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Spin and orbital frustration in $FeSc_2S_4$ probed by ^{45}Sc NMR

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We report on ^{45}Sc NMR experiments in the geometrically frustrated spinels $FeSc_2S_4$ and $MnSc_2S_4$. The temperature dependences of line shift $K(T)$, linewidth $\Delta(T)$, spin-spin relaxation rate $1/T_2(T)$, and spin-lattice relaxation rate $1/T_1(T)$ are deduced. The manganese compound reveals the behavior of a long-range ordered antiferromagnet, but with the onset of critical spin fluctuations at unusually high temperatures of 40 T_N. $K(T)$ of $FeSc_2S_4$ exhibits a cusplike maximum, a hallmark of spin frustration. Orbital fluctuations strongly enhance $1/T_1(T)$ at elevated temperatures. Toward lowest temperatures these fluctuations slow down resulting in an increase of $1/T_2(T)$. The exponential decrease of $1/T_1(T)$ results from the opening of a spin gap $\Delta = 0.2$ meV, a characteristic feature of a spin liquid.

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Spin liquids and orbital liquids evolve in magnetic systems characterized by strongly frustrated exchange interactions. In structurally ideal and stoichiometric compounds, these exotic ground states stem from geometrical frustration (GF), which is well studied for the spin degree of freedom.[1] But GF also can govern the orbital sector. In this case, the orbitals of structurally perfect compounds, which are expected to undergo a Jahn-Teller (JT) (Ref. 2) or Kugel-Khomskii[3] derived orbital-ordering phase transition, remain disordered down to the lowest temperatures. Along these lines, Feiner *et al.*[4] proposed a spin-orbital liquid to occur in $LiNiO_2$.

Recently, measurements of specific heat and magnetization in $FeSc_2S_4$ and $MnSc_2S_4$ (Ref. 5) demonstrated that the tetrahedrally coordinated A-site cation of the spinel structure is strongly frustrated. Both compounds have the normal cubic spinel structure with the ions carrying the internal degrees of freedom residing solely on the A site. The iron compound reveals spin and orbital degrees of freedom, whereas the manganese spinel is a spin-only system. Both manifest strong GF of the spin degree of freedom, with $FeSc_2S_4$ showing one of the largest frustration parameters ever observed.[5] Additionally, experimental evidence for a glassy freezing of the orbital moments has been provided.[6] The freezing of an orbital liquid into an orbital glass has unambiguously been demonstrated for $FeCr_2S_4$.[7]

In this paper, we study the spin and orbital frustration in $FeSc_2S_4$ utilizing nuclear magnetic resonance (NMR). Due to hyperfine interactions of the resonant nuclei with the spin degree of freedom, the line shift K probes the local susceptibility of the magnetic moments. In addition, the resonant nuclei possessing an electric quadrupole moment are sensitive to the surrounding charge distribution[8] which either results from the ligand field of ionic charges or from the shape of electron orbitals.[9] In both cases, the interaction of the nuclear quadrupole moment with the electrical field gradient (EFG) of the charge distribution can yield a broadening or splitting of the NMR spectra into a central line and satellites.

Polycrystalline $FeSc_2S_4$ ($Fd\bar{3}m$, lattice constant $a = 10.519$ Å, fractional coordinate $z=0.255$) and $MnSc_2S_4$ ($Fd\bar{3}m$, $a=10.621$ Å, $z=0.257$) were from the same batches studied previously.[5] The $3d$ manifold of the tetrahedrally coordinated A-site cation exhibits a lower doublet and an excited triplet. Mn^{2+} reveals a half-filled d shell with spin $S = \frac{5}{2}$ and a zero orbital moment. Fe^{2+} ($S=2$) has a hole in the lower doublet and, hence, is JT active. Therefore, long-range orbital order is expected at low temperatures which, however, could not be detected down to 50 mK.[5] The paramagnetic susceptibilities follow a Curie-Weiss (CW) law with CW temperatures $\Theta_{CW}=-22.9$ K for the Mn and $\Theta_{CW}=-45.1$ K for the Fe compound, respectively.[5] For the NMR experiment the samples were powdered and immersed into paraffin. The ^{45}Sc nuclei ($I=7/2$, $\gamma/2\pi=10.343$ MHz/T, $Q=-0.22$ barn) were probed by a spin-echo technique. As the ^{45}Sc nuclei carry an electric quadrupole moment Q, an interaction with an EFG at the B site is expected. The measurements were carried out with a phase coherent spectrometer using the field-sweep method at the constant irradiation frequencies of $\omega_0/2\pi=10$, 35, and 90 MHz, corresponding to an applied magnetic field of ≈9.5, 33, and 85 kOe, respectively. The bulk susceptibility $\chi(T)$ was measured for $1.7 < T < 400$ K (for details see Refs. 5 and 6).

Figure 1 shows the field-swept spectra of the ^{45}Sc nuclei residing on the octahedral B site of $FeSc_2S_4$ and $MnSc_2S_4$ at 90 MHz. The spectra were recorded using a pulse sequence with long pulses (100 μs − τ_D − 200 μs, pulse separation time $\tau_D=180$ μs), in order to get a narrow irradiation width which is necessary to resolve quadrupole satellites. But neither the manganese nor the iron compound exhibits a splitting into satellites. The powder patterns exhibit almost Gaussian lines which strongly broaden and shift to lower fields with decreasing temperature. Both compounds reveal slight deviations from a perfect packing ($z=0.25$) and, hence, the Sc site has local trigonal symmetry. This effect explains the slight asymmetry observed in the Mn compound and has been studied in more detail in Ref. 10. Lowering the temperature, the intensity of the spectral line of $FeSc_2S_4$ strongly decreases, as was checked by measurements in a $^3He/^4He$ dilution refrigerator. This wipeout of intensity is due to fast nuclear relaxation when the electronic spin dynamics slows down.

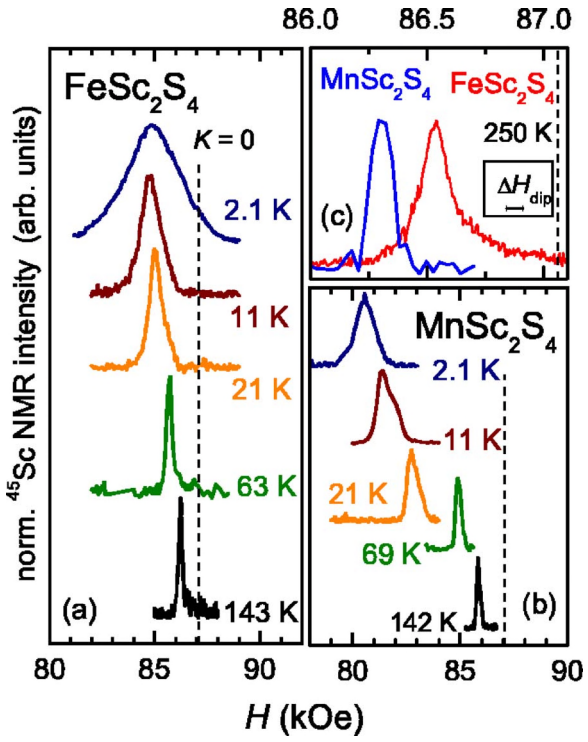

FIG. 1. (Color online) ^{45}Sc-NMR spectra of $FeSc_2S_4$ (a) and $MnSc_2S_4$ (b) at 90 MHz for different temperatures. The dashed lines mark $K=0$ as determined from $ScCl_3$. (c) Spectra of $MnSc_2S_4$ and $FeSc_2S_4$ at $T=250$ K. The bar denotes the linewidth contribution ΔH_{dip} due to a nuclear dipole-dipole interaction.

The inhomogeneous slowing down of spin fluctuations is a common phenomenon of disordered and frustrated systems and has been observed in spin glasses,[11], in high-T_c cuprates,[12] and in frustrated magnets.[13] For temperatures $T<1$ K, we observed a second signal with a paramagnetic line shift $K(T)$. From the ratio of the Curie constants of the majority signal and the second signal we obtained that 1.3% of the nuclei contribute to the second signal.

The temperature dependences of the line shifts $K(T)$ of the spectral lines together with the bulk susceptibilities $\chi(T)$ for $FeSc_2S_4$ and $MnSc_2S_4$ are plotted in Fig. 2. At elevated temperatures, the local susceptibilities $K(T)$ of both compounds closely follow the temperature dependence of $\chi(T)$. From the inverse line shift $1/K(T)$ (cf. inset of Fig. 2) we obtained CW temperatures in perfect agreement with Ref. 5. In $MnSc_2S_4$, the local susceptibility $K(T)$ and the bulk susceptibility $\chi(T)$ trace each other within the complete temperature range. The kink around $T_N \approx 2$ K marks the onset of long-range magnetic order.[5] In $FeSc_2S_4$, $K(T)$ significantly deviates from the CW law already at $T \lesssim 40$ K and becomes temperature independent at the lowest temperatures for all applied fields $H<85$ kOe. This behavior of $K(T)$ is a hallmark of strong spin frustration, as was identified in a number of frustrated spin systems.[13–15] The slightly enhanced values of $\chi(T)$ with respect to $K(T)$ at low temperatures are attributed to defect contributions affecting the bulk, but not the local susceptibility. However, competing with this view a further explanation could be given involving the orbital degree of freedom: the transferred hyperfine fields at the ^{45}Sc nuclei are governed by the spins of the Fe^{2+} ions which are coupled via exchange interactions. These exchange interactions strongly depend on the orbital orientations and it could well be that orbital fluctuations or orbital glassiness[6] give rise to effective changes of the hyperfine coupling and suppress the local susceptibility $K(T)$.

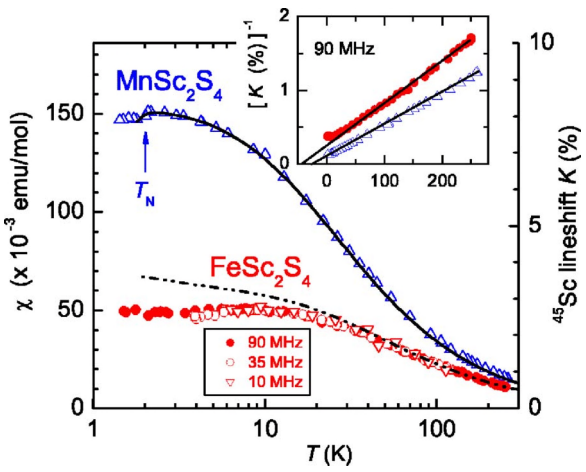

FIG. 2. (Color online) Bulk susceptibility $\chi(T)$ (dashed and solid lines, 1 kOe) and line shift $K(T)$ (symbols) of $FeSc_2S_4$ and $MnSc_2S_4$, respectively. $T_N \approx 2$ K of $MnSc_2S_4$ is marked by an arrow. Inset: inverse line shift $1/K(T)$; the lines indicate CW laws with $\Theta_{CW}=-45$ K ($FeSc_2S_4$) and -23 K ($MnSc_2S_4$).

Figure 3 shows the temperature dependences of the ^{45}Sc linewidth $\Delta H(T)$. For $MnSc_2S_4$, $\Delta H(T)$ nicely scales with the bulk susceptibility $\chi(T)$ indicating the usual magnetic broadening which is expected in powder samples due to field inhomogeneities.[16] Below $T_N \approx 2$ K, a drastic increase of $\Delta H(T)$ sets in. Recently, this discontinuous increase has been identified to be due to the superposition of two spectra of magnetically inequivalent Sc sites in the antiferromagneti-

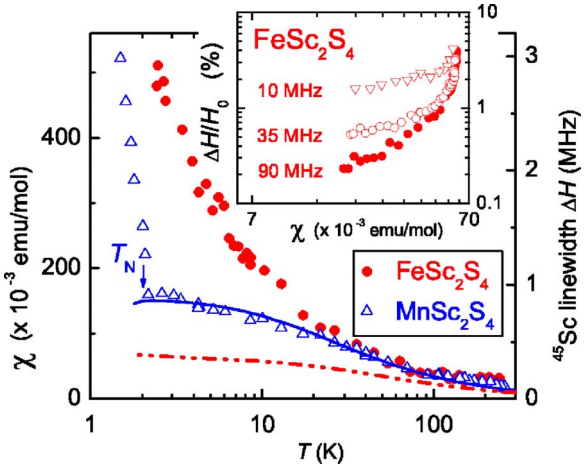

FIG. 3. (Color online) Bulk susceptibility $\chi(T)$ (dashed and solid lines, 1 kOe) and ^{45}Sc-NMR linewidth $\Delta H(T)$ (symbols) of $FeSc_2S_4$ and $MnSc_2S_4$, respectively, at 90 MHz. Inset: logarithmic plot of $\Delta H/H_0$ vs χ of $FeSc_2S_4$ for different frequencies ($\omega_0/2\pi$) and/or applied fields H_0 (see text).

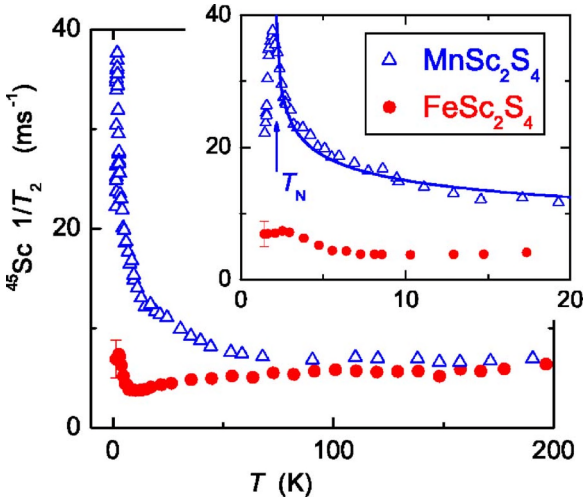

FIG. 4. (Color online) Spin-spin relaxation rates $1/T_2(T)$ of $FeSc_2S_4$ (circles) and $MnSc_2S_4$ (triangles) at 90 MHz. Inset: the line is a fit of a divergent behavior (T_N=2 K) for $MnSc_2S_4$ (see text).

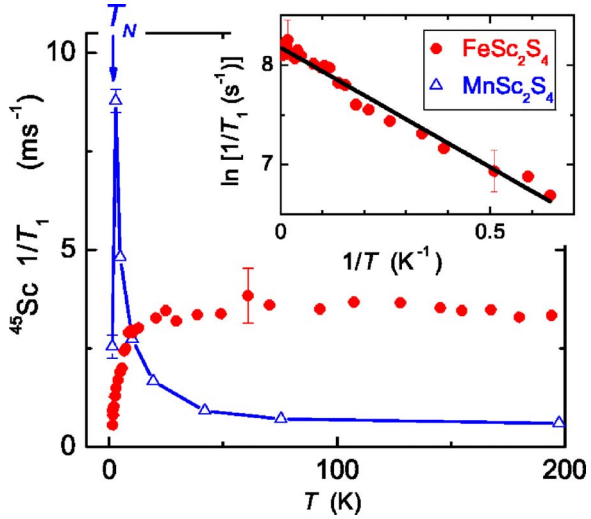

FIG. 5. (Color online) Spin-lattice relaxation rates $1/T_1(T)$ of $FeSc_2S_4$ (circles) and $MnSc_2S_4$ (triangles) at 90 MHz. Inset: Arrhenius plot of $1/T_1(T)$ for $FeSc_2S_4$. The solid line fits an activated behavior $1/T_1 \propto \exp(-\Delta/k_BT)$ with Δ=0.2 meV.

cally long-range ordered state of the Mn^{2+} moments.[10] For $FeSc_2S_4$, however, $\Delta H(T)$ remarkably exceeds the bulk susceptibility $\chi(T)$, indicating an additional broadening mechanism. The inset shows the relative linewidth $\Delta H(T)/H_0$ vs $\chi(T)$ with the temperature T as an implicit parameter. In the case of magnetic broadening, $\Delta H(T)/H_0$ vs $\chi(T)$ is expected to scale with the irradiation frequencies $\omega_0/2\pi$ and/or applied fields H_0.[13] Toward low values of $\Delta H(T)/H_0$ and χ, i.e., high temperatures, the leveling off of $\Delta H(T)/H_0$ for different $\omega_0/2\pi$ and/or H_0 indicates that a frequency and/or field independent broadening mechanism is active and the relative linewidth $\Delta H(T)/H_0$ cannot be explained based on magnetic effects only.

Therefore, we attribute this contribution of ΔH to the interaction between the electric quadrupole moment Q of the probing nuclei and an EFG at the scandium site (B site). Indeed, the drastic increase of ΔH resembles the temperature dependence of the EFG at the A site deduced from the quadrupole splitting in Mössbauer experiments,[17] where the enormous increase of the EFG toward lower temperatures has been explained taking into account the effects of second order spin-orbit coupling and random strains on the vibronic e doublet ground state.[17] Dielectric spectroscopy indicates that the orbital reorientation drastically slows down and is well below 1 MHz for $T<75$ K.[6] Hence, viewed from the time scale set by the NMR experiment, the charge distribution of orbitals appears to be almost frozen in producing a static EFG at the probing nuclear site.

Figure 4 presents the temperature dependences of the spin-spin relaxation rates $1/T_2(T)$ of $FeSc_2S_4$ and $MnSc_2S_4$. At high temperatures both compounds exhibit temperature independent rates and almost identical values of $1/T_2$ resulting from exchange narrowing due to fast spin fluctuations. Lowering the temperature, the spin-spin relaxation in the manganese compound diverges and shows a peak at T_N as is usually observed in antiferromagnets (AFM).[18] A fit of a critical behavior $1/T_2 \propto [(T-T_N)/T_N]^{-\alpha}$ with T_N=2 K and α=0.23 (for $2<T<70$ K) is shown in the inset of Fig. 4. This value roughly meets the theoretical prediction α=0.3 for a three-dimensional (3D) Heisenberg AFM.[19] But it has clearly to be stated that critical exponents are only defined near T_N and in zero magnetic fields. In contrast, the spin-spin relaxation rate $1/T_2(T)$ in the iron compound decreases toward low temperatures, exhibits a minimum at around 10 K, and slightly increases again at lowest temperatures. As there is no long-range magnetic order in $FeSc_2S_4$,[5,20] this increase of $1/T_2(T)$ for $T<10$ K does not indicate the vicinity of a magnetically ordered state, but more likely is due to a release of the exchange narrowing mechanism as orbital fluctuations or orbital glassiness[6] weaken the exchange interaction toward low temperatures.

Finally, the temperature dependences of the spin-lattice relaxation rates $1/T_1(T)$ are shown in Fig. 5. In $MnSc_2S_4$, $1/T_1(T)$ exhibits the common behavior of long-range ordered AFMs with a divergent relaxation rate at the magnetic ordering temperature T_N=2 K. At high temperatures, $1/T_1(T)$ levels off at a constant value of $1/T_1 \approx 0.6$ ms^{-1} which is slightly below the value reported recently.[10] In $FeSc_2S_4$, $1/T_1(T)$ at elevated temperatures is temperature independent with a value of $1/T_1 \approx 3$ ms^{-1}, strongly enhanced when compared to $MnSc_2S_4$. In the case of a predominant nuclear relaxation mechanism provided by fluctuations of localized spins, $1/T_1(T)$ in the high-temperature limit is $1/T_{1\infty} = \sqrt{2\pi}(\gamma g \mu_B A_{hf}/z')^2 z' S(S+1)/(3\omega_{ex})$ with the exchange frequency of local spins $\omega_{ex}=k_B|\Theta_{CW}|/[\hbar\sqrt{zS(S+1)/6}]$.[10,21] The constants z=4 and z'=6 define the numbers of exchange-coupled local spins and that of local spins interacting with the probing nuclei, respectively.[10] From a plot K versus χ (not shown) we checked that $MnSc_2S_4$ as well as $FeSc_2S_4$ exhibit the same value of the hyperfine coupling constant $A_{hf} \approx 3$ kOe/μ_B. Due to the lower spin value and the higher value of the Curie-Weiss temperature in the case of $FeSc_2S_4$, the relaxation rate in the high-temperature limit

is expected to be approximately three times *smaller* for $FeSc_2S_4$, which is in strong conflict with the observation in Fig. 5. This demonstrates the crucial role of the orbital fluctuations contributing to the nuclear spin-lattice relaxation rate. Toward lower temperatures, $1/T_1(T)$ in $FeSc_2S_4$ decreases and can be described by an activated behavior $1/T_1(T) \propto \exp(-\Delta/k_B T)$, indicating the opening of a gap $\Delta = 0.2$ meV (cf. inset of Fig. 5). The opening of a spin gap is theoretically expected in spin liquids at low temperatures.[22] Recently, inelastic neutron scattering identified cooperative spin excitations with a similar value of the spin gap.[20]

The very different behavior of the spin-lattice relaxation in these two frustrated magnets can be explained in terms of the dynamic susceptibility in a crude approximation, $1/T_1(T) \propto (T/\omega)\chi''(\omega)$. For low frequencies the dynamic susceptibility is expressed via $\chi'' = \chi_0/\Gamma$, with χ_0 the static susceptibility and Γ the electron magnetic relaxation rate.[18,19] For high temperatures $T > \Theta_{CW}$, Γ is constant and χ_0 can be approximated by a Curie law. In this case, $1/T_1(T)$ is temperature independent as actually observed in both compounds. At low temperatures, in $MnSc_2S_4$ and close to T_N, a critical decrease of $\Gamma(T)$ leads to a divergence of $1/T_1(T)$.[18] In the strongly frustrated magnet a spin liquid will be formed with an almost constant $\Gamma$and temperature independent χ_0. In this case, $1/T_1$ should linearly decrease on decreasing temperature. The actually observed exponential decrease of $1/T_1(T)$ in $FeSc_2S_4$ can only be explained by the opening of a spin gap at low temperatures.

In conclusion, we performed ^{45}Sc NMR in strongly frustrated $FeSc_2S_4$ with JT active *A*-site Fe^{2+} cations and compared the results with the spin-only homolog $MnSc_2S_4$. In the manganese compound, with $T_N \approx 2$ K and moderate frustration, the linewidth, line shift, and magnetic relaxation rates exhibit the behavior of long-range ordered AFMs, however, with the onset of spin fluctuations at 40 T_N. The experimental results in $FeSc_2S_4$ differ significantly: The local susceptibility $K(T)$ exhibits a crossover from the CW law at elevated temperatures to a temperature independent behavior as it is a fingerprint of strongly frustrated spin systems. One has to keep in mind the additional fluctuating orbital degree of freedom suppressing long-range magnetic order in $FeSc_2S_4$. The strongly enhanced high-temperature values of the spin-lattice relaxation rates $1/T_1$ in $FeSc_2S_4$ compared to $MnSc_2S_4$ have to be ascribed to these orbital fluctuations. The contrasting temperature dependences of $1/T_2$ and $1/T_1$ demonstrate that we probed the slowing down of the orbital degree of freedom in $FeSc_2S_4$.

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