

High-Pressure Synthesis, Crystal Structure, and Physical Properties of a Spinel Compound $\text{Co}_{0.7}\text{Al}_2\text{S}_4$

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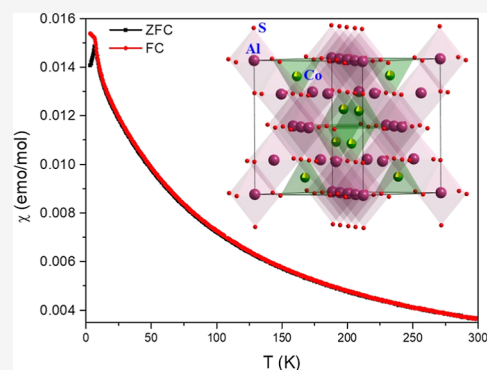


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Supporting Information

ABSTRACT: In this paper, we report on the discovery of a spinel compound, $\text{Co}_{0.7}\text{Al}_2\text{S}_4$, which was synthesized at high-pressure. The systematic characterizations were carried out by structural, magnetic, and heat capacity measurements. The compound crystallizes into a cubic structure with the space group $Fd\bar{3}m$ (no. 227) and the lattice constant $a = 9.9580(1)$ Å. Magnetic susceptibility measurements suggest that $\text{Co}_{0.7}\text{Al}_2\text{S}_4$ exhibits a spin glass ground state, freezing at $T_f \sim 7.2$ K with a Weiss temperature $T_\theta \sim -115.9$ K, which is verified by ac magnetic susceptibility and heat capacity measurements. The frustration parameter f for $\text{Co}_{0.7}\text{Al}_2\text{S}_4$ is calculated to be about 16.6, based on the formula $f = |T_\theta/T_f|$, indicating that $\text{Co}_{0.7}\text{Al}_2\text{S}_4$ is a high-frustration magnet. Specific heat data displays a T^2 dependence below the freezing temperature, which is different from the linear dependence observed in a common spin glass system. Compared with the similar compound CoAl_2O_4 , it is suggested that the vacancies in the Co sites should be responsible for the occurrence of the spin glass behavior of $\text{Co}_{0.7}\text{Al}_2\text{S}_4$.



1. INTRODUCTION

The AB_2X_4 system (A = divalent cation, B = trivalent cation, and X = chalcogens) has attracted much attention because it gives rise to abundant materials, which crystallizes into various crystal structures, such as cubic and hexagonal structure, and displays plentiful and exotic physical properties.^{1–3} One of the most widely studied structures among the AB_2X_4 system is the spinel structure because of its unique structure and novel properties.^{4–6} In terms of crystal structure, which is shown in Figure 1a, spinel compounds undergo a cubic structure with a space group of $Fd\bar{3}m$ (no. 227). The B-site cations, coordinated by six chalcogens, form a pyrochlore lattice, which is known to result in very strongly geometrical frustration (see Figure 1b).³ In contrast, the A site cations are surrounded by four chalcogens to form an AX_4 tetrahedron. As shown in Figure 1c, the A sublattice undergoes a diamond-like structure, which does not exhibit geometrical frustration with only nearest neighbor exchange interaction J_1 . However, a substantial spin frustration arises because of the competition between next-nearest-neighbor exchange interaction J_2 and the nearest neighbor exchange interaction J_1 .⁷ Therefore, when the A-site position is occupied with magnetic atoms, rich and novel magnetic ground states occur, such as spin liquid and spin ice.^{8,9}

As typical A-site spinel compounds, where magnetic atoms occupy A-site cations but the B-site position is occupied by nonmagnetic atoms, the Al-based spinel oxides have been studied widely because of their unique magnetic ground

state.^{10–13} For example, Long-range antiferromagnetic order is formed at the Néel temperature $T_N \sim 40$ K in MnAl_2O_4 .⁶ FeAl_2O_4 exhibits a spin freezing transition with a memory effect, different from canonical spin-glass behavior;^{6,9} CoAl_2O_4 is reported to undergo a spin-liquid ground state or coexisting phases of spin liquid and spin glass,^{14,15} and CuAl_2O_4 also display a spin glass-like feature but a possible orbital liquid state.^{16,17} Owing to the smaller electronegativity of sulfur, the Al-based spinel sulfides possibly show various physical properties compared with the Al-based spinel oxides. However, it is reported that MAl_2S_4 (M = Mn, Fe, Co) do not crystallize into a spinel structure like MAl_2O_4 but into a layered trigonal structure when oxygen atoms are replaced by sulfur atoms, owing to the structural instability of sulfide lattice resulting from the strong polarizing capacity of Al^{3+} .²

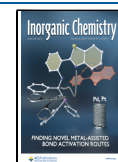
Very recently, a high pressure technique, which is able to shorten atomic distance and initiate chemical reactions forbidden at ambient pressure,¹⁸ is applied to attempt to grow the Al-based spinel sulfides.¹⁹ Fortunately, FeAl_2S_4 with a spinel structure is successfully prepared at high pressure. It is reported to be a spin-liquid candidate, but a cation inversion

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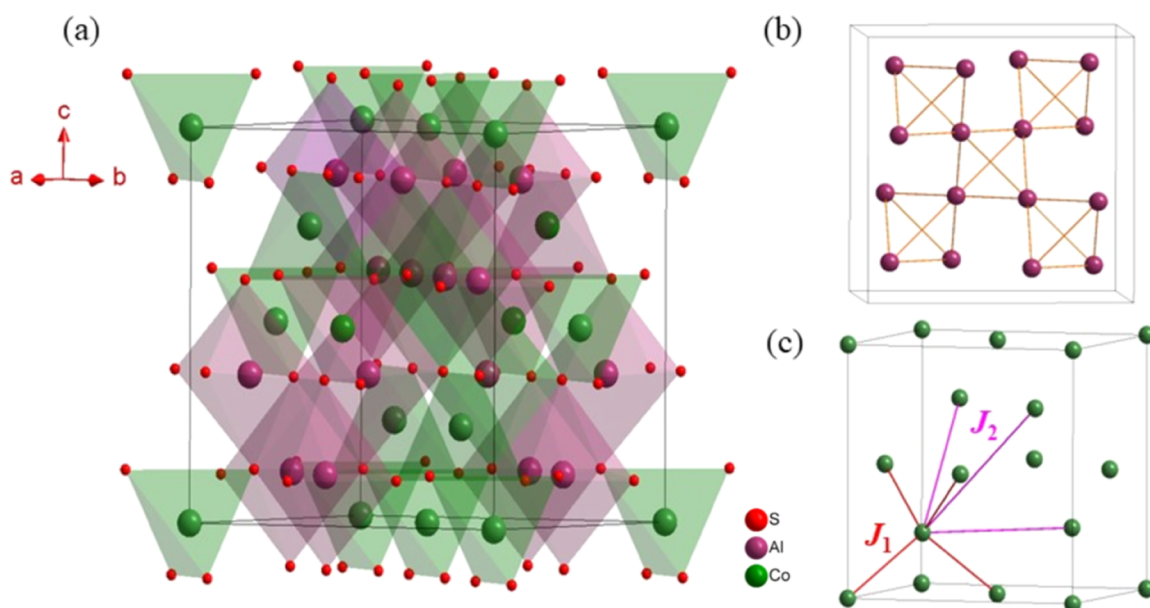


Figure 1. (a) Crystal structure of spinel compounds AB_2X_4 ; (b) B sublattice of the spinel structure, forming a pyrochlore lattice; (c) two exchange interactions J_1 and J_2 shown in the A sublattice, forming a diamond lattice.

results in a spin glass behavior, freezing at ~ 10.5 K, which inspires researchers to explore other more Al-based spinel sulfides.¹⁹ In this paper, we also set out to conduct an exploratory work at high pressure and report the synthesis, crystal structure, and physical properties on the Al-based spinel sulfide $Co_{0.7}Al_2S_4$.

2. EXPERIMENTAL SECTION

A new spinel compound $CoAl_2S_4$ was tried to be synthesized at high pressure like $FeAl_2S_4$ [19]. The starting materials Co (Alfa, 99.9%), Al (Alfa, 99.9%), and S (Alfa, 99.9%) were homogeneously mixed at the elementary ratio of stoichiometric $CoAl_2S_4$ and then pressed into a pellet. The pellet was put into a cubic-anvil-type high-pressure apparatus and then sintered at 5.5 GPa and 1300 °C for 30 min. Finally, the polycrystalline sample was obtained. The powder X-ray diffraction (PXRD) of the sample was measured and is plotted in Figure 2. The result

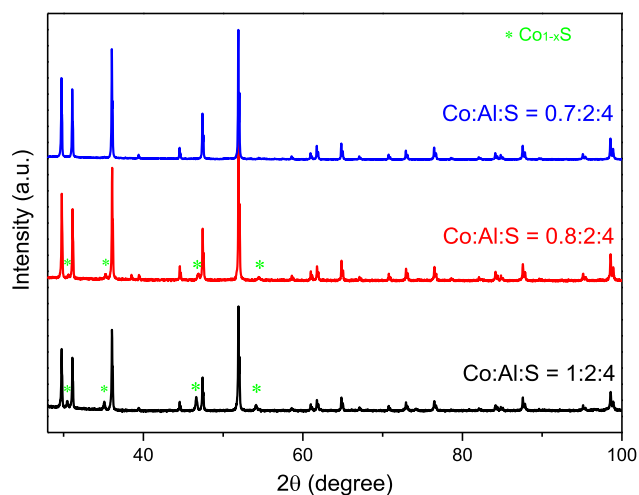


Figure 2. Room-temperature PXRD of compounds prepared at the different molar ratio of Co/Al/S. The impurities phase of $Co_{1-x}S$ is denoted by the green asterisks.

shows that the main diffraction peaks can be indexed using a cubic spinel structure like $FeAl_2S_4$,¹⁹ but an obvious impurity phase of $Co_{1-x}S$ is included,²⁰ which is denoted by the green asterisks also as shown in Figure 2. Then, we tried to decrease the content of Co and carried out the synthesis to prepare the pure compound, of which the details are the same as the above. The PXRDs of the products are also shown in Figure 2, which indicates that as the content of Co decreases, the impurity phase also decreases and even disappeared when the content of Co decreases to 0.7. Based on the above results, the occupation ratio in the Co sites of our sample is considered to be 0.7, and the molecular formula should be changed to $Co_{0.7}Al_2S_4$.

PXRD measurements were performed on a Rigaku Ultima VI (3 KW) diffractometer using Cu $K\alpha$ radiation ($\lambda = 1.54060$ Å) generated at 40 kV and 40 mA at room temperature. The Rietveld refinements on the PXRD were carried out by using GSAS software packages. The chemical composition of $Co_{0.7}Al_2S_4$ was measured by energy dispersive X-ray spectroscopy (EDX). Magnetic measurements were performed by using a superconducting quantum interference device (SQUID). Heat capacity and ac magnetic susceptibility measurements were carried out on a physical property system (PPMS).

3. RESULTS AND DISCUSSION

A polycrystalline sample of $Co_{0.7}Al_2S_4$ was successfully prepared at high pressure. The chemical composition of $Co_{0.7}Al_2S_4$ was determined by EDX, as shown in Figure S1. The average atomic ratio of Co/Al/S is obtained to be 0.71:2.02:3.94, which is very close to the stoichiometric ratio of $Co_{0.7}Al_2S_4$. Figure 3a shows the Rietveld refinement of PXRD for $Co_{0.7}Al_2S_4$, which was synthesized at an elementary stoichiometric ratio. The results show that $Co_{0.7}Al_2S_4$ crystallizes into a spinel structure and adopts the space group of $Fd\bar{3}m$ (no. 227) with the lattice constants of $a = b = c = 9.9580(1)$ Å. During the refinement, the occupation ratio of Co is constrained to be 0.7. The refinement smoothly converges to $\chi^2 = 4.74$, $R_p = 1.2\%$, and $R_{wp} = 2.1\%$.

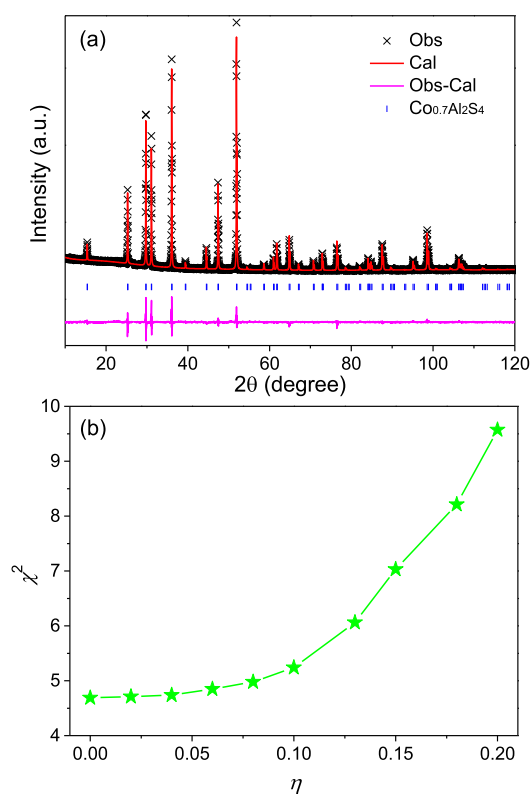


Figure 3. (a) Powder X-ray diffraction patterns with the refinements of $\text{Co}_{0.7}\text{Al}_2\text{S}_4$. (b) Site inversion parameter η dependence of Goodness-of-fit parameter χ^2 , which are obtained by single-phase Rietveld refinement of XRD of $\text{Co}_{0.7}\text{Al}_2\text{S}_4$.

Furthermore, an A/B site inversion, where B (or A) atoms occupy the A (or B) site, is common in a spinel compound [3]. Hence, in order to confirm the percentage of cation inversion, refinement of the X-ray diffraction data was performed, supposing the stoichiometric formula $(\text{Co}_{0.7-\eta}\text{Al}_\eta)(\text{Al}_{2-\eta}\text{Co}_\eta)\text{S}_4$, where η is the inversion parameter. The details are described in ref 19.¹⁹ The goodness-of-fit parameter χ^2 which was obtained by Rietveld refinements of the PXRD, as a function of inversion parameter η is displayed in Figure 3b. The result shows that as the inversion parameter η increases, the value of χ^2 also gradually increases, and the value of χ^2 increases to 9.5 with the inversion parameter $\eta \sim 0.2$, which indicates that no inversion occurs in $\text{Co}_{0.7}\text{Al}_2\text{S}_4$, different from the similar compound FeAl_2S_4 with an inversion parameter $\eta \sim 0.22$.¹⁹ The crystallographic data of $\text{Co}_{0.7}\text{Al}_2\text{S}_4$ without site inversion are obtained and summarized in Table 1. Furthermore, the refined value u of the sulfur position 32e (u, u, u) is obtained to be 0.2424(2) for $\text{Co}_{0.7}\text{Al}_2\text{S}_4$, deviating from the ideal spinel value with $u = 0.25$, which is common in AB_2X_4 spinels.³

The compound CoAl_2S_4 (AP) synthesized at ambient pressure possesses a layered trigonal structure and adopts the

space group $P\bar{3}m1$,² while $\text{Co}_{0.7}\text{Al}_2\text{S}_4$ prepared at high pressure crystallizes into a cubic structure with the space group of $Fd\bar{3}m$, though the vacancies occur in the Co sites. A structure field map has been proposed by Haeuseler using mean values of pseudopotential radii for AB_2S_4 compounds with different structures to clarify the structure difference in AB_2S_4 systems, which successfully predicts some new compounds and explains the absence of others.²¹ Several compounds have been added into the map followed by Haeuseler (see the Figure 3 of ref 19).¹⁹ It is seen that the AB_2S_4 compound would crystallize into a spinel structure, when the value of \bar{R}_σ , which is defined in ref 19, exceeds a critical value ~ 0.91 . Indeed, the orbital radii of anions should be easier to compress under high pressure and then could result in a larger \bar{R}_σ , which provides a possibility to synthesize more new spinel compounds. Recently, spinel FeAl_2S_4 has been synthesized at 5.5 GPa and exhibits a cation inversion but no vacancies like CoAl_2O_4 , which is reported that the inversion parameter increases as the synthetic temperature increases.²² When the spinel compound CoAl_2S_4 is attempted to be prepared at 5.5 GPa like FeAl_2S_4 , the spinel compound $\text{Co}_{0.7}\text{Al}_2\text{S}_4$ with some vacancies in the Co sites was successfully prepared. As shown in Figure 3 of ref 19, the value of \bar{R}_σ of CoAl_2S_4 is about 0.69, which is smaller than that of FeAl_2S_4 (~ 0.73), indicating that it needs higher pressure to compress atoms and thus prepare the spinel compound CoAl_2S_4 .¹⁹ It seems that the cation inversion is dependent on the temperature, while the vacancy is determined by the pressure. Hence, it is speculated that the pressure, which is applied to prepare the CoAl_2S_4 , is not large enough, and then cause the formation of the vacancies in the Co sites, and the spinel compound CoAl_2S_4 without any vacancies could be prepared under higher pressure.

To investigate the magnetic behavior, the temperature dependence of magnetic susceptibility for $\text{Co}_{0.7}\text{Al}_2\text{S}_4$ was measured at a low field of 100 Oe in both zero-field-cooled (ZFC) and field-cooled (FC) modes, as shown in Figure 4a. It is shown that the ZFC and FC curves are overlapped in the high temperature region, but begin to diverge when the temperature cools to $T_f \sim 7.2$ K. The ZFC curve displays a peak at T_f while the FC curve increases continuously but at a lower rate, displaying a λ -shape, which indicates that $\text{Co}_{0.7}\text{Al}_2\text{S}_4$ probably exhibits a spin glass behavior with the freezing temperature $T_f \sim 7.2$ K. Furthermore, Figure 4a also displays the inverse susceptibility $1/\chi$ versus temperature. It is obvious that the $1/\chi$ curve displays a straight line in the high-temperature range of 175–300 K, which indicates that the magnetic susceptibility of $\text{Co}_{0.7}\text{Al}_2\text{S}_4$ can be described by the Curie-Weiss law $1/\chi = (T - T_\theta)/C$, where T_θ is the Weiss temperature and C is the Curie constant. After linearly fitting the magnetic susceptibility between 175 and 300 K, the values of T_θ and C are obtained to be -115.9 K and 1.50 emu K/mol, respectively. The negative sign of T_θ suggests that the dominant interaction in $\text{Co}_{0.7}\text{Al}_2\text{S}_4$ is antiferromagnetic. According to the formula $\mu_{\text{eff}} = \sqrt{8C} \mu_B$, the effective moment

Table 1. Crystallographic Parameters for $\text{Co}_{0.7}\text{Al}_2\text{S}_4$ ^a

site	Wyck	x	y	z	Occ	$U_{\text{iso}}(\text{\AA}^2)$
Co	8a	0.375	0.375	0.375	0.7	0.0136(1)
Al	8a	0	0	0	1	0.0196(0)
S	32e	0.2424(2)	0.2424(2)	0.2424(2)	1	0.0235(2)

^aSpace group $Fd\bar{3}m$ (no. 227), $a = 9.9580(1)$ \AA, $Z = 8$. $V = 987.45(2)$ \AA³, $\chi^2 = 4.74$, $R_p = 1.2\%$, $R_{\text{wp}} = 2.1\%$.

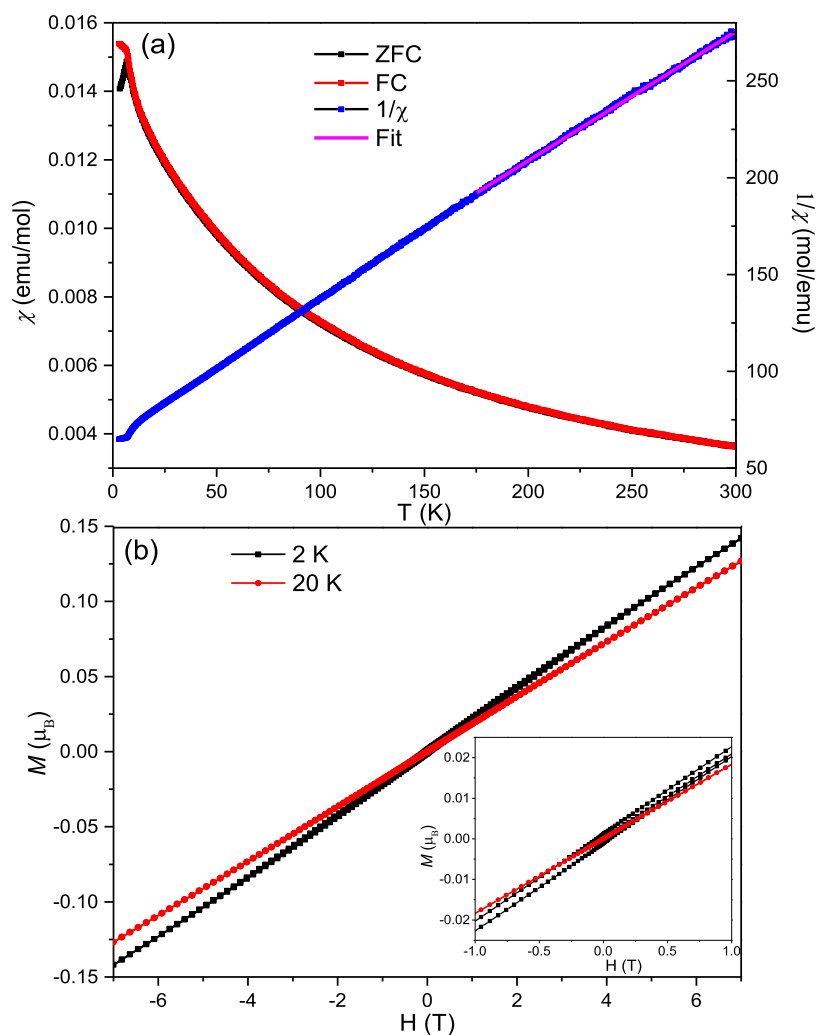


Figure 4. (a) Temperature dependence of magnetic susceptibility of $\text{Co}_{0.7}\text{Al}_2\text{S}_4$ and the reverse susceptibility versus temperature. The magenta line is the fit between 175 and 300 K using the Curie–Weiss law. (b) Magnetization as a function of field measured at 2 K. The inset shows the low magnetic field part.

μ_{eff} can be calculated to be $4.95 \mu_B/\text{Co}$, which is larger than the theoretically spin-only value of $3.87 \mu_B$ for Co^{2+} . However, it is a typical phenomenon for Co^{2+} because of the large g factor, which is considered to result from the strong spin–orbital coupling and the large anisotropy.^{23,24} The g factor is calculated to be 2.5 using the formula $\mu_{\text{eff}}^2 = g^2 S(S + 1)$, which lies in the range of 2.2–2.6 for a typical Co^{2+} system.^{23,24} In addition, we can see that the Weiss temperature $T_\theta \sim -115.9$ K and freezing temperature $T_f \sim 7.2$ K of $\text{Co}_{0.7}\text{Al}_2\text{S}_4$ both are slightly larger than those of the spinel compound CoAl_2O_4 ($T_\theta \sim -104$ K and $T_f \sim 4.8$ K).⁶ In general, the Weiss temperature is closely related to the spin coupling strength. Moreover, it seems that the freezing temperature also depends on the spin exchange interaction, for example, in the sequence of CoAl_2O_4 , FeAl_2O_4 , and MnAl_2O_4 , the spin coupling strength increases due to the increase of spin values. As a result, the Weiss temperature and ordering temperature (freezing temperature T_f or T_N) increases.⁶ In general, the spin coupling strength relies on orbital overlap, which is related to the covalent component. When O atoms in CoAl_2O_4 are substituted by S atoms, the covalent component of the bands between Co (Al) and S increases and thus leads to a larger spin exchange interaction,

although there are some vacancies in $\text{Co}_{0.7}\text{Al}_2\text{S}_4$, which results in the slight increase in the Weiss temperature T_θ and freezing temperature T_f in contrast to those of CoAl_2O_4 .

Furthermore, compared with the freezing temperature $T_f \sim 7.2$ K, the Weiss temperature $T_\theta \sim -115.9$ K of $\text{Co}_{0.7}\text{Al}_2\text{S}_4$ is extremely large, resulting in a large frustration parameter $f \sim 16.6$, which can be calculated by the equation $f = |T_\theta/T_f|$. Generally, it can be considered as a highly frustrated magnet, when its frustration parameter f is larger than 5–10.^{25,26} Hence, the large frustration parameter $f \sim 16.6$ of $\text{Co}_{0.7}\text{Al}_2\text{S}_4$ indicates that strong frustration occurs in $\text{Co}_{0.7}\text{Al}_2\text{S}_4$. The isothermal magnetization measurements on $\text{Co}_{0.7}\text{Al}_2\text{S}_4$ were carried out at 2 and 20 K, and the obtained curves are plotted in Figure 4b. The magnetization dependence of magnetic field at 20 K is linear, while the isothermal magnetization curve at 2 K exhibits little magnetic hysteresis with a small coercive force but nonsaturated magnetization behavior, shown in the inset of Figure 4b, which is also common in a spin glass system.^{19,27}

To confirm the spin-glass behavior of $\text{Co}_{0.7}\text{Al}_2\text{S}_4$, we performed the ac magnetic susceptibility measurements at four frequencies, ranging from 133 to 6333 Hz. Figure 5a shows the temperature dependence of the real part of the ac susceptibility χ' . All the ac susceptibility χ' curves exhibit a

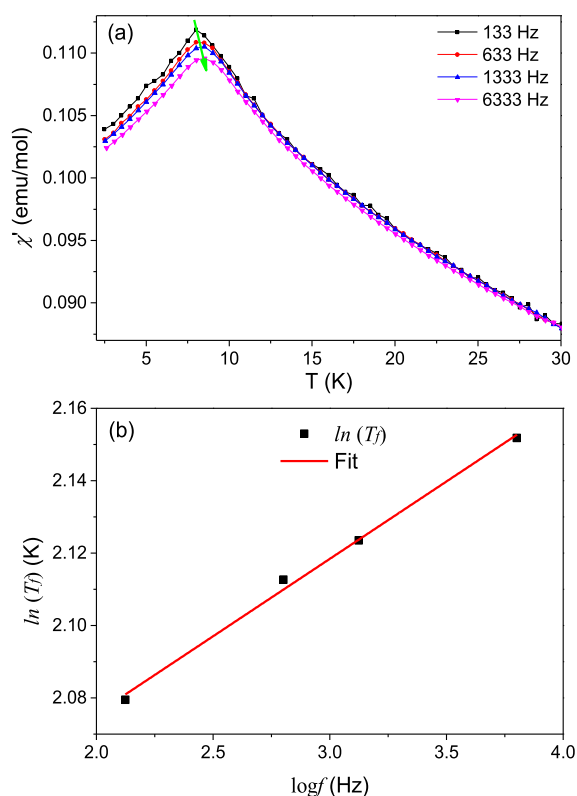


Figure 5. (a) Real part of ac magnetic susceptibility (χ') measured at four frequencies. (b) $\ln T_f$ versus $\log f$ for $\text{Co}_{0.7}\text{Al}_2\text{S}_4$.

peak at 8.0–8.6 K, which is close to the freezing temperature T_f . It is observed that as the frequency increases, the maximum value of ac susceptibility decreases, but the temperature at the peak increases, which suggests that the freezing temperature T_f is sensitive to the frequency, confirming the spin glass ground state of $\text{Co}_{0.7}\text{Al}_2\text{S}_4$. In order to characterize the spin glass, the parameter $K = \Delta T_f / (T_f \Delta \log f)$ is applied to describe the response of susceptibility in the frequency. Figure 5b exhibits the $\ln T_f$ versus $\log f$, which gives rise to the value of the parameter K to be 4.3×10^{-2} , lying in the range of $5 \times 10^{-3} - 8 \times 10^{-2}$ for a typical spin glass system.²⁴

The specific heat $C(T)$ curve as a function of temperature for $\text{Co}_{0.7}\text{Al}_2\text{S}_4$ measured in the range of 2–50 K is shown in Figure 6. Obviously, there is a weak shoulder at the temperature slightly larger than the magnetic ordering temperature T_b , indicating spin-glass freezing. Furthermore, the inset of Figure 6 shows the $C(T)/T$ vs T curve, where the anomaly is more obvious, affirming a magnetic phase transition. It is worth noting that the specific heat $C(T)$ exhibits a nonlinear temperature dependence but approaches 0 strictly following a T^2 dependence below the cusp observed above the freezing temperature, which is unlike that observed in canonical spin glass systems.²⁸ Furthermore, T^2 dependence has also been found in similar spinel compound, such as CoAl_2O_4 and CuAl_2O_4 ,^{6,17} and observed in other geometrically frustrated spin glass with a Kagome structure.²⁷ The observed T^2 dependence in $\text{Co}_{0.7}\text{Al}_2\text{S}_4$ remains an open question like CoAl_2O_4 , but it is speculated that it may originate from local strain because of residual spin–orbital coupling.⁶

In a A-site spinel system, where the magnetic ions occupying the A site form a diamond lattice, there occurs a competition between the nearest-neighbor (J_1) and next-nearest-neighbor

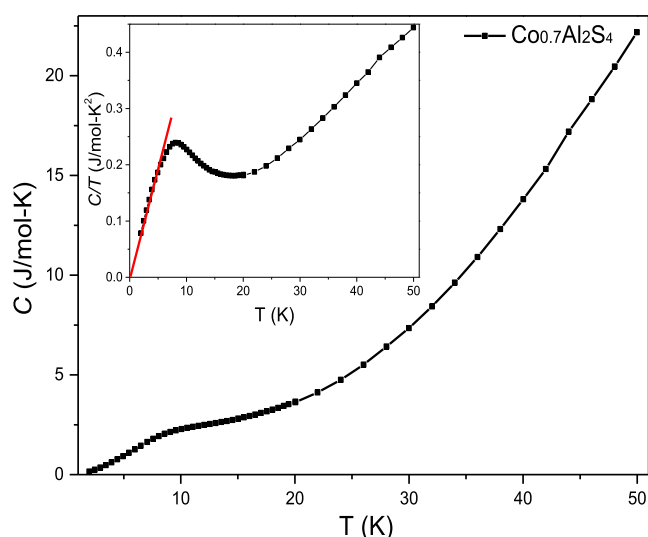


Figure 6. Specific heat of $\text{Co}_{0.7}\text{Al}_2\text{S}_4$ in the range of 2–50 K. The inset is the C/T vs T curve.

(J_2) exchange interaction, as shown in Figure 1c. The competition is argued to give rise to magnetic frustration and novel magnetic states with high degeneracy generated when $J_2/J_1 > 0.125$, such as a spin liquid.⁷ For the typical A-site spinel CoAl_2O_4 , it is reported to be a spin liquid state considering a minimal cation inversion parameter, while the ground state changes into a spin glass state at the low temperature when the cation inversion parameter exceeds 0.1, originating from cation inversion, which can introduce random exchange, lift the degeneracy in the spin liquid, and thus result in a spin glass state.^{22,29} The synthesized spinel $\text{Co}_{0.7}\text{Al}_2\text{S}_4$ displays a spin glass ground state with the Weiss temperature $T_\theta \sim -115.9$ K and freezing temperature $T_f \sim 7.2$ K. Based on mean field approximation, the mean-field exchange parameter J_{MF} of $\text{Co}_{0.7}\text{Al}_2\text{S}_4$ can be estimated to be 11.6 K based on the equation $T_\theta = 2zJS(S+1)/3$, where $z = 4$ is the tetrahedral coordination of the Co ion and $S = 3/2$ is the spin for Co^{2+} , which is close to that of CoAl_2O_4 ($J_{\text{MF}} \sim 10.4$ K).⁶ The theoretical phase diagram of the diamond lattice was carried out by Bergman et al. (see the Figure 3 of ref 7),⁷ employing unit vectors for the spin and scaled exchange constants $J_1 = J_{\text{MF}}S(S+1)$. Hence, we can obtain $J_1 = 43.5$ K and $T_f/J_1 = 0.161$ of $\text{Co}_{0.7}\text{Al}_2\text{S}_4$, and then according to the Figure 3 of ref 7, the ratio of the next-nearest-neighbor (J_2) and nearest-neighbor (J_1) exchange interaction J_2/J_1 can be calculated to be 0.137,⁷ which is slightly larger than the critical ratio of 0.125 and indicates that $\text{Co}_{0.7}\text{Al}_2\text{S}_4$ should display a spin-liquid behavior like CoAl_2O_4 . However, for CoAl_2O_4 , cation inversion hinders the appearance of the spin liquid and results in the spin glass state in CoAl_2O_4 . For $\text{Co}_{0.7}\text{Al}_2\text{S}_4$, there is no cation inversion, but the vacancies in the Co sites occur. In general, vacancies play an important role in the magnetic properties of frustrated magnets and could induce a spin-glass state.³⁰ Furthermore, in a system with randomly located magnetic moments, it is known that the magnetic transition temperature increases as the density of the moments increases. Hence, diluting the spins by the vacancies in $\text{Co}_{0.7}\text{Al}_2\text{S}_4$ not only lowers the spin glass transition temperature but also decreases the contribution to the magnetic susceptibility. Based on above results, we speculate that the vacancies in the

Co sites prevent the formation of the spin-liquid state but give rise to the spin glass behavior in $\text{Co}_{0.7}\text{Al}_2\text{S}_4$.

4. CONCLUSIONS

In conclusion, we have successfully synthesized the new spinel compound $\text{Co}_{0.7}\text{Al}_2\text{S}_4$ with large vacancies in the Co sites at high pressure. $\text{Co}_{0.7}\text{Al}_2\text{S}_4$ displays a spin glass ground state at freezing temperature $T_f \sim 7.2$ K with a large Weiss temperature $T_\theta \sim -115.9$ K, giving rise to a large frustration parameter $f \sim 16.6$, which suggests that strong frustration occurs in $\text{Co}_{0.7}\text{Al}_2\text{S}_4$. Furthermore, the ratio of the next-nearest-neighbor (J_2) and nearest-neighbor (J_1) exchange interaction of $\text{Co}_{0.7}\text{Al}_2\text{S}_4$ is estimated to be 0.137, slightly larger than the critical ratio of 0.125, which indicates that it should be a spin-liquid candidate. However, the vacancies in the Co sites result in the formation of the spin glass state of $\text{Co}_{0.7}\text{Al}_2\text{S}_4$.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.inorgchem.3c03529>.

Energy dispersive X-ray spectrum collected on CoAl_2S_4 polycrystalline samples (PDF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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