Spin and Orbital Frustration in $MnSc_2S_4$ and $FeSc_2S_4$

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Crystal structure, magnetic susceptibility, and specific heat were measured in the normal cubic spinel compounds $MnSc_2S_4$ and $FeSc_2S_4$. Down to the lowest temperatures, both compounds remain cubic and reveal strong magnetic frustration. Specifically the Fe compound is characterized by a Curie-Weiss (CW) temperature $\Theta_{CW} = -45$ K and does not show any indications of order down to 50 mK. In addition, the Jahn-Teller ion Fe^{2+} is orbitally frustrated. Hence, $FeSc_2S_4$ belongs to the rare class of spin-orbital liquids. $MnSc_2S_4$ is a spin liquid for temperatures $T > T_N \approx 2$ K.

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Frustration characterizes the inability of a system to satisfy all pairwise interactions and to establish unique long-range order. Instead, a highly degenerate ground state is formed. Frustration combined with site disorder is the key concept to describe spin glasses in diluted magnets [1]. But frustration can also govern pure compounds due to geometrical constraints only [2]. Geometrical frustration yields a variety of different ground states which depend on the nature of the exchange interaction, the magnetic anisotropy, and the magnitude of the spin. Spin-liquid (SL) [3] or spin-ice states [4,5], spin clusters or spin loops [6,7], as well as singlet formation [8] were experimentally observed or theoretically predicted.

Geometric frustration has been intensively investigated in the spin sector. However, frustration of the orbital degrees of freedom will be even more dominant: Orbital order is established via the Jahn-Teller (JT) effect [9] or via a purely electronic exchange mechanism, as proposed by Kugel and Khomskii [10]. The exchange mechanisms in orbitally degenerate systems are strongly frustrated and even in cubic lattices the orbitals may remain disordered down to $T = 0$ K forming an orbital liquid (OL) state [11–13]. An OL has been proposed for $LaTiO_3$ [14,15] and a spin-orbital liquid (SOL) for $LiNiO_2$ [16], but new experiments suggested an orbitally ordered state in $LaTiO_3$ [17,18] and questioned the SOL for $LiNiO_2$ [19]. Hence it remains a challenge to search for further realizations of a SL, OL, and SOL.

Here we present experimental results on $MnSc_2S_4$ and $FeSc_2S_4$ revealing strong spin-frustration effects. Additionally, the Fe ion is JT active and due to its geometrically frustrated network, $FeSc_2S_4$ is expected to be also orbitally frustrated. We thus have the interesting case to compare two similar systems: the Mn compound, characterized by a half-filled $3d$ shell and zero orbital moment, being a prime candidate for a pure SL, while the Fe compound is expected to bear the characteristics of a SOL.

It is well known that the B sites in the normal spinels AB_2X_4 form a pyrochlore lattice which is a paramount example for geometrically frustrated networks. Here we demonstrate that A-site spinels also reveal frustration, in the spin as well as in the orbital sector. The A-site ions in the normal spinel form a diamond lattice, i.e., two face centered cubic (fcc) lattices at (0, 0, 0) and (1/4, 1/4, 1/4). The magnetic superexchange interactions between the A ions are weakly antiferromagnetic and the corresponding exchange paths involve at least five ions [20]. Within one fcc sublattice, the 12 nearest neighbors (NN) are connected via two equivalent A-X-B-X-A exchange paths, including nearly rectangular X-B-X bonds of nonmagnetic ions. Considering the entire lattice, the exchange between the two A-site sublattices is transferred as follows: the four NN are connected via six A-X-B-X-A exchange paths again including nearly rectangular X-B-X bonds. Twelve third-next nearest neighbors (third-NNN) are coupled via one A-X-B-X-A exchange path, including a 180° X-B-X bond. Note that the NNN in the entire lattice corresponds to the NN within each sublattice. We conclude that each fcc sublattice is coupled antiferromagnetically and, hence, is frustrated. In addition, the two sublattices are coupled again antiferromagnetically, strongly enforcing the frustration effects.

The synthesis of $MnSc_2S_4$ and $FeSc_2S_4$ is described in Refs. [21–23]. The magnetic susceptibility for $4.2 < T < 300$ K was investigated by Pawlak and Duczmal [24] and the absence of long-range magnetic order in both compounds has been noted. A structural investigation [23] using single crystalline $MnSc_2S_4$ and polycrystalline $FeSc_2S_4$ confirmed the normal spinel structure (space group $Fd\bar{3}m$) with Mn(Fe) and Sc occupying only A and B sites, respectively. Already from earlier Mössbauer experiments on $FeSc_2S_4$ it had been concluded that the iron ions occupy the A sites only and that any long-range magnetic or JT ordering is absent [25]. The crystal field splits the d-electron manifold of the divalent cations A^{2+}

at the tetrahedral sites into an excited triplet (t_2) and a lower doublet (e). The Mn^{2+} ion reveals a half-filled d shell with a spin value $S = 5/2$ and zero orbital moment. The Fe^{2+} ion with $S = 2$ exhibits a hole in the lower doublet and, hence, is JT active.

Polycrystalline $\mathrm{MnSc_2S_4}$ and $\mathrm{FeSc_2S_4}$ were prepared by sintering stoichiometric mixtures of the pure elements in evacuated, sealed silica ampoules at 900 °C during 5 d. To reach good homogeneity the synthesis was repeated several times with subsequent regrinding, pressing, and firing. The powdered samples were investigated by standard x-ray techniques using CuK_α radiation. Representative room-temperature spectra are shown in Fig. 1. From a detailed Rietveld refinement (solid lines in Fig. 1) the lattice constant a and the fractional coordinate z of the sulfur atom were determined as $a = (10.621 \pm 0.007)$ Å, $z = 0.2574 \pm 0.0005$ for the Mn compound and $a = (10.519 \pm 0.007)$ Å, $z = 0.2546 \pm 0.0005$ for the Fe compound, respectively. The deviation of the sulfur parameter z from the ideal value 1/4 indicates a slight trigonal distortion of the octahedra around the B sites, while the tetrahedra remain undistorted. This slight trigonal distortion yields X-B-X bonds of 92.3° for the Fe compound and 93.6° for the Mn compound in good agreement with Ref. [23]. To search for structural phase transitions in the JT-active compound $\mathrm{FeSc_2S_4}$ we performed a diffraction analysis down to 100 K. We found no indications of a structural distortion (see the [333] Bragg reflection in the inset of Fig. 1, which remains resolution limited at all temperatures) and even the positions of the sulfur atoms within the unit cell remained constant within experimental uncertainties.

The susceptibility measurements were performed with a commercial SQUID magnetometer for temperatures $1.7 \le T \le 400$ K and in external fields up to 50 kOe. The specific-heat experiments were conducted in noncommercial setups using a quasiadiabatic method for $2.5 < T < 30$ K and an ac technique for $15 < T < 200$ K in a ^{4}He cryostat. Below 2.5 K we measured in a ^{3}He/^{4}He dilution refrigerator with a relaxational method.

Figure 2 shows the inverse susceptibilities of $\mathrm{MnSc_2S_4}$ (triangles up) and $\mathrm{FeSc_2S_4}$ (triangles down) for $1.7 \le T \le 400$ K. We observed perfect Curie-Weiss (CW) laws with CW temperatures $\Theta_{\mathrm{CW}} = (-45.1 \pm 1)$ K for the iron and $\Theta_{\mathrm{CW}} = (-22.9 \pm 0.8)$ K for the manganese compound, respectively. Paramagnetic moments of $\mu_{\mathrm{eff}} = (5.12 \pm 0.1)\mu_{\mathrm{B}}$ for $\mathrm{FeSc_2S_4}$ and $\mu_{\mathrm{eff}} = (5.77 \pm 0.12)\mu_{\mathrm{B}}$ for $\mathrm{MnSc_2S_4}$ were determined. Here we took the average of a series of measurements of different batches, where we used as grown samples and samples tempered in vacuum as well as in sulfur atmosphere. Despite these different treatments, we observed marginal changes of μ_{eff} and Θ_{CW} only, which are included in the error bars given above. For Fe^{2+} ($3d^6$, high spin), the experimentally determined value of μ_{eff} is higher than the spin-only value of $4.90\mu_{\mathrm{B}}$. This signals an enhancement due to spin-orbit coupling, resulting in an effective g value of 2.09, typically observed in iron compounds with Fe^{2+}.

A closer look at the susceptibilities $\chi(T)$ reveals slight deviations from a CW law below 4 K in the Fe compound, but the absence even of any spin-glass ordering is demonstrated by field cooled (FC) and zero-field cooled (ZFC) cycles of $\chi(T)$ at low fields (10 Oe) revealing no

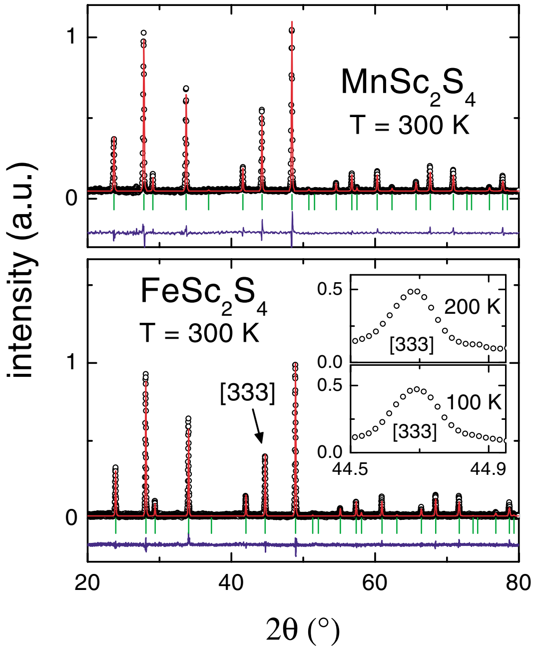

FIG. 1 (color online). Diffraction pattern of $\mathrm{MnSc_2S_4}$ (upper frame) and $\mathrm{FeSc_2S_4}$ (lower frame). The solid lines represent fits of a Rietveld analysis. The difference spectra shown below the data demonstrate the absence of any impurity phases. Inset: [333] reflection at 100 and 200 K, respectively.

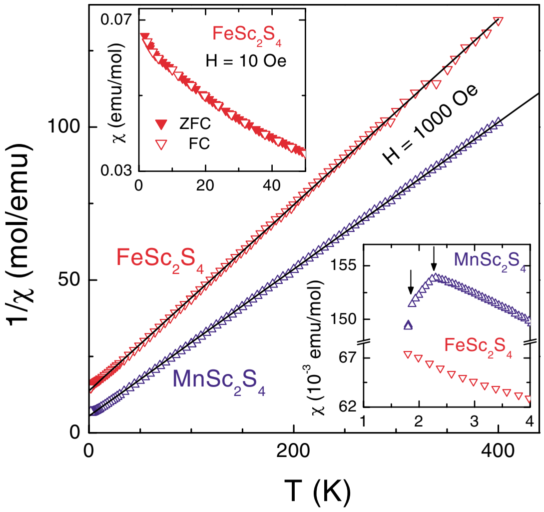

FIG. 2 (color online). Inverse susceptibility $1/\chi(T)$ of $\mathrm{MnSc_2S_4}$ (triangles up) and $\mathrm{FeSc_2S_4}$ (triangles down). The solid lines are linear fits with a Curie-Weiss law $\chi = C/(T - \Theta_{\mathrm{CW}})$. Upper inset: FC and ZFC susceptibility loop measured in $\mathrm{FeSc_2S_4}$ at 10 Oe. Lower inset: susceptibility $\chi(T)$ vs T at low temperatures.

significant splitting (see the upper inset of Fig. 2). In $MnSc_2S_4$ the clear onset of antiferromagnetic (AFM) order is demonstrated in the lower inset of Fig. 2. There, $\chi(T)$ exhibits a peak at the ordering temperature $T_{N1} = 2.1$ K and an additional downturn for $T < T_{N2} = 1.8$ K.

Figure 3 documents the molar heat capacity for temperatures $0.05 < T < 200$ K. As the results cover almost four decades in temperature, for representation purposes we plotted C/T vs T on logarithmic scales. The results are compared to nonmagnetic $CdIn_2S_4$ to get an estimate of the phonon contributions. Below 200 K, in the Fe and Cd compound no specific-heat anomalies can be detected, indicating the absence of structural ($CdIn_2S_4$) or structural/magnetic ($FeSc_2S_4$) phase transitions. Together with the diffraction pattern (lower frame of Fig. 1) it is clear that $FeSc_2S_4$ remains cubic (no JT distortion) and paramagnetic down to 50 mK. In all samples the lattice-derived specific heat dominates above 20 K. However, it is impressive to see how, in the geometrically frustrated systems, the heat capacity is enhanced towards low temperatures, having in mind that the characteristic magnetic temperatures are 23 and 45 K for the Mn and Fe compound, respectively. For $MnSc_2S_4$, a double peak close to 2 K in $C(T)/T$ indicates two subsequent magnetic phase transitions which also have been observed in $\chi(T)$ (cf. lower inset of Fig. 2). The magnetic order of $MnSc_2S_4$ most probably results from residual magnetic interaction only, as any coupling to the lattice in this spin-only system must be negligible. Below 0.4 K, nuclear contributions dominate and the increase in $C(T)/T$ can be accounted for by assuming a hyperfine term of ^{45}Sc in an internal field of 15 kOe due to the magnetic order of the manganese moments.

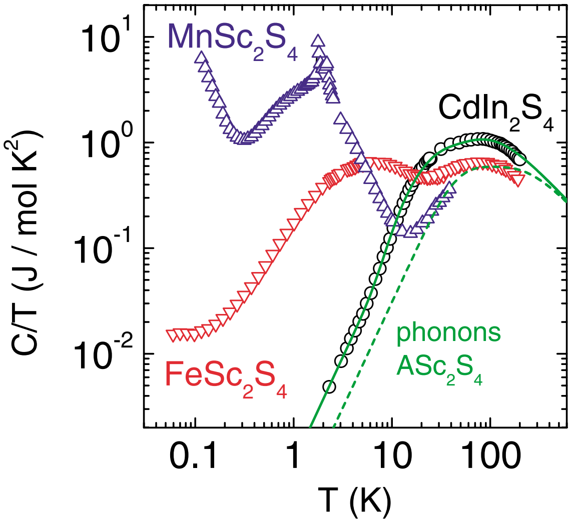

FIG. 3 (color online). Specific heat $C(T)/T$ for $MnSc_2S_4$ (triangles up), $FeSc_2S_4$ (triangles down), and $CdIn_2S_4$ (circles). The solid line represents the calculated specific heat of the nonmagnetic reference compound $CdIn_2S_4$. The dashed line gives the estimated phonon contribution for ASc_2S_4 (A = Mn, Fe).

$FeSc_2S_4$ reveals a broad peak close to 6 K which often is observed in geometrically frustrated magnets [2] indicating soft collective modes. On further decreasing temperatures, $C(T)/T$ decreases reaching a constant value below 0.2 K. The lack of any hyperfine contribution signals the absence of internal magnetic fields. The constant value of $C(T)/T$ below 0.2 K suggests a linear term in $C(T)$ which often is observed in spin glasses [1]. The increase of the heat capacity between $0.3 < T < 2$ K is close to $T^{2.5}$, a power-law behavior that also has been observed in $LiNiO_2$ another potential candidate for a SOL. As documented in Fig. 3, $FeSc_2S_4$ does not order down to 50 mK, despite the fact that Fe reveals a strong spin-spin interaction and is JT active. Hence, the ground state indeed has to be characterized as SOL. In this case the magnetic (spin) frustration parameter $f = -\Theta_{CW}/T_N$ is of the order of 1000 and one of the largest values reported so far [2]. In $MnSc_2S_4$, the magnetic ordering temperature of 2 K and the CW temperature of -23 K yields $f = 11.5$.

In order to get an estimate of the magnetic contribution to the specific heat we calculated the lattice specific heat of $CdIn_2S_4$ and scaled it to the two magnetic compounds under investigation. The phonon contribution of $CdIn_2S_4$ can well be parametrized (solid line in Fig. 3) using a Debye term and three Einstein contributions, with a Debye temperature of 154 K and Einstein temperatures of 90, 244, and 350 K. This assumption is corroborated by the fact that in $CdIn_2S_4$ the lowest IR-active mode is at 69 cm^{-1} (99 K), while the highest IR mode was detected at 304 cm^{-1} (438 K) [26]. In this simulation we fixed the number of internal degrees of freedom to 21, according to seven atoms in the unit cell. We also assumed a reasonable weight distribution between these modes. Keeping this weight distribution fixed, we tried to describe the phonon contribution of $MnSc_2S_4$ and $FeSc_2S_4$ which should be practically identical due to the similar masses of Mn and Fe. The dashed line in Fig. 3 was calculated using a Debye temperature of 190 K and Einstein temperatures of 190, 420, and 550 K. This seems to be reasonable taking into consideration the much lower masses of Fe/Mn and Sc as compared to Cd and In, respectively.

Using this phonon contribution we estimated the purely magnetic contributions C_m of the heat capacity. The results are shown in Fig. 4(a) as C_m/T vs T up to 60 K in a semilogarithmic representation. We see that above 30 K the magnetic contribution vanishes for $MnSc_2S_4$, while even at 60 K there are some finite contributions in C_m/T for $FeSc_2S_4$. Because of the experimental and model dependent uncertainties we confine the discussion to temperatures $T < 60$ K, where our results are significant.

From C_m/T we calculated the magnetic entropy S_m which is plotted in Fig. 4(b). We found that for $MnSc_2S_4$ only 30% of the expected entropy for a spin $S = 5/2$ system is recovered at T_N. The full entropy is reached at $T \approx -\Theta_{CW}$. For $FeSc_2S_4$ the entropy slowly increases with increasing temperature reaching $S_m = R\ln(5)$

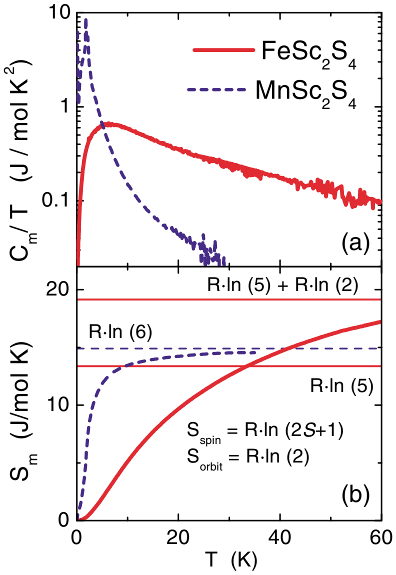

FIG. 4 (color online). (a) Magnetic contribution of the specific heat C_m/T vs T for MnSc$_2$S$_4$ and FeSc$_2$S$_4$. (b) Magnetic entropy of MnSc$_2$S$_4$ and FeSc$_2$S$_4$. The horizontal lines give the magnetic entropy S_m which is theoretically expected for the spin and orbital degrees of freedom (see text).

corresponding to a $S = 2$ system at $T \approx 30$ K. It further increases significantly towards $S_\mathrm{m} = R\ln(5) + R\ln(2)$, where the latter term characterizes the entropy of the orbital doublet of the JT-active e levels. From the entropy S_m in Fig. 4(b) we attribute MnSc$_2$S$_4$ to a SL for temperatures $2 < T < 23$ K, whereas in the case of FeSc$_2$S$_4$ an additional contribution to S_m comes from the frustrated orbital state. Therefore, FeSc$_2$S$_4$ can be considered as a SOL for $T < 45$ K.

In conclusion, we investigated the thiospinel systems MnSc$_2$S$_4$ and FeSc$_2$S$_4$ and found strong frustration effects. MnSc$_2$S$_4$ is a spin-only system with $S = 5/2$, characterized by a spin-frustration parameter $f \approx 10$ showing AFM order at low temperatures and bearing the characteristics of a spin liquid between $T_\mathrm{N} \approx 2$ K and $-\Theta_\mathrm{CW} \approx 23$ K. FeSc$_2$S$_4$ ($S = 2$, JT active) reveals frustration both in the spin and in the orbital sector. The spin-frustration parameter $f > 900$ is one of the largest ever observed. The orbital frustration is evidenced by the entropy which significantly exceeds the spin value of $R\ln(5)$. FeSc$_2$S$_4$ has to be characterized as a spin-orbital liquid below 45 K. In this case, any kind of spin order, including canonical spin-glass behavior, can be excluded on the basis of the temperature dependence of the FC and ZFC susceptibilities and heat capacity.

The question remains why these two similar systems behave so differently: This problem can be tackled only by taking into account the orbital degrees of freedom coupled to the spins. MnSc$_2$S$_4$ is a spin-only system with no orbital degrees of freedom, supported by preliminary ESR experiments yielding no indication of any anisotropy in the resonance absorption. At some finite temperature some residual exchange interactions (e.g., NNN interactions or magnetic dipolar interactions) establish long-range magnetic order. FeSc$_2$S$_4$ exhibits orbital degeneracy and our results demonstrate indeed [11] that orbital degeneracy does drastically increase quantum fluctuations and thereby suppresses long-range magnetic order.

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