic field.

Specific heat measurements were carried out by a relaxation method using a Quantum Design PPMS system on the cold-pressed $\text{Na}_2\text{FeSbO}_5$ sample. The data were collected at zero magnetic field and under applied field of $9$ T in the temperature range $2 – 300$ K.

Electron spin resonance (ESR) studies were carried out using an X-band ESR spectrometer CMS 8400 (ADANI) ($f = 9.4$ GHz, $B \leq 0.7$ T) equipped with a low-temperature mount, operating in the range $T = 6 – 420$ K. The effective g-factor of our sample has been calculated with respect to an external reference for the resonance field. We used BDPA ($a$,g - bisdiphenyline-b-phenylallyl) $g_{\text{eff}} = 2.00359$, as a reference material.

3. RESULTS AND DISCUSSION

3.1. Synthesis

The bulk, polycrystalline $\text{Na}_2\text{FeSbO}_5$ can readily be synthesized in air at $1000$ °C and was found to remain stable without any noticeable decomposition. The PXRD pattern matched well with the reported pattern indicating an orthorhombic lattice ($a \approx 10.896$ Å; $b \approx 15.718$ Å; $c \approx 5.325$ Å) resembling a brownmillerite structure (Figure 1). Commonly, this structure with composition, $\text{Ca}_2\text{FeAlO}_5$, which many oxides including $\text{Ca}_2\text{Fe}_2\text{O}_5$ adopt has been known to crystallize in orthorhombic symmetry with unit cell dimensions, $\sqrt{2}a_p \times 4a_p \times \sqrt{2}a_p$ ($a_p =$ perovskite unit cell parameter of $\sim 4$ Å).\textsuperscript{44}

This structure is built up of alternating layers of vertex-linked $\text{MO}_6$ ($\text{M} =$ metal) octahedra and $\text{MO}_4$ tetrahedra. Several structural variations are possible based on how the chains of corner-sharing $\text{MO}_4$ tetrahedra are ordered. Accordingly, brownmillerites can have a range of structures with different lattice parameters and space groups.\textsuperscript{45} A brownmillerite superstructure $\text{Ca}_2\text{FeCoO}_5$ (S.G. Pbcm) has the unit cell dimensions of $a = 5.3652(3)$ Å; $b =$
Figure 1. Le Bail profile fit of PXRD pattern of Na$_2$FeSbO$_5$ in orthorhombic space group \textit{Pbna} (No. 60). Observed (blue), calculated (pink), and difference (green) plots are shown, and Bragg reflections are indicated by light blue tick marks.

11.0995(5) Å; and \( c = 14.7982(7) \) Å.\textsuperscript{46} Our attempts to match the observed PXRD pattern of Na$_2$FeSbO$_5$ using the structural model of Ca$_2$FeCoO$_5$ were not successful.

Subsequently, we carried out experiments to grow single crystals. Trial experiments based on high temperature (1200 °C) melting and slow cooling resulted in the formation of NaFeO$_2$ and Fe$_2$O$_3$. Further explorations were carried out by the utilization of fluxes such as NaCl, Na$_2$CO$_3$, non-eutectic mixture of Na$_2$CO$_3$ and K$_2$CO$_3$, Na$_2$SO$_4$ as well as an equimolar mixture of Na$_2$SO$_4$ and K$_2$SO$_4$. The crystal growth temperature varied from 1000 to 1200 °C. Use of Na$_2$SO$_4$ as flux led to single crystals of Na$_2$FeSbO$_5$ of appreciable quality after washing with hexane.

3.2. Structure

Single crystal measurements using several crystals, obtained from different batches using Na$_2$SO$_4$ flux yielded the orthorhombic lattice parameters \( a = 15.6991(9) \) Å; \( b = 5.3323(4) \) Å; \( c = 10.8875(6) \) Å with \( a \) axis being the highest cell dimension. The systematic absences suggested the possible space groups, \textit{Pbna, Pmma, Pnma, Pnnm, Pmm2, Pmc2},
Pmn2, Pca2, and P222. SHG measurements performed on the polycrystalline sample of Na₂FeSbO₅ did not show any significant SHG response with respect to KDP and implied the possibility of the structural solution in a centrosymmetric space group. Out of the various centrosymmetric space groups, the space group Pbna (No. 60) was confirmed to be the correct one (Tables 1, 2 and S1).

The Sb1, Sb2, Na1 and Na2 were located at 4c positions (site symmetry, 2) with the Fe1, Na3 and all the five oxygen atoms (O1 to O5) occupying the general positions (Table 2). The Sb1 and Sb2 atoms form Sb1O₆ and Sb2O₆ octahedra respectively, which alternate along the b direction by sharing their edges (through O2 and O4) to form zigzag chains (Figure 2). The Fe atoms make FeO₄ tetrahedra by sharing their corners (O5) to form zigzag chains along b. The zigzag chains of edge-sharing SbO₆ octahedra are connected with those of FeO₄ tetrahedra by sharing corners (O1 and O3) to form the three-dimensional (3D) framework of Na₂FeSbO₅, which exhibits the connectivity of -Sb1-O1-Fe-O3-Sb2-O3-Fe-O1-Sb1- along the c direction (Figure 2). In addition to the O2 and O4 atoms, the octahedral coordination around Sb1 and Sb2 is completed by the O1 and O3 atoms respectively (Table 3). The sodium atoms, Na1, Na2 and Na3 are located at the pockets of the 3D FeSbO₅ framework (Figures 2, 3). In essence, Na₂FeSbO₅ has the zigzag chains of edge-sharing SbO₆ octahedra condensed with those of corner-sharing FeO₄ tetrahedra by sharing their corners (Figure 4), with two distinct mirror-related configurations for the zigzag chains of corner-sharing FeO₄ tetrahedra (L and R) as found for the brownmillerite structure.⁴⁶

Table 1. Crystal data and structure refinement parameters for Na₂FeSbO₅ based on single crystal X-ray diffraction measurements at 150 K.

| Property                        | Value         |
|---------------------------------|---------------|
| Formula weight (g/mol)          | 303.58        |
| Crystal system                  | Orthorhombic  |
| Space group, Z                  | Pbna, 8       |
| a [Å]                           | 15.6991(9)    |
| b [Å]                           | 5.3323(4)     |
| c [Å]                           | 10.8875(6)    |
| Atom  | Wyckoff position | x/a       | y/b       | z/c       | SOF | U_{eq}(\text{Å}^2) |
|-------|------------------|-----------|-----------|-----------|-----|-------------------|
| Sb1   | 4c               | 0.22241(9)| 0.2500    | 0.5000    | 1.0 | 0.0110(5)         |
| Sb2   | 4c               | 0.32697(9)| -0.2500   | 0.5000    | 1.0 | 0.0101(5)         |
| Fe    | 8d               | -0.05821(12)| -0.2596(4)| 0.2751(2) | 1.0 | 0.0105(6)         |
| Na1   | 4c               | 0.0934(7) | -0.2500   | 0.5000    | 1.0 | 0.0303(3)         |
| Na2   | 4c               | 0.4509(6) | 0.2500    | 0.5000    | 1.0 | 0.0263(3)         |
| Na3   | 8d               | 0.3218(5) | 0.3139(14)| 0.7545(6) | 1.0 | 0.0248(17)        |

**Table 2.** Atomic coordinates and isotropic equivalent displacement parameters for Na$_2$FeSbO$_5$ based on single crystal X-ray diffraction measurements at 150 K.
The +5 oxidation state of Sb is supported by bond valence sum (BVS) calculations yielding 5.28 and 5.31 respectively for Sb1 and Sb2. The FeO₄ tetrahedra was found to be distorted having four different Fe-O bond lengths varying from 1.83 to 1.91 Å with O-Fe-O angles varying from 107.45° to 123.18° (Table S2, Supporting Information). Here again, the calculated BVS was 2.91, matching well with +3 oxidation state of iron. The charge balancing counter cations (Na1, Na2 and Na3) are having irregular octahedral oxygen coordinations. The Na1, Na2 and Na3 atoms form distorted octahedra; the Na1 and Na2 have three different Na-O bond lengths ranging from 2.37 to 2.67 Å, and the Na3 have six different Na-O bond lengths (2.19 to 2.74 Å) (Table 3).

|    |   |   |   |   |   |
|----|---|---|---|---|---|
| O1 | 8d | 0.1376(6) | 0.121(2) | 0.6120(9) | 1.0 | 0.018(2) |
| O2 | 8d | 0.3156(6) | 0.067(2) | 0.5932(9) | 1.0 | 0.016(2) |
| O3 | 8d | 0.4170(7) | -0.1342(19) | 0.3857(10) | 1.0 | 0.014(2) |
| O4 | 8d | 0.2377(6) | -0.0692(19) | 0.4036(9) | 1.0 | 0.013(2) |
| O5 | 8d | 0.0423(6) | -0.0995(19) | 0.3085(10) | 1.0 | 0.015(2) |

Figure 2. Ball and stick representation of the crystal structure highlighting the FeSbO₅ framework of Na₂FeSbO₅. The Na⁺ ions are not included for clarity.
Figure 3. (a) Ball and stick representation of the crystal structure of Na$_2$FeSbO$_5$ showing the coordination environments of the cations. (b) Corresponding polyhedral representation in the $ac$ plane.

Table 3. Selected bond distances (in Å) of Na$_2$FeSbO$_5$ and bond valence sum (BVS) values calculated for the Sb$^{5+}$, Fe$^{3+}$ and Na$^+$ cations.

| Atoms    | Bond distance (Å) | BVS   |
|----------|-------------------|-------|
| Sb1–O4   | 2.014(10) × 2     |       |
| Sb1–O1   | 1.933(10) × 2     | 5.28  |
| Sb1–O2   | 2.030(10) × 2     |       |
| Sb2–O2   | 1.980(11) × 2     |       |
| Sb2–O3   | 1.982(10) × 2     | 5.31  |
| Sb2–O4   | 1.999(10) × 2     |       |
| Fe–O5    | 1.831(10)         |       |
| Fe–O5    | 1.865(10)         | 2.91  |
| Fe–O1    | 1.901(11)         |       |
| Fe–O3    | 1.914(11)         |       |
| Na1–O5   | 2.374(11) × 2     |       |
| Na1–O1   | 2.423(11) × 2     | 0.99  |
| Na1–O4   | 2.676(14) × 2     |       |
|                |   |          |
|----------------|---|----------|
| Na2–O3         |   | 2.455(11) |
| Na2–O3         |   | 2.497(13) |
| Na2–O2         |   | 2.548(13) |
| Na3–O2         |   | 2.196(12) |
| Na3–O1         |   | 2.279(12) |
| Na3–O4         |   | 2.561(12) |
| Na3–O5         |   | 2.491(12) |
| Na3–O4         |   | 2.283(12) |
| Na3–O3         |   | 2.735(12) |

Finally, the Le Bail PXRD pattern of the bulk crystallites possessing hexagonal morphology (Figure S1, Supporting Information) confirms the formation of single phase; the reflections match well with the orthorhombic space group (Figure 1). Further confirmation was also obtained by comparison between the PXRD pattern of the bulk polycrystalline sample Na$_2$FeSbO$_5$ with those generated from the single crystal measurements and with those generated from the single crystal structure solution in Figure S2 (Supporting Information).

Figure 4. Crystal structure of Na$_2$FeSbO$_5$ in the $bc$ plane. (a) Zigzag octahedral chain made up of edge shared Sb$_2$O$_{10}$ units at $z = 0$. (b) Zigzag chains of corner-sharing FeO$_4$ terahedra at $z = 0.25$. (c) Octahedral chains at $z = 0.50$. (d) Tetrahedral chain at $z = 0.75$. All the chain orientations are shown in the $ab$ plane.
3.3. Magnetic susceptibility

The dc magnetic susceptibility $\chi = M/B$ measured at different magnetic fields are presented in Fig. 5(a). The clearest feature is a step-like anomaly at around 100 K at $B = 0.1$ T. Below this temperature the magnetic susceptibilities $\chi(T)$, recorded in zero-field-cooled (ZFC) and field-cooled (FC) regimes at low fields, diverge appreciably. This bifurcation tends to close with increasing the strength of the external field and completely disappears at $B = 9$ T. The $\chi(T)$ measured at $B = 1$ T exhibits an additional anomaly at $\sim 30$ K, the presence of which can be readily recognized by the derivative curve $d\chi/dT(T)$ (see lower inset in Fig. 5(a)). At the same time, there is no sign for a conventional long-range magnetic ordering down to 2 K. As can be seen from Fig. S3 in the Supporting Information, the inverse magnetic susceptibility $1/\chi$ as well as the product $\chi T$ clearly demonstrate the absence of the Curie-Weiss type behavior up to the highest temperature reached in the experiment. Attempts to describe the $\chi(T)$ using the Curie-Weiss law, which crucially depends on the temperature interval used, resulted in unrealistic parameters.

In order to explore the spin dynamic behavior, we have performed ac magnetic susceptibility measurements. It is obvious from Fig. 5(b) that there are two smooth but distinct spin-crossover peaks at $T_{f1}$ and $T_{f2}$ in the real $\chi'$ and imaginary $\chi''$ parts of the ac magnetic susceptibility, which are both frequency dependent. The values $T_{f1}$ and $T_{f2}$, estimated from the real part $\chi'$ at 0.5 Hz, are approximately 80 and 35 K, respectively. With increasing the frequency, the curves shift to high temperatures. In the investigated frequency range, the magnitude of this shift as measured by the factor $\Delta T/\Delta(\log\omega)$ as in canonical spin glasses, is 0.04 for $T_{f1}$ and 0.02 for $T_{f2}$. The two critical temperatures differ slightly from those determined from the anomalies in the dc $\chi(T)$ measured at $B = 1$ T (Fig.5(a)). The corresponding anomalies on the imaginary part $\chi''$ occur at 73 K and 22 K. Such a decrease in the temperature where the imaginary $\chi''$ peak occurs is characteristic of insulating spin-
Figure 5. Magnetic susceptibility measured for Na$_2$FeSbO$_5$: (a) Temperature dependence of the $dc$ magnetic susceptibility $\chi = M/B$ recorded in the ZFC (blue open symbols) and FC (black filled symbols) regimes at various fields along with dynamic magnetic susceptibility $\chi_{ESR}$ obtained from ESR measurements (magenta filled symbols). (b) Real $\chi'$ and imaginary $\chi''$ parts of the $ac$ magnetic susceptibility at various frequencies.

The activation energies for the two different relaxation processes can be determined using the Arrhenius law:

$$\omega = \omega_0 \exp\left[-\frac{E_a}{k_B T_f}\right]$$

Here $\omega = 2\pi f$ is the driving frequency of our $\chi_{ac}$-measurements, and $T_f$ the peak temperature. Using the Arrhenius plot, ln(\omega) vs 1/$T_f$, we obtain $E_{a1} = 1680 \pm 10$ K for the “high”-temperature freezing, and $E_{a2} = 940 \pm 10$ K for the “low”-temperature freezing (Fig. S4).
It is interesting to note that such an unusual spin dynamics has been observed earlier for several quasi 1D magnetic systems associated with the formation of “partially disordered antiferromagnetic structure”, which can be considered as a spin liquid like state. Examples include KCr$_3$As$_3$, Sr$_{1-x}$Ca$_x$Ni$_2$V$_2$O$_8$, Ca$_3$CoRhO$_6$, ([MnTPP][TCNE]) and FeMgBO$_4$. In a representative system FeMgBO$_4$ consisting of zigzag chains of magnetic ions Fe$^{3+}$, impurities break the magnetic chains. Mössbauer experiments show that the spins of the broken zigzag chains are frozen at low temperature. However, the specific heat measurements show no anomaly, and neutron diffraction measurements on powder samples no Bragg peaks. This indicates the spin glass nature of FeMgBO$_4$.

The frequency dependence of $T_f$ can be described by the critical “slowing down” mechanism of spin dynamics, which is described by

$$\tau(T_f) = \tau_0 \left( \frac{T_f}{T_g} - 1 \right)^{z\nu}$$

(2)

where $\tau$ is the spin-relaxation time ($\tau = 1/f$), $T_g$ the critical temperature for spin-glass ordering at $f \to 0$, $z\nu$ the dynamical exponent, and $\tau_0$ the characteristic time scale for the spin dynamics. Plots log$\tau$ vs. log$[(T_e/T_g)-1]$ are shown in Fig. 6. These plots are best described by the $T_{g1} = 70 \pm 5$ K and $T_{g2} = 30 \pm 5$ K. From the intercept and slope of the fitted straight line, we obtain $\tau_0^1 \sim 10^{-8}$ s, $z\nu_1 = 7$ and $\tau_0^2 \sim 10^{-11}$ s, $z\nu_2 = 10$. The value of $z\nu$ is in good agreement with those reported experimentally and theoretically for low-dimensional spin-glass magnetic systems.

3.4. Magnetization isotherms

The full magnetization isotherm $M(B)$ at $T = 1.8$ K in external fields from -7 T to 7 T (Fig. 7) has a characteristic feature of spin-glass compounds, namely, an S-shape, implying the presence of a weak ferromagnetic component in the exchange interactions. It also shows a tiny hysteresis with a residual magnetization reaching $M_r \approx 0.002\mu_B$/f.u. (lower inset of Fig. 7). Such a behavior may suggest the freezing of spins. Within this range of the applied
Figure 6. Plots of \( \log \tau \) vs \( \log [(T/T_g)-1] \) for the two relaxation processes of \( \text{Na}_2\text{FeSbO}_5 \) at low temperatures. The solid lines represent the least-square fit to the experimental data.

Figure 7. The full \( M(B) \) isotherm at \( T = 1.8 \) K for \( \text{Na}_2\text{FeSbO}_5 \). Insets: \( M(B) \) isotherms at various temperatures and the zoomed-in central part of \( M(B) \) at \( T = 1.8 \) K.

Magnetic fields, the magnetization isotherm does not display saturation and the magnetic moment is still far below the theoretically expected saturation value for the high spin state \( \text{Fe}^{3+} \) (\( S = 5/2 \)) ion: \( M_S = gS\mu_B \approx 5 \mu_B \). With increasing temperature, the magnetization
isotherms $M(B)$ gradually straighten, demonstrating the decrease in the ferromagnetic correlation contribution (upper inset of Fig. 7). No additional magnetic field induced features were detected in the whole temperature range investigated. All the phenomena observed consistently point to a spin-glass state at low temperatures.

3.5. Specific heat

The temperature dependence of the specific heat $C_p(T)$ for Na$_2$FeSbO$_5$ at $B = 0$ T and 9 T is shown in Fig. 8. Over the whole temperature range studied, the specific heat data show no $\lambda$-type anomaly that can indicate a transition to a magnetically ordered state, which is in good agreement with the temperature dependence of magnetic susceptibility. The number of atoms per formula unit in Na$_2$FeSbO$_5$ is $\nu = 9$, so a classical Dulong-Petit saturation value is expected to be $C = 3R\nu = 224 \text{ J/(mol K)}$, where $R = 8.31 \text{ J/mol K}$ is the gas constant. In low

Figure 8. The temperature dependence of the specific heat $C_p(T)$ at $B = 0$ T (black circles) and at $B = 9$ T (green diamonds) measured for Na$_2$FeSbO$_5$. The upper inset highlights a Schottky-type anomaly on $C_p(T)$ at low temperatures. The lower inset shows the $C_p(T)$ at $B = 0$ T in the low temperature range and its approximation, where the green dash-dotted line corresponds to the lattice contribution to the specific heat $C_{ph}$, the violet dashed line the magnetic contribution to the specific heat $C_m$, and the red line their sum.
temperature range, the $C_p(T)$ shows a weak broad maximum (Schottky-type anomaly) at $T_{Sch} \approx 5$ K, which corresponds most likely to a trace amount of some defects in the Na$_2$FeSbO$_5$.

The application of an external magnetic field does not practically affect the character of the $C_p(T)$ dependence, but slightly shifts the $T_{Sch}$ value to lower temperatures (upper inset in Fig. 8). To get some quantitative estimations, we approximated low-temperature part of specific heat by the sum of the phonon term $C_{ph}$ (in the frame of Debye model) and the magnetic contribution $C_m$ from the Schottky-type anomaly $C_{ph} = \beta T^3 + nC_{Sch}$, where $n$ is the concentration of defects responsible for the Schottky anomaly with energy gap $\Delta$,\textsuperscript{60}

$$C_{Sch} = R \left( \frac{\Delta}{T} \right)^2 \frac{e^{\left( \frac{\Delta}{T} \right)}}{1 + e^{\left( \frac{\Delta}{T} \right)}}$$ (1)

As can be seen from the lower inset of Fig. 8, the red solid curve gives a reasonable description of the experimental data with the parameters $n \approx 9.8\%$, $\beta = 1.77 \times 10^{-4}$ J/(mol K$^4$), and $\Delta = 9.9 \pm 0.1$ K at zero magnetic field. The external field $B = 9$ T reduces the energy gap down to $\Delta = 8.5 \pm 0.1$ K. The estimated energy gap is in reasonable agreement with the position of $T_{Sch} = 0.42 \Delta$.\textsuperscript{60} Using the parameter $\beta$, the Debye temperature $\Theta_D$ is estimated to be $460 \pm 10$ K.

### 3.6. Mössbauer spectroscopy

The $^{57}$Fe Mössbauer spectra of Na$_2$FeSbO$_5$ recorded above 105 K (Fig. 9) can be described as a superposition of two quadrupole doublets, Fe(1) and Fe(2), corresponding to the high-spin ferric ions Fe$^{3+}$ at tetrahedral and octahedral sites, respectively.\textsuperscript{61} The second Fe(2) doublet can arise either from the Fe$^{3+}$ ions substituted for the Sb$^{5+}$ ions at 4c positions, or from the Fe$^{3+}$ ions located on the surface of the sample grains.

Due to the fact that the contribution of the Fe(2) subspectrum is small (~4%), it is difficult to accurately determine its hyperfine parameters; therefore, this contribution will not
discussed further. The parameters of both quadrupole doublets are collected in Table 4 and can be assigned to the high-spin Fe$^{3+}$ ($3d^5$, $S = 5/2$) cations in octahedral and tetrahedral oxygen coordination sites, which are in good agreement with the parameters found for other iron-containing oxides.\textsuperscript{62} It is important to note that, according to the Mössbauer spectroscopy data, practically all iron ions (95-96\%) are at the tetrahedral sites, consistent with the crystal structure.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure9.png}
\caption{$^{57}$Fe Mössbauer spectra of Na$_2$FeSbO$_5$ recorded in the paramagnetic temperature range above $T^* = 104$ K.}
\end{figure}
Below 105 K, the spectra broaden and show six lines characteristic of magnetic hyperfine interactions (see Fig. S5(a)). A Zeeman structure with broadened components evidences the existence of a distribution of hyperfine magnetic fields $H_{\text{hf}}$ at the $^{57}$Fe nuclei, as often observed in spin-glasses. In the first stage of the spectral analysis, we reconstructed the magnetic hyperfine field distribution $p(H_{\text{hf}})$ (Fig. S5(b)), assuming a linear correlation between the quadrupolar shift ($\varepsilon_Q$) of the Zeeman components and the value of $H_{\text{hf}}$. From the temperature dependences of the mean field $\langle H_{\text{hf}}(T) \rangle$ and dispersion $D_{p(H_{\text{hf}})}(T) = \sqrt{\sum p(H_{\text{hf}})(H_{\text{hf}} - \langle H_{\text{hf}} \rangle)^2 \delta H_{\text{hf}}}^{1/2}$ (Fig. 10) of the resulting distributions $p(H_{\text{hf}})$, we evaluated the temperature $T^* = 104(4)$ K, at which the magnetic hyperfine structure totally vanishes. The temperature $T^*$ cannot be considered as a Néel or Curie temperature because, according to magnetic and thermodynamic measurements, no long-range order is present in Na$_2$FeSbO$_5$. This effect can be associated with the characteristic Mössbauer hyperfine Larmor frequency of $\sim$280 MHz instead a spin freezing temperature ($T_g$).

Table 4. Hyperfine parameters of the $^{57}$Fe Mössbauer spectra of Na$_2$FeSbO$_5$ at different temperatures.

| $T$ (K) | Subspectrum | $\delta$ (mm/s) | $\Delta$ (mm/s) | $\Gamma$ (mm/s) | $I$ (%) |
|---------|-------------|----------------|----------------|----------------|--------|
| 300     | Fe(1)       | 0.21(1)        | 0.74(1)        | 0.26(1)        | 95.6(3) |
|         | Fe(2)       | 0.46(1)        | 0.72(2)        | 0.26(1)*       | 4.5(3)  |
| 110     | Fe(1)       | 0.29(1)        | 0.77(1)        | 0.29(1)        | 94.3(9) |
|         | Fe(2)       | 0.55(1)        | 0.90(4)        | 0.29(1)*       | 5.7(9)  |

$\delta$ is an isomer shift, $\Delta$ is a quadrupole splitting, $\Gamma$ is a linewidth and $I$ is a relative intensity.

*The values were fixed.
The temperature dependence of $<H_{hf}(T)>$ was described by Brillouin function (Fig. 10):

$$
<H_{hf}(T)> = H_{hf}(0)B_S \left[ \frac{\sigma(T) \cdot S}{\tau \cdot (S+1)} \right],
$$

(3)

where $S = 5/2$ for the Fe$^{3+}$ ion, $\sigma = <H_{hf}(T)>/H_{hf}(0)$ is the reduced field, $\tau = T/T^*$ is the reduced temperature, and $H_{hf}(0)$ is the “saturation” hyperfine magnetic field. The approximated saturation value of $H_{hf}(0) \approx 346$ kOe is anomalously low for high-spin ferric ions in tetrahedral oxygen environment for which $H_{hf}(0)$ is about 480-520 kOe, corrected for covalence effects. This spin reduction (~ 30 %) cannot be caused by crystal field or covalency effects only and may be attributed to zero-point spin reduction, which has been predicted in quasi-one-dimensional systems to be large.

In the temperature range $40 \text{ K} < T < T^*$, the spectra clearly demonstrate relaxation behavior (Fig. 11). We observe an increase in the ratio $\omega_{1,6}/\omega_{3,4}$ of the split between 1$^{st}$ - 6$^{th}$ ($\omega_{1,6}$) and 3$^{rd}$ - 4$^{th}$ ($\omega_{3,4}$) lines, thus evidencing the presence of anisotropic hyperfine field fluctuations. This ratio should not depend on temperature in absence of fluctuation effects. It

\[\text{Figure 10. Temperature dependence of the average hyperfine field } <H_{hf}(T)> \text{ and dispersion } D_p(H) \text{ (inset) of the distributions } p(H_{hf}). \text{ The solid blue curve corresponds to the fit using the Brillouin function with } S = 5/2.\]
Figure 11. $^{57}$Fe Mössbauer spectra of Na$_2$FeSbO$_5$ recorded at $T < T_0$ (left side) where the solid blue lines are the simulations of the experimental spectra using a stochastic relaxation model, and in the range $T_0 < T < T^*$ (right side) where the solid lines are the simulations of the experimental spectra as the superposition of the magnetic (blue line) and paramagnetic (orange area) subspectra.
is important, that such behavior even in the presence of a static magnetically split spectra series cannot occur. These features can be interpreted by persistence of slow collective magnetic fluctuations below $T^*$, which is quite reasonable considering the low-dimensional and frustrated topology of the Fe$^{3+}$ spins in the Na$_2$FeSbO$_3$ structure.

We used the stochastic model of ionic spin relaxation to simulate the magnetic relaxation spectra. Earlier, this model was used to explain the shape of the $^{57}$Fe Mössbauer spectra of the ferrites demonstrating a geometric frustration and spin-glass-like behavior.$^6$ The computation procedure can be found in Refs. 67, 68. The $^6$S state of the Fe$^{3+}$ ion splits into six levels driven by the Zeeman interaction with the Weiss magnetic field $H_W$; the ratio of the thermal population of the successive Zeeman levels is given by $s = \exp(-2\mu_B H_W/k_B T)$. The thermal average $\langle S_z(T) \rangle$ of the Fe$^{3+}$ ion is given by

$$\langle S_z(T) \rangle = \frac{2.5 + 1.5s + 0.5s^2 - 0.5s^3 - 1.5s^4 - 2.5s^5}{1 + s + s^2 + s^3 + s^4 + s^5}$$  (4)

The rate of flipping between the ionic levels, $\Omega_e$, is related to the relaxation time $\tau$ by the relation $\tau = [7(1 + s)\Omega_e]^{-1}$. All quantities appearing in the formula of the Mössbauer lineshape, except $s$ (or $\tau$) and $\Omega_e$, are obtained by fitting the spectrum at 17 K. The lineshape of the spectrum depends not only on the “static” hyperfine parameters ($\delta$, $\epsilon_Q$, $\Gamma$), but also on the “dynamical” parameters: $s$, $\Omega_e$, and $H_{hf}$ (the saturated hyperfine field when $s \to 0$). At higher temperatures, only $s$ and $\Omega_e$ are treated as variable parameters. A satisfactory description of the spectra at all temperatures (Fig. 11) was achieved only assuming that there is a continuous distribution of averaged population $s = \exp(-\Delta/kT)$, where $\Delta$ is an energy gap between two neighboring relaxation levels. Fig. 12 represents the thermal variation of the selected distributions $p(\Delta)$ reconstructed by the fits of the spectra shown in Fig. 11. The physical origin of the observed $\Delta$ gap distributions can be the anisotropy of exchange interactions as often observed in spin-glasses systems.$^{69-71}$
Figure 12. Temperature dependence of the distribution $p(\Delta/k_B)$ of the energy gap ($\Delta/k_B$) between two adjacent relaxation levels in the stochastic relaxation model (see text). The distribution at 40 K was scaled down by factor 2.5 for the convenience of perception.

The observed thermal variation of $\tau^{-1}(T)$ (see the inset in Fig. 13) can be fitted to the sum of a temperature independent spin-spin term ($\tau^{-1})_0$ and an exponential term associated with a two-phonon process through the excited states, the Orbach process\textsuperscript{72}: $\tau^{-1}(T) = (\tau^{-1})_0 + B \cdot \exp(-U/k_BT)$, with the energy of an excited crystal field level $U$. The fit yields: $(\tau^{-1})_0 = 7.3(2) \times 10^7$ s$^{-1}$, $B = 4.5 \times 10^9$ s$^{-1}$ and $U = 41(9)$ meV. Fig. 13 represents the temperature dependence of $<S_z(T)>$ in accordance to Eq.(4). This dependence agrees qualitatively with the thermal variation of the mean field $<H_{hf}(T)> \propto <S_z(T)>$ (Fig. 10) obtained from the $p(H_{hf})$ distribution analysis. The observed thermal variation of $\Omega_S(T)$ (insert in Fig. 13) is fitted as a constant value $8.89(3) \times 10^6$ s$^{-1}$, thus indicating that the only spin-spin relaxation occurred in the Na$_2$FeSbO$_5$ lattice.
Figure 13. Temperature dependence of $<S_z(T)>$ of the Fe$^{3+}$ ions, determined from the values of the thermal population ($s$) of the successive Zeeman levels where the red solid line corresponds to fit using the Brillouin function with $S = 5/2$. Inset: the rate ($\Omega_e$) of flipping between the ionic levels and inverse value of the relaxation time ($\tau$). The solid line corresponds to fit according to: $(\tau^{-1})_0 + B \exp(-U/k_B T)$ (see text).

The $T^*$ value found from Mössbauer spectra appears to be noticeably higher (by $\sim 20\%$) than that ($T_{f1} \approx 80$ K) obtained from the measurements of magnetic $ac$ susceptibility, but agrees well with anomaly in $dc \chi(T)$ (Fig. 5). A generic feature of spin-glasses is the critical low (Eq. 2) expected for the characteristic frequency ($\omega = 2\pi f$) of the measurement. Fig. 6 shows the dependence of the frequency $\omega$ on a log scale with the temperature calculated using $T_g(0) = 70(5)$ K. We included the “freezing” temperature $T^* = 104(4)$ K measured by the present $^{57}$Fe Mössbauer study in order to sweep a larger frequency range. A characteristic frequency $\Omega_e \approx 8.89(3) \cdot 10^6$ s$^{-1}$ deduced from analysis of relaxation spectra (Fig. 11) was used. The critical scaling is seen to be satisfactorily obeyed over 10 orders of magnitude for $\omega$, with reasonable physical values $\omega_0 = 10^8$ Hz and $z\nu = 7.0(5)$. 


It is clearly seen that as the $T^*$ temperature is approached from below (starting with $T_0 = 79$ K), a paramagnetic component ($\text{Fe}^{\text{par}}$) coexisted with the magnetic spectrum ($\text{Fe}^{\text{mag}}$), continuous to show the presence of ionic spin relaxation, appears (Fig. 11) and sharply grows in intensity ($I$) with temperature (Fig. 13). The transformation of the magnetic spectrum into a paramagnetic one requires that the magnetic sublattice splits into superparamagnetic clusters with more rapid than the nuclear Larmor precession period $\tau_L (\sim 10^{-8} \text{ s})^{73,74}$ fluctuations of the magnetization. Therefore, the spin freezing in the $\text{Na}_2\text{FeSbO}_5$ lattice occurs via cluster formation. The observed rapid development of a paramagnetic doublet $\text{Fe}^{\text{par}}$ is characteristic for a gradual decrease of short range ordering up to temperature $T^*$ where all clusters are successively deblocked. We speculate that the formation of “clusters” reflecting the spin glass state of $\text{Na}_2\text{FeSbO}_5$ may be described by a random coupling of strongly correlated quasi-one-dimensional $\text{Fe-Fe}$ chain segments due to frustration of various magnetic interactions.

3.7. ESR spectroscopy

The ESR spectra of $\text{Na}_2\text{FeSbO}_5$ powder samples measured at various temperatures are presented in Fig. 14. The ESR line shape has a rather complex character and changes radically with the temperature variation. At high temperatures the Lorentzian shape line with a $g$-factor $g = 2$, typical for high-spin state Fe$^{3+}$ ions in tetrahedral coordination, is observed. When temperature decreases the strong distortion of the ESR spectrum is observed. The experimental spectra are relatively broad, hence two circular components of the exciting linearly polarized microwave field on both sides of $B = 0$ should be included to standard Lorenzian profile for proper fitting of the line shape $^{75}$:

$$
\frac{dP}{dB} \propto \frac{dB}{dB} \left[ \frac{\Delta B}{\Delta B^2 + (B - B_r)^2} + \frac{\Delta B}{\Delta B^2 + (B + B_r)^2} \right]
$$

(5)

where $P$ is the power absorbed in the ESR experiment, $B$ the magnetic field, $B_r$ the resonance
field, and $\Delta B$ the line width. A satisfactory description can be achieved by using one, two and three Lorentzian lines in the temperature ranges of $6 - 30$ K, $220 - 450$ K and $40 - 220$ K, respectively. The results of ESR line shape fitting are shown by the solid curves in Fig. 14, which shows a good agreement between the fitted curves and the experimental data.

Representative examples of the ESR spectrum decomposition are given in Fig. 15. The main contributions to the absorption come from the two main resonance modes, the $L_1$ and $L_2$ lines (the green and blue curves in Fig. 15, respectively). Moreover, the dominating contribution brings $L_1$ mode over the whole investigated temperature range, which allows us to assign the $L_1$ mode to the signal from the zigzag chains of corner-sharing FeO$_4$ tetrahedra, and the $L_2$ mode to fragments of these chains. The latter manifest themselves as separate paramagnetic subsystem.

**Figure 14.** Temperature dependence of the first derivative absorption line for Na$_2$FeSbO$_5$.

The black circles are experimental data, the lines are results of fitting by the sum of two ($T > 225$ K, (a)) or three ($T < 225$ K, (b)) Lorentzians, where each of Lorentzian is given by eq.5.
For both $L_1$ and $L_2$ lines in whole temperature range, the position of the resonance field $B_r$ practically does not change. This indicates the absence of a long-range magnetic ordering down to 6 K. Thus, the ESR data agree well with the static magnetization and specific heat data.

In addition, a careful analysis of the ESR spectra reveals the appearance of another $L_3$ line, whose amplitude also rapidly grows with decreasing $T$, and the resonant field is strongly shifted towards weaker fields, in contrast to the resonance fields of $L_1$ and $L_2$ lines that remain practically unchanged over the entire temperature range. The strong shift of the resonance field for the $L_3$ line indicates the presence of the internal magnetic field, which changes the resonance conditions. It is usually characteristic of a magnetic ordering. In this case, however, it is obvious that this ordering does not capture the whole volume of a sample and most probably responds to the formation of limited ordered areas (linear clusters).

At $T < 20$ K, the main $L_1$ line dominates the spectra, while the $L_2$ and $L_3$ lines practically disappear: the position of the resonance for $L_3$ obviously falls out of the investigated magnetic field range, while the presence of $L_2$ becomes hidden in the background of more intensive $L_1$ line due to the strong broadening of the $L_1$ and $L_2$ lines. Additionally, at lowest temperatures one can see two weak satellite signals at $g_4 \approx 4.1$ and $g_5 \approx 5.6$ (see inset in Fig. 14b) on the background of the main $L_1$ mode. Similar ESR response has been observed earlier in other Fe$^{3+}$ containing oxides$^{76}$ and signal at $g \approx 4.2$ has been related to the median Kramers doublet from Fe sites, which are located in either tetrahedral or octahedral distorted coordination. This interpretation has been supported by Loveridge and Parke$^{77}$, and a similar behaviour has been observed experimentally for Na$_4$FeSbO$_6$. Following by this interpretation, we assume that the major signals at $g_1 = 2$ and $g_5 = 5.6$ are typical for Fe$^{3+}$ ions in tetrahedral oxygen coordination, while the signal at $g_4 = 4.2$ might be associated with Fe$^{3+}$ ions in rhombohedrally distorted environments.
Figure 15. ESR spectra of Na$_2$FeSbO$_5$ at different temperatures. The black circles represent the experimental data ((a): 360 < T < 430 K, (b): 200 < T < 300 K, (c): 120 < T < 180 K, (d): 20 < T < 100 K), and the curves the results of the fitting with each Lorentzian given by Eq.(5). The green, blue and magenta curves represent the resolved components of the ESR spectra, and the red solid line the sum of the components.
The values of the linewidth $\Delta B$ and effective g-factor derived from the fitting analyses for the ESR spectra of Na$_2$FeSbO$_5$ are collected in Figs. 16-17. In the temperature range of $T > 100$ K, the $L_1$ and $L_2$ curves are characterized by an isotropic temperature-independent effective g-factor $g = 2.00 \pm 0.05$, while the g-factor of the $L_3$ curve is very close to the value $g_3 = 2.2$ (Fig. 16). With decreasing temperature, the temperature dependence of $g(T)$ becomes noticeably different; at $T^* = 100(5)$ K, the g-factor of the $L_1$ curve exhibits a small jump reaching $g_1 = 2.1$, the g-factor of the $L_2$ curve stays almost unchanged, and that of the $L_3$ curve sharply increases. Such behaviors of $g(T)$ are in qualitative agreement with the presence of the main anomaly on the dc/ac magnetic susceptibility and Mössbauer data, below which spin-freezing ordering occurs.

The temperature dependences of the ESR linewidth for the $L_1$, $L_2$ and $L_3$ curves are shown in Fig. 17. The linewidth $\Delta B$ monotonically increases over the entire $T$-range, except

![Figure 16](image-url)

**Figure 16.** The temperature dependence of the effective g-factor for Na$_2$FeSbO$_5$. The green, blue and magenta circles are obtained from the three Lorentzian fits for $L_1$, $L_2$ and $L_3$, respectively. The inset shows a zoomed-in view in the low temperature range. The dashed line indicates the critical point of the observed anomaly.
for $100 \, K > T > 210 \, K$, where a wide step-like transition to another dynamic regime is observed. The linewidths $\Delta B_2$ and $\Delta B_3$ remain almost temperature-independent down to $\approx 210K$ and $\approx 100K$, respectively, and then increase progressively. Such a critical line broadening for all components is indicative of the development of strong spin-spin correlations and slowing down of spins at low temperatures.$^{78,79}$ The same line broadening over the wide temperature range was reported for many other antiferromagnetic compounds, including classical and low-dimensional ones as well as for spin-glass materials.$^{80-85}$

The integral ESR intensity, $\chi_{\text{ESR}}$, which is known to be proportional to the concentration of paramagnetic centres, estimated by the double integration was found to agree well with the FC static magnetic susceptibility $\chi(T)$ and also exhibits a step-like anomaly at $T^* \approx 100 \, K$ (Fig. 5(a)).

![Figure 17](image)

**Figure 17.** The temperature dependence of the ESR linewidth for Na$_2$FeSbO$_5$. The green, blue and magenta circles are obtained from the three Lorentzian fits for $L_1$, $L_2$ and $L_3$, respectively. The dashed lines indicate the critical temperatures, where anomalies are observed. Yellow area denoted as SR corresponds to the region with the short range fluctuations.
Obviously, the temperature dependence of the ESR parameters implies the significant role of the short-range magnetic correlations at temperatures below 210 K and confirms a transition to slow dynamic regime, i.e., spin-glass state at low temperature.

3.8. Density functional analysis of magnetic structure

To explain the observed magnetic properties of the Na$_2$FeSbO$_5$, we determine its spin exchange interactions by carrying out energy-mapping analysis based on DFT calculations. The chains of corner-sharing FeO$_4$ tetrahedra lie in the $bc$-plane as depicted in Fig. 18, where the red, cyan, green and yellow circles represent the Fe, O(1), O(3) and O(5) atoms, respectively. As shown in Fig. 19a, the spin exchange paths of interest are the nearest-neighbour (NN) intrachain spin exchange $J_1$ as well as the NN interchain exchanges paths $J_2$ and $J_3$. The structural parameters associated with the exchange paths $J_1$ – $J_3$ are summarized in Table 5. To determine the values of $J_1$ – $J_3$, we carry out spin-polarized DFT calculations using a (2a, b, c) supercell for Na$_2$FeSbO$_5$ for the four ordered spin states defined in Fig. 19 by employing the projected augmented wave method encoded in the Vienna Ab Initio Simulation Package (VASP) with the generalized gradient approximation of Perdew, Burke and Ernzerhof for the exchange-correlation functionals with a plane wave cutoff energy of 450 eV, a set of $2\times4\times8k$-points, and a threshold $10^{-6}$ eV for energy convergence. The DFT plus on-site repulsion U (DFT+U) method was employed at $U^{\text{eff}} = U - J = 3$ and 4 eV to describe the electron correlation in the Fe 3$d$ states. Given the spin Hamiltonian,

$$H_{\text{spin}} = \sum_{i<j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j$$

where $\mathbf{S}_i$ and $\mathbf{S}_j$ are the spins at magnetic ion sites $i$ and $j$, respectively, with the spin exchange constant $J_{ij} = J_1$, $J_2$ or $J_3$. Then, the total spin exchange energies of the four ordered spin states are given by
\[
E_{FM} = \left( -16J_1 - 8J_2 - 8J_3 \right) \left( \frac{N^2}{4} \right)
\]

\[
E_{AF1} = \left( 16J_1 - 8J_2 - 8J_3 \right) \left( \frac{N^2}{4} \right)
\]

\[
E_{AF2} = \left( 16J_1 + 8J_2 - 8J_3 \right) \left( \frac{N^2}{4} \right)
\]

\[
E_{AF3} = \left( 16J_1 - 8J_2 + 8J_3 \right) \left( \frac{N^2}{4} \right)
\]

per supercell (2a, b, c), where \( N = 5 \), i.e., the number of unpaired spins at each Fe\(^{3+}\) ion site.

Thus, by mapping the relative energies of these four states determined by the spin exchange parameters onto the corresponding energies determined by the DFT+U calculations, we obtain the values of \( J_1 - J_3 \) summarized in Table 6. The spin exchanges \( J_1 - J_3 \) are all antiferromagnetic (AFM). The intrachain spin exchange \( J_1 \) is much stronger than the two interchain spin exchanges \( J_2 \) and \( J_3 \). Magnetically, Na\(_2\)FeSbO\(_5\) is best described as a 1D chain system forming the AFM chains made up of the spin exchanges \( J_1 \) along the \( b \)-direction. This agrees with the magnetic properties of Na\(_2\)FeSbO\(_5\) discussed in the previous sections.

![Figure 18. Chains of corner-sharing FeO\(_4\) tetrahedra in the \( bc \)-plane, where the red, cyan, green and yellow circles represent the Fe, O(1), O(3) and O(5) atoms, respectively.](image)

| \( \) | \( Fe...Fe (\text{Å}) \) | \( O...O (\text{Å}) \) | \( \angle \text{Fe-O...O (°)} \) | \( \angle \text{O...O-Fe (°)} \) |
| --- | --- | --- | --- | --- |
| \( J_1 \) | 3.233 | | 111.9 | 111.9 |
| \( J_2 \) | 4.898 | 2.800 | 111.9 | 111.9 |
| \( J_3 \) | 5.991 | 2.778 | 131.6 | 131.6 |

Table 5. Geometrical parameters associated with the spin exchange paths \( J_1, J_2 \) and \( J_3 \) of Na\(_2\)FeSbO\(_5\)
Table 6. Spin exchange parameters (in $k_B$K) of Na$_2$FeSbO$_5$ obtained from GGA+U calculations

|       | $U_{\text{eff}} = 3$ eV | $U_{\text{eff}} = 4$ eV |
|-------|-------------------------|-------------------------|
| $J_1$ | 215.2                   | 181.1                   |
| $J_2$ | 3.23                    | 2.65                    |
| $J_3$ | 4.47                    | 3.81                    |

![Graphical representation](image)

(a) FM  
(b) AF1  
(c) AF2  
(d) AF3

Figure 19. Ordered spin arrangements of the FM (a), AF1 (b), AF2 (c) and AF3 (d) states used to extract the values of $J_1 - J_3$. The grey and white circles indicate the spin up and down sites of Fe$^{3+}$ ions.

Using interface provided by the JASS code$^{94}$ we simulated temperature dependence of magnetic susceptibility using quantum Heisenberg model for weakly coupled antiferromagnetic spin 5/2 chains. We used quantum Monte-Carlo (QMC) method as realized by the Loop algorithm in the ALPS package$^{95}$ to simulate 8x4x4 cell. The exchange parameters obtained in the GGA+U calculations for $U_{\text{eff}} = 4$ eV were used. Number of sweeps was set up to be equal $10^6$. Results are presented in Fig. 20, which shows that the considered
spin model does not order until very lowest temperatures used in the calculations (5 K). There is a broad susceptibility maximum reflecting presence of the short-range spin correlations very typical for low-dimensional spin systems, weakly coupled Heisenberg chains in particular. These correlations are seen in Mössbauer and ESR spectra. On another hand, temperature behavior of the calculated susceptibility is very different from what is seen in the experiment, see Fig. 5. Theory and experiment can be reconciled if we take into account fragmentation of the chains, as suggested by the ESR. Due to segmentation, the system should rather be considered not as a network of the chains, but as a set of weakly coupled chain fragments (of different lengths), which obviously results in the Curie-like behavior at low temperatures seen in the experiment. At higher temperature these tails subside, but there is still a contribution from those chains, which remain unbroken. Because of large intra-chain exchange coupling the correlation maximum for these chains lies very high in temperature – at $T_{\text{max}} \approx 850$ K, much higher than the experimentally investigated temperature range in the present work. This explains why the observed magnetic susceptibility does not obey the Curie-Weiss law up to 400 K.

Figure 20. Calculated temperature dependence of the magnetic susceptibility of weakly coupled spin 5/2 chains with intra-chain ($J_{\text{intra}} = 181$ K) and inter-chain ($J_{\text{intra}} = 3$ K) exchanges.
4. CONCLUDING REMARKS

Single crystals of Na$_2$FeSbO$_5$ were obtained by using sodium sulphate flux. In this quasi-one-dimensional oxide, zigzag chains of edge-sharing SbO$_6$ octahedra are condensed with chains of corner-sharing FeO$_4$ tetrahedra. The $^{57}$Fe Mössbauer spectra indicate that all high-spin Fe$^{3+}$ ions occupy equivalent sites in the distorted tetrahedral oxygen coordination. The magnetization, specific heat and ESR data indicate the absence of a long-range magnetic order down to 2 K and extended temperature range of the short-range magnetic correlations. There is neither saturation nor magnetic field induced features on the magnetization isotherms in the whole investigated temperature range. At the same time overall bulk magnetic studies demonstrated a spin-glass-type behavior at low temperatures, which is directly confirmed by $ac$ magnetic susceptibility, which manifested a unique two-step freezing at $T_{f1} \sim 80$ K and $T_{f2} \sim 35$ K. Low temperature Mössbauer spectra also reveal a spin-glass behavior below temperature $T^* \sim 104$ K. The theoretical fits of the line shapes in accordance with the stochastic model of ionic spin relaxation show agree well with the experimental MS data. The appearance of a spin-glass transition is supported by frequency dependence of the freezing temperature over a wide frequency range. The spectra just below $T^*$ in the range $T_{f1} < T < T^*$ demonstrate an appearance of quadrupole doublet coexisting with the magnetic subspectrum and sharply growing in intensity with temperature. Such behaviour demonstrates that the spin freezing in the Na$_2$FeSbO$_5$ lattice occurs via cluster formation. The ESR data yield a complicated picture concerning the coexistence of different magnetic sublattices, which tentatively correspond to the signals from the ordered and disordered FeO$_4$ tetrahedral 1D spin chain clusters. In full agreement with Mössbauer spectra data, both the static magnetic susceptibility and the integral ESR intensity reveal a clear anomaly at $T^* \sim 100$ K. The spin exchanges determined by the mapping analysis based on DFT calculations show a strong 1D AFM character with the main intrachain exchange of $\sim 200$ K and small interchain interaction.
of ~3 K. Our results seem to be related to the fluctuations enhanced by the weakened interchain coupling leading to fractionalization of linear chain clusters and freezing the system into spin-cluster ground state.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website. It contains the figures of FESEM, EDX, comparative PXRD patterns, $dc$ magnetic susceptibility $\chi$ and its inverse value $1/\chi$, Arrhenius plots $\ln(\omega)$ vs $1/T$ and $^{57}$Fe Mössbauer spectra at different temperatures; the tables of bond angles and anisotropic displacement parameters.

Accession codes

CCDC -1858526 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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REFERENCES

(1) Melot, B.C.; Tarascon, J.M. Design and preparation of materials for advanced electrochemical storage. *Acc. Chem. Res.* **2013**, *46*, 1226-1238.

(2) Mather, G.C.; Smith, R.I.; Skakle, J.M.S.; Fletcher, J.G.; Castellanos, M.A.; Gutierrez, M.P.; West, A.R. Synthesis and structures of the partially ordered rock salt phases, Li$_3$M$_2$XO$_6$: M = Mg, Co, Ni; X = Nb, Ta, Sb. *J. Mater. Chem.* **1995**, *5*, 1177-1182.

(3) Greaves, C.; Katib, S.M.A. The structural chemistry of Li$_3$Zn$_2$MO$_6$ (M = Sb, Bi) and related phases. *Mat. Res. Bull.* **1990**, *25*, 1175-1182.

(4) Skakle, J.M.S.; Castellanos, M.A.; T(548,571),(579,602); West, A.R. Synthesis of Li$_3$Cu$_2$SbO$_6$, a new partially ordered rock salt structure. *J. Solid State Chem.* **1997**, *131*, 115-120.

(5) Mather, G.C.; West, A.R. Continuous order-disorder transition in Li$_3$Ni$_2$NbO$_6$ and Cr-doped Li$_3$Ni$_2$NbO$_6$ rock salt structures. *J. Solid State Chem.* **1996**, *124*, 214-219.

(6) Berthelot, R.; Schmidt, W.; Muir, S.; Eilertsen, J.; Etienne, L.; Sleight, A.W.; Subramanian, M.A. New layered compounds with honeycomb ordering: Li$_3$Ni$_2$BiO$_6$, 
Li$_3$NiM’BiO$_6$ (M’ = Mg, Cu, Zn), and the delafossite Ag$_3$Ni$_2$BiO$_6$. *Inorg. Chem.* **2012**, *51*, 5377-5385.

(7) Smirnova, O.A.; Nalbandyan, V.B.; Petrenko, A.A.; Avdeev, M. Subsolidus phase relations in Na$_2$O-CuO-Sb$_2$O$_7$ system and crystal structure of new sodium copper antimonate Na$_3$Cu$_2$SbO$_6$. *J. Solid State Chem.* **2005**, *178*, 1165-1170.

(8) Viciu, L.; Huang, Q.; Morosan, E.; Zandbergen, H.W.; Greenbaum, N.I.; McQueen, T.; Cava, R.J. Structure and basic magnetic properties of the honeycomb lattice compounds Na$_2$Co$_2$TeO$_6$ and Na$_3$Co$_2$SbO$_6$. *J. Solid State Chem.* **2007**, *180*, 1060-1067.

(9) Politaev, V.V.; Nalbandyan, V.B.; Petrenko, A.A.; Shukaev, I.L.; Volotchaev, V.A.; Medvedev, B.S. Mixed oxides of sodium, antimony (5+) and divalent metals (Ni, Co, Zn or Mg). *J. Solid State Chem.* **2010**, *183*, 684-691.

(10) Seibel, E.M.; Roudebush, J.H.; Wu, H.; Huang, Q.; Ali, M.N.; Ji, H.; Cava, R.J. Structure and magnetic properties of the $\alpha$-NaFeO$_2$-Type honeycomb compound Na$_3$Ni$_2$BiO$_6$. *Inorg. Chem.* **2013**, *52*, 13605-13611.

(11) Kumar, V.; Bhardwaj, N.; Tomar, N.; Thakral, V.; Uma, S. Novel lithium-containing honeycomb structures. *Inorg. Chem.* **2012**, *51*, 10471-10473.

(12) Nalbandyan, V.B.; Avdeev, M.; Evstigneeva, M.A. Crystal structure of Li$_4$ZnTeO$_6$ and revision of Li$_3$Cu$_2$SbO$_6$. *J. Solid State Chem.* **2013**, *199*, 62-65.

(13) Zvereva, E.A.; Nalbandyan, V.B.; Evstigneeva, M.A.; Koo, H.-J.; Whangbo, M.-H.; Ushakov, A.V.; Medvedev, B.S.; Medvedeva, L.I.; Gridina, N.A.; Yalovega, G.E.; Churikov, A.V.; Vasiliev, A.N.; Büchner, B. Magnetic and electrode properties, structure and phase relations of the layered triangular-lattice tellurate Li$_4$NiTeO$_6$. *J. Solid State Chem.* **2015**, *225*, 89-96.

(14) Bhardwaj, N.; Gupta, A.; Uma, S. Evidence of cationic mixing and ordering in the honeycomb layer of Li$_4$MSbO$_6$ (M (III) = Cr, Mn, Al, Ga) (S.G. C2/c) oxides. *Dalton Trans.* **2014**, *43*, 12050-12057.
(15) Zvereva, E.A.; Savelieva, O.A.; Titov, Ya.D.; Evstigneeva, M.A.; Nalbandyan, V.B.; Kao, C.N.; Lin, J.-Y.; Presniakov, I.A.; Sobolev, A.V.; Ibragimov, S.A.; Abdel-Hafiez, M.; Krupskaya, Yu.; Jahne, C.; Tan. G.; Klingeler, R.; Buchner, B.; Vasiliev, A.N. A new layered triangular antiferromagnet \( \text{Li}_4\text{FeSbO}_6 \): spin order, field-induced transitions and anomalous critical behaviour. *Dalton Trans.* **2013**, *42*, 1550-1566.

(16) Politaev, V.V.; Nalbandyan, V.B. Subsolidus phase relations, crystal chemistry and cation-transport properties of sodium iron antimony oxides. *Solid State Sci.* **2009**, *11*, 144-150.

(17) Zvereva, E.A.; Presniakov, I.A.; Whangbo, M.-H.; Koo, H.-J.; Frantsuzenko, T.V.; Savelieva, O.A.; Sobolev, A.V.; Nalbandyan, V.B.; Shih, P.-S.; Chiang, J.-C.; Lee, J.-M.; Chen, J.-M.; Lin, J.-Y.; Buechner, B.; Vasiliev, A.N. Crucial Role of Site Disorder and Frustration in Unusual Magnetic Properties of Quasi-2D Triangular Lattice Antimonate \( \text{Na}_4\text{FeSbO}_6 \). *Appl. Magn. Reson.* **2015**, *46*, 1121–1145.

(18) Schmidt, W.; Berthelot, R.; Etienne, L.; Wattiaux, A.; Subramanian, M.A. Synthesis and characterization of \( \text{O}_3\text{Na}_3\text{LiFeSbO}_6 \): A new honeycomb ordered layered oxide. *Mat. Res. Bull.* **2014**, *50*, 292-296.

(19) Yuan, D.; Liang, X.; Wu, L.; Cao, Y.; Ai, X.; Feng, J.; Yang, H. A honeycomb-layered \( \text{Na}_3\text{Ni}_2\text{SbO}_6 \) : A high-rate and cycle-stable cathode for sodium-ion batteries. *Adv. Mater.* **2014**, *26*, 6301-6306.

(20) Sathiya, M.; Ramesha, K.; Rousse, G.; Foix, D.; Gonbeau, D.; Guruprakash, K.; Prakash, A. S.; Doublet, M. L.; Tarascon, J.-M. \( \text{Li}_4\text{NiTeO}_6 \) as a positive electrode for Li-ion batteries. *Chem. Commun.* **2013**, *49*, 11376-11378.

(21) McCalla, E.; Sougrati, M.T.; Rousse, G.; Berg, E.J.; Abakumov A.; Recham, N.; Ramesha, K.; Sathiya, M.; Dominko, R.; Tendeloo, G.V.; Novak, P.; Tarascon, J-M. Understanding the roles of anionic redox and oxygen release during electrochemical cycling of Lithium-rich layered \( \text{Li}_4\text{FeSbO}_6 \). *J. Am. Chem. Soc.* **2015**, *137*, 4804-4814.
(22) Xu, J.; Assoud, A.; Soheilnia, N.; Derakhshan, S.; Cuthbert, H. L.; Greedan, J. E.; Whangbo, M.-H.; Kleinke, H. Synthesis, structure, and magnetic properties of the layered copper (II) oxide Na$_2$Cu$_2$TeO$_6$. *Inorg. Chem.* **2005**, *44*, 5042-5046.

(23) Derakhshan, S.; Cuthbert, H. L.; Greedan, J. E.; Rahaman, B.; Saha-Dasgupta, T. Electronic structures and low-dimensional magnetic properties of the ordered rocksalt oxides Na$_3$Cu$_2$SbO$_6$ and Na$_2$Cu$_2$TeO$_6$. *Phys. Rev. B.* **2007**, *76*, 104403-104407.

(24) Miura, Y.; Hirai, R.; Kobayashi, Y.; Sato, M. Spin-gap behaviour of Na$_3$Cu$_2$SbO$_6$ with distorted honeycomb structure, *J. Phys. Soc. Japan*. **2006**, *75*, 084707-084712.

(25) Koo, C.; Zvereva, E.A.; Shukaev, I.L.; Richter, M.; Stratan, M.I.; Vasiliev, A.N.; Nalbandyan, V.B.; Klingeler, R. Static and Dynamic Magnetic Response of Fragmented Haldane-like Spin Chains in Layered Li$_3$Cu$_2$SbO$_6$. *J. Phys. Soc. Japan*. **2016**, *85*, 084702.

(26) Zvereva, E.A.; Stratan, M.I.; Ovchenkov, Y.A.; Nalbandyan, V.B.; Lin, J.-Y.; Vavilova, E.L.; Iakovleva, M.F.; Abdel-Hafiez, M.; Silhanek A.V.; Chen, X.-J.; Stroppa, A.; Picozzi, S.; Jeschke, H. O.; Valentí, R.; Vasiliev, A.N. Zigzag antiferromagnetic quantum ground state in monoclinic honeycomb lattice antimonates, A$_3$Ni$_2$SbO$_6$ (A=Li, Na). *Phys. Rev. B*. **2015**, *92*, 144401.

(27) Schmidt, W.; Berthelot, R.; Sleight, A.W.; Subramanian, M. A. Solid solution studies of layered honeycomb-ordered phases O$_3$-Na$_3$M$_2$SbO$_6$ (M = Cu, Mg, Ni, Zn). *J. Solid State Chem.* **2013**, *201*, 178-185.

(28) Zvereva, E.A.; Stratan, M.I.; Shukaev, I.L.; Nalbandyan, V.B.; Vasiliev, A.N. Effect of a Structural Disorder on the Magnetic Properties of the Sodium–Cobalt Tellurate Na$_{3.70}$Co$_{1.15}$TeO$_6$. *J. Exp. Theor. Phys.* **2017**, *124*, 612-616.

(29) Zvereva, E.A.; Evstigneeva, M.A.; Nalbandyan, V.B.; Savelieva, O.A.; Ibragimov, S.A.; Volkova, O.S.; Medvedeva, L.I.; Vasiliev, A.N.; Klingeler, R.; Buechner, B. Monoclinic honeycomb-layered compound Li$_3$Ni$_2$SbO$_6$: preparation, crystal structure and magnetic properties. *Dalton Trans.* **2012**, *41*, 572-580.
(30) Kurbakov, A.I.; Korshunov, A.N.; Podchezertsev, S.Yu.; Malyshev, A.L.; Evstigneeva, M.A.; Damay, F.; Park, J.; Koo, C.; Klingeler, R.; Zvereva, E.A.; Nalbandyan, V.B. Zigzag spin structure in layered honeycomb Li$_3$Ni$_2$SbO$_6$: A combined diffraction and antiferromagnetic resonance study. Phys. Rev. B. 2017, 96, 024417.

(31) Zvereva, E.A.; Stratan, M.I.; Ushakov, A.V.; Nalbandyan, V.B.; Shukaev, I.L.; Silhanek, A.V.; Abdel-Hafiez, M.; Streltsov, S.V.; Vasiliev, A.N. Orbitally induced hierarchy of exchange interactions in zigzag antiferromagnetic state of honeycomb silver delafossite Ag$_3$Co$_2$SbO$_6$. Dalton Trans. 2016, 45, 7373 – 7384.

(32) Gupta, A.; Kumar, V.; Uma, S. Interesting cationic (Li$^+$/Fe$^{3+}$/Te$^{6+}$) variations in new rocksalt ordered structures. J. Chem. Sci. 2015, 127, 225–233.

(33) Uma, S.; Gupta, A. Synthesis and characterization of new rocksalt superstructure type layered oxides Li$_{4.5}$M$_{0.5}$TeO$_6$ (M(III)=Cr, Mn, Al, Ga). Mat. Res. Bull. 2016, 76, 118-123.

(34) Berry, F.J.; Sarson, M.I.; Tejada, J.; Labarta, A.; Rodriguez, R.; Obradors, X. Spin glass-type behaviour in iron antimonate: The identification of unusual phenomena at low temperatures in low magnetic fields. J. Solid State Chem. 1990, 87, 237-240.

(35) Retuerto, M.; Alonso, J.A.; Martínez-Lope M.J.; Garcia-Hernandez, M.; Krezhov, K.; Spirov, I.; Ruskov, T.; Fernandez-Diaz, M.T. Crystal structure and magnetism of the 6H hexagonal double perovskites Ba$_2$FeSbO$_6$ and Ba$_2$CoSbO$_{6.5}$. A neutron diffraction and Mossbauer spectroscopy study. Eur. J. Inorg. Chem. 2008, 14, 2286-2294.

(36) Whitaker, M.J.; Marco, J.F.; Berry, F.J.; Raith, C.; Blackburn, E.; Greaves, C. Structural and magnetic characterization of the pyrochlores Bi$_{2-x}$Fe$_x$(FeSb)O$_7$, (x = 0.1, 0.2, 0.3), Nd$_{1.8}$Fe$_{0.2}$(FeSb)O$_7$ and Pr$_2$(FeSb)O$_7$. J. Solid State Chem. 2013, 198, 316-322.

(37) Rigaku oxford diffraction 2018, Crysalis Pro software system version, Rigaku Corporation, Oxford, USA.

(38) De Meulenaer, J.; Tompa, H. The absorption correction in crystal structure analysis. Acta Crystallogr. 1965, 19, 1014.
(39) Sheldrick, G.M. SHELXL97, Program for crystal structure refinement, University of Gottingen, Germany, 1997.

(40) Farrugia, L.J. WINGX suite for small-molecule single-crystal crystallography. J. Appl. Cryst. 1999, 32, 837-838.

(41) Putz, H.; Brandenburg, K. Crystal and molecular structure visualization; Diamond (version 3.0), Crystal Impact, Gbr, Bonn, Germany, 2004.

(42) Coelho, A.A. TOPAS User Manual, version 3.1; Bruker AXS GmbH: Karlsruhe, Germany, 2003, 1-68.

(43) Matsnev, M.E.; Rusakov, V.S. SpectrRelax: An application for Mössbauer spectra modeling and fitting. AIP Conf. Proc. 2012, 1489, 178.

(44) Berggren, J. Refinement of the crystal structure of Dicalcium ferrite, Ca$_2$Fe$_2$O$_5$. Acta Chem. Scand. 1971, 25, 3616-3624.

(45) Parsons, T.G; Hondt, H.D; Hademann, J; Hayward, M.A. Synthesis and Structural Characterization of La$_{1-x}$A$_x$MnO$_{2.5}$ (A = Ba, Sr, Ca) Phases: Mapping the Variants of the Brownmillerite Structure. Chem. Mater. 2009, 21, 5527-5538.

(46) Ramezanipour, F.; Greedan, J.E.; Grosvenor, A.P.; Britten, J.F.; Cranswick, L.M.D; Garlea, V.O. Intralayer cation ordering in a brownmillerite superstructure: Synthesis, Crystal, and magnetic structures of Ca$_2$FeCoO$_5$. Chem. Mater. 2010, 22, 6008-6020.

(47) Brown, I.D. Valence- A program for calculating bond valences. J. Appl. Cryst. 1996, 29, 479-480.

(48) Binder, K.; Young A.P. Spin glasses: Experimental facts, theoretical concepts, and open questions, Rev. of Mod. Phys. 1986, 58, 801.

(49) Mydosh, J.A. Spin Glasses, An Experimental Introduction, Taylor & Francis, London, 1993.
(50) Balanda, M. AC Susceptibility Studies of Phase Transitions and Magnetic Relaxation: Conventional, Molecular and Low-Dimensional Magnets. *Acta Phys. Pol. A* **2013**, *124*, 964-976.

(51) Bao, J.-K.; Li, L.; Tang, Z.-T.; Liu, Y.; Li, Y.-K.; Bai, H., Feng, C.M.; Xu, Z.-A.; Cao, G.-H. Cluster spin-glass ground state in quasi-one-dimensional KCr$_3$As$_3$. *Phys. Rev. B* **2015**,

(52) Bera, A.K.; Yusuf, S.M. Quantum phase transition from a spin-liquid state to a spin-glass state in the quasi-one-dimensional spin-1/2 system Sr$_{1-x}$Ca$_x$Ni$_2$V$_2$O$_8$. *Phys. Rev. B* **2012**, *86*, 024408.

(53) Sampathkumaran, E.V.; Niazi, A. Superparamagnetic-like ac susceptibility behaviour in the partially disordered antiferromagnetic compound Ca$_3$CoRhO$_6$. *Phys. Rev. B* **2002**, *65*, 180401.

(54) Etzkorn, S.J.; Hibbs, W.; Miller, J.S.; Epstein, A.J. Viscous behaviour in a quasi-1D fractal cluster glass. *Phys. Rev. Lett.* **2002**, *89*, 207201.

(55) Wiedenmann, A.; P. Burlet. Magnetic behaviour of imperfect quasi one dimensional insulators FeMgBO$_4$ and FeMg$_2$BO$_5$: spin glass systems? *J. Phys. Colloques* **1978**, *39*, C6-720-C6-722.

(56) Gunnarsson, K.; Svedlindh, P.; Nordblad, P.; Lundgren, L.; Aruga, H.; Ito, A. Dynamics of an Ising spin-glass in the vicinity of the spin-glass temperature. *Phys. Rev. Lett.* **1988**, *61*, 754.

(57) Sandlund, L.; Granberg, P.; Lundgren, L.; Nordblad, P.; Svedlindh, P.; Cowen, J.A.; Kenning, G. G. Dynamics of Cu-Mn spin-glass films, *Phys. Rev. B* **1989**, *40*, 869.

(58) Kirkpatrick, S.; Sherrington, D. Infinite-ranged models of spin-glasses. *Phys. Rev. B*. **1978**, *17*, 4384.

(59) Campbell, I.A. Ordering and relaxation in spin glasses. *Phys. Rev. B* **1986**, *33*, 3587(R).

(60) Tari, A. The specific heat of matter at low temperatures. *Imperial Collage press: London*, 2003.
(61) Menil, F. Systematic trends of the $^{57}$Fe Mössbauer isomer shifts in (FeO$_n$) and (FeF$_n$) polyhedra. Evidence of a new correlation between the isomer shift and the inductive effect of the competing bond T-X ($\rightarrow$ Fe) (where X is O or F and T any element with a formal positive charge). *J. Phys. Chem. Solids.* **1985**, *46*, 763-789.

(62) Geller, S.; Grant, R.W.; Gonser, U. Crystal chemistry and magnetic structures of substituted Ca$_2$[Fe](Fe)O$_5$. *Prog. Solid State Chem.* **1978**, *5*, 5.

(63) Meyer, C.; Hartmann-Boutron, F.; Gros, Y.; Campbell, I.A. Mössbauer effect measurements on an AuFe spin glass. *J. Magn. Magn. Mater.* **1985**, *46*, 254-256.

(64) Gupta, G.P.; Dickson, D.P.E.; Johnson, C.E. One dimensional antiferromagnetism in K$_2$FeF$_5$: a single crystal Mössbauer study. *J. Phys. C: Solid State Phys.* **1978**, *11*, 215-225.

(65) Van der Woude, F.; Dekker, A.J. The relation between magnetic properties and the shape of Mössbauer spectra. *Phys. Stat. Soli B.* **1965**, *9*, 775-786.

(66) Bhargava, S.C.; Mulder, F.M.; Thiel, R.C.; Kulshreshtha, S.K. Magnetic behaviour of Co$_{0.5}$Zn$_{0.5}$FeCrO$_4$: A Mössbauer study. *Hyperfine Interact.* **1990**, *54*, 459-466.

(67) Bhargava, S.C.; Morrish, A.H.; Kunkel, H.; Li, Z.W. Spin-glass ordering in a spinel ferrite, Mg(Al, Fe)$_2$O$_4$. *J. Phys.: Cond. Matter.* **2000**, *12*, 9667-9687.

(68) Gaunt, P. Magnetic viscosity in ferromagnets. I. Phenomenological theory. *Phil. Mag.* **1976**, *34*, 775-780.

(69) Gibbs, M.R.J.; Evetts, J.E.; Leake, J.A. Activation energy spectra and relaxation in amorphous materials. *J. Mater. Sci.* **1983**, *18*, 278-288.

(70) Hoon, S.R.; Shelton, A.; Tanner, B.K. Time-dependent resistivity in carbon fibre sheets. *J. Mater. Sci.* **1985**, *20*, 3311-3319.

(71) Orbach, R. Spin-lattice relaxation in rare-earth salts. *Proc. Roy. Soc. A.* **1961**, *264*, 458-484.

(72) Gütlich, P.; Bill, E.; Trautwein, A.X. Mössbauer Spectroscopy and Transition Metal Chemistry (Fundamentals and Applications). *Springer*, **2012**.
(73) Molinier, M.; Frommen, C.; Massa, W.; Pebler, J. Magnetism of alkalitetrafluoromanganates (III) AMnF$_4$ (A = K, Rb, Cs): Neutron diffraction, Mössbauer and magnetization investigations. *Z. Naturforsch.* 1993, *48a*, 1054-1072.

(74) Bean, C.P.; Rodbell, D.S. Magnetic disorder as a first-order phase transformation. *Phys. Rev.* 1962, *126*, 104-115.

(75) Joshi, J.P.; Bhat, S.V. On the analysis of broad Dysonian electron paramagnetic resonance spectra. *J. Magn. Res.* 2004, *168*, 284-287.

(76) Kurkjian, C.R.; Sigety, E.A. Coordination of Fe$^{3+}$ in Glass, *Phys. Chem. Glasses*, 1968, 9, 73.

(77) Loveridge D.; Parke, S. Electron spin resonance of Fe$^{3+}$, Mn$^{2+}$ and Cr$^{3+}$ in glasses. *Phys. Chem. Glasses*, 1971, 12, 19-27.

(78) Kawasaki, K. Anomalous Spin Relaxation near the Magnetic Transition. *Prog. Theor. Phys.*, 1968, *39*(2), 285 – 311.

(79) Kawasaki, K. Ultrasonic attenuation and ESR linewidth near magnetic critical points. *Phys. Lett.A*, 1968, *26A*(11), 543.

(80) Causa, M.T.; Tovar, M.; Obradors, X.; Labarta, A.; Tejada, J. Electron-spin resonance in the spin-glass-like system Fe$_{1-x}$Ga$_x$SbO$_4$. *Phys. Rev. B* 1991, *44*, 4455-4460.

(81) Likodimos, V.; Guskos, N.; Glenis, S.; Szymczak, R.; Bezkovnyi, A.; Wabia, M.; Typek, J.; Gasiorek, G.; Kurzawa, M.; Rychlowska-Himmel, I.; Blonska-Tabero, A. Magnetic properties of the antiferromagnetic site-disordered vanadate Zn$_2$FeV$_3$O$_{11}$. *Eur. Phys. J. B* 2004, *38*, 13-18.

(82) Guskos, N.; Likodimos, V.; Glenis, S.; Zolnierkiewicz, G.; Typec, J.; Szymczak, R.; Blonska-Tabero, A. Magnetic frustration in the site ordered Mg$_3$Fe$_6$(VO$_4$)$_6$ vanadate. *J. Appl. Phys.* 2007, *101*, 103922.

(83) Oseroff, S.B. Magnetic susceptibility and EPR measurements in concentrated spin-glasses: Cd$_{1-x}$Mn$_x$Te and Cd$_{1-x}$Mn$_x$Se. *Phys. Rev. B.* 1982, *25*, 6584.
(84) Viticoli, S.; Fiorani, D.; Nogués M.; Dormann, J.L. Magnetic resonance of the insulating spin-glass spinel solid solution CdCr$_{2x}$In$_{2-2x}$S$_4$ $(0.25 \leq x \leq 0.85)$. Phys. Rev. B. **1982**, 26, 6085.

(85) Zvereva, E.A; Savelieva, O.A.; Primenko, A.E.; Ibragimov, S.A.; Slyn’ko, E.I.; Slyn’ko, V.E. Anomalies in electron spin resonance spectra of Ge$_{1-x}$Mn$_x$Te diluted magnetic semiconductors. *J. Appl. Phys.* **2010**, *108*, 093923.

(86) Whangbo, M.-H.; Koo, H.-J.; Dai, D. Spin exchange interactions and magnetic structures of extended magnetic solids with localized spins: theoretical descriptions on formal, quantitative and qualitative levels. *J. Solid State Chem.* **2003**, *176*, 417-481.

(87) Xiang, H. J.; Lee, C.; Koo, H.-J.; Gong X. G.; Whangbo, M.-H. Magnetic properties and energy-mapping analysis. *Dalton Trans.* **2013**, *42*, 823-853.

(88) Whangbo, M.-H.; Xiang, H.J. Magnetic Properties from the Perspectives of Electronic Hamiltonian: Spin Exchange Parameters, Spin Orientation and Spin-Half Misconception, in *Handbook in Solid State Chemistry, Volume 5: Theoretical Descriptions*, Dronskowski, R., Kikawa, S., Stein, A., eds., *Wiley*, pp 285-343, 2017.

(89) Kresse, G.; Hafner, J. *Ab initio* molecular dynamics for liquid metals. *Phys. Rev. B.* **1993**, *47*, 558-561.

(90) Kresse, G.; Furthmüller, J. Efficiency of *ab-initio* total energy calculations for metals and semiconductors using a plane-wave basis set. *Comput. Mater. Sci.* **1996**, *6*, 15-60.

(91) Kresse, G.; Furthmüller, J. Efficient iterative schemes for *ab initio* total-energy calculations using a plane-wave basis set. *Phys. Rev. B.* **1996**, *54*, 11169-11186.

(92) Perdew, J.P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865-3868.

(93) Dudarev, S.L.; Botton, G.A.; Savrasov, S.Y.; Humphreys, C.J.; Sutton, A.P. Electron-energy-loss spectra and the structural stability of nickel oxide: An LSDA+U study. *Phys. Rev. B.* **1998**, *57*, 1505-1509.

(94) Streltsov, S.V.; Pchelkina, Z.V.; Igoshev, P.A.; Gapontsev, V.V. www.jass-code.org.
(95) Bauer, B.; Carr, L.D.; Evertz, H.G.; Feiguin, A.; Freire, J.; Fuchs, S.; Gamper, L.; Gukelberger, J.; Gull, E.; Guertler, S.; Hehn, A.; Igarashi, R.; Isakov, S.V.; Koop, D.; Ma, P.N.; Mates, P.; Matsuo, H.; Parcollet, O.; Pawłowski, G.; Picon, J.D.; Pollet, L.; Santos, E.; Scarola, V.W.; Schollwöck, U.; Silva, C.; Surer, B.; Todo, S.; Trebst, S.; Troyer, M.; Wall, M.L.; Werner, P.; Wessel, S. The ALPS project release 2.0: open source software for strongly correlated systems. *J. Stat. Mech. Theory Exp.* **2011**, P05001.

(96) Carlin, R.L. Magnetochemistry. *Springer-Verlag*, 1986.

(97) Smith, T.; Friedberg, S.A. Linear Chain Antiferromagnetism in CsMnCl₃·2H₂O. *Phys. Rev.* **1968**, *176*, 660-665.