

Spin and orbital frustration in FeSc_2S_4 probed by ^{45}Sc NMRN. Büttgen,¹ A. Zymara,¹ C. Kegler,¹ V. Tsurkan,^{1,2} and A. Loidl¹¹*Experimentalphysik V, Center for Electronic Correlations and Magnetism, Universität Augsburg, D-86159 Augsburg, Germany*²*Institute of Applied Physics, Academy of Sciences of Moldova, MD 2028 Chisinau, Republic of Moldova*

(Received 24 March 2005; published 26 April 2006)

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.

DOI: 10.1103/PhysRevB.73.132409

PACS number(s): 75.50.Bb, 71.70.Ej, 75.40.Gb, 76.60.-k

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-Khomskii³ 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 distribution⁸ 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 $\Theta_{\text{CW}} = -22.9$ K for the Mn and $\Theta_{\text{CW}} = -45.1$ 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 $\approx 9.5, 33,$ 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 ($100 \mu\text{s} - \tau_D - 200 \mu\text{s}$, pulse separation time $\tau_D = 180 \mu\text{s}$), 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 $^3\text{He}/^4\text{He}$ dilution refrigerator. This wipeout of intensity is due to fast nuclear relaxation when the electronic spin dynamics slows down.

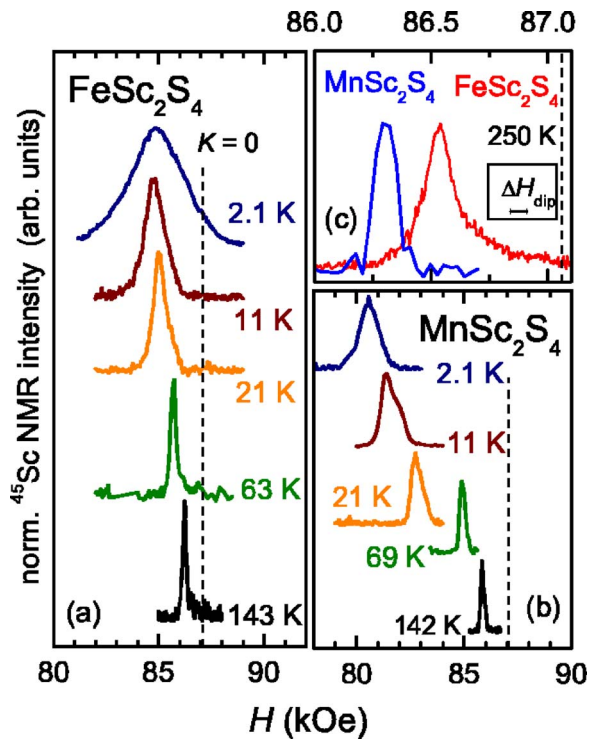


FIG. 1. (Color online) ^{45}Sc -NMR spectra of FeSc_2S_4 (a) and MnSc_2S_4 (b) at 90 MHz for different temperatures. The dashed lines mark $K=0$ as determined from ScCl_3 . (c) Spectra of MnSc_2S_4 and FeSc_2S_4 at $T=250$ K. The bar denotes the linewidth contribution ΔH_{dip} due to a nuclear dipole-dipole 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 $T \leq 40$ 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 de-

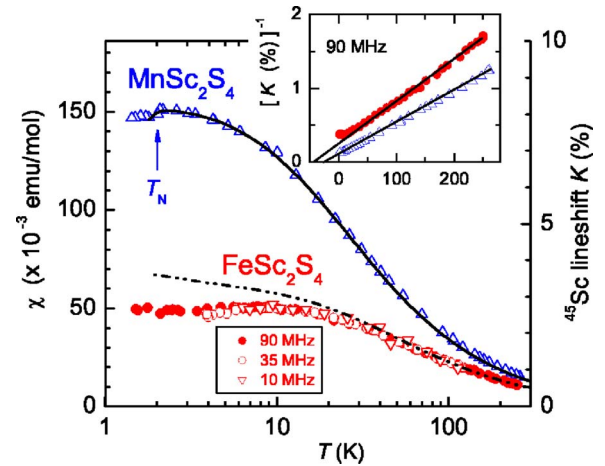


FIG. 2. (Color online) Bulk susceptibility $\chi(T)$ (dashed and solid lines, 1 kOe) and line shift $K(T)$ (symbols) of FeSc_2S_4 and MnSc_2S_4 , respectively. $T_N \approx 2$ K of MnSc_2S_4 is marked by an arrow. Inset: inverse line shift $1/K(T)$; the lines indicate CW laws with $\Theta_{\text{CW}}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

gree 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 glassiness⁶ give rise to effective changes of the hyperfine coupling and suppress the local susceptibility $K(T)$.

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-

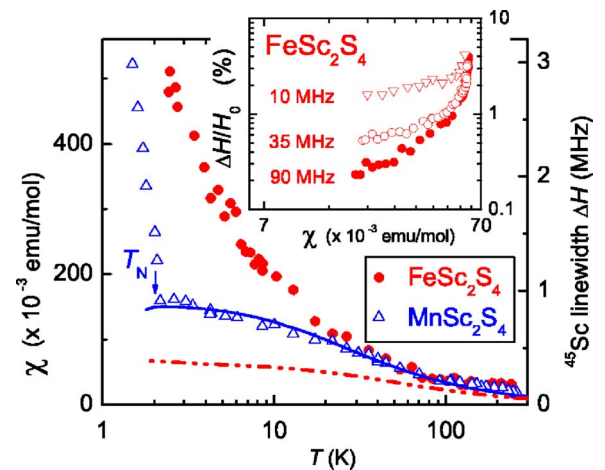


FIG. 3. (Color online) Bulk susceptibility $\chi(T)$ (dashed and solid lines, 1 kOe) and ^{45}Sc -NMR linewidth $\Delta H(T)$ (symbols) of FeSc_2S_4 and MnSc_2S_4 , respectively, at 90 MHz. Inset: logarithmic plot of $\Delta H/H_0$ vs χ of FeSc_2S_4 for different frequencies ($\omega_0/2\pi$) and/or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

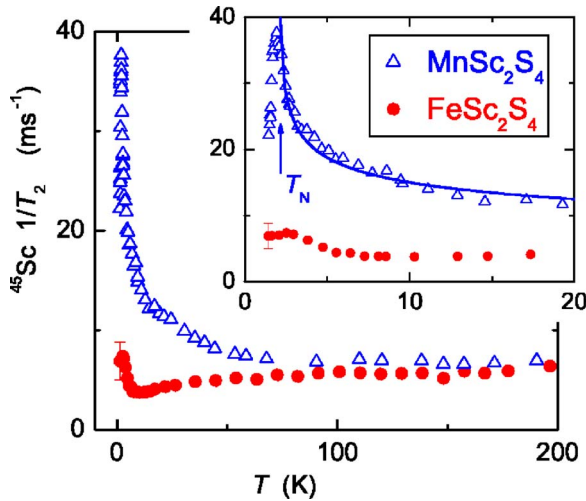


FIG. 4. (Color online) Spin-spin relaxation rates $1/T_2(T)$ of FeSc_2S_4 (circles) and MnSc_2S_4 (triangles) at 90 MHz. Inset: the line is a fit of a divergent behavior ($T_N=2$ K) for MnSc_2S_4 (see text).

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

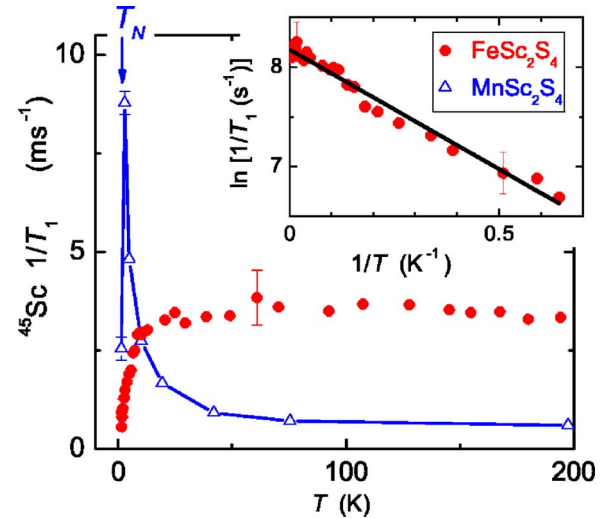


FIG. 5. (Color online) Spin-lattice relaxation rates $1/T_1(T)$ of FeSc_2S_4 (circles) and MnSc_2S_4 (triangles) at 90 MHz. Inset: Arrhenius plot of $1/T_1(T)$ for FeSc_2S_4 . The solid line fits an activated behavior $1/T_1 \propto \exp(-\Delta/k_B T)$ with $\Delta=0.2$ meV.

$\alpha=0.23$ (for $2 < T < 70$ K) is shown in the inset of Fig. 4. This value roughly meets the theoretical prediction $\alpha=0.3$ 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 glassiness⁶ 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 $1/T_{1\infty} = \sqrt{2\pi}(\gamma\mu_B A_{\text{hf}}/z')^2 z' S(S+1)/(3\omega_{\text{ex}})$ with the exchange frequency of local spins $\omega_{\text{ex}} = k_B |\Theta_{\text{CW}}| / [\hbar \sqrt{z} S(S+1)/6]$.^{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 $A_{\text{hf}} \approx 3$ 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 $T > \Theta_{\text{CW}}$, 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 Γ 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 .

We are indebted to H.-A. Krug von Nidda for fruitful discussions. This work was supported by the BMBF via VDI/EKM, FKZ 13N6917-A and by the DFG through the Sonderforschungsbereich SFB 484 (Augsburg).

-
- ¹A. P. Ramirez, in *Handbook of Magnetic Materials*, edited by K. H. J. Buschow (Elsevier, Amsterdam, 2001), Vol. 13, p. 423.
- ²H. A. Jahn and E. Teller, Proc. R. Soc. London, Ser. A **161**, 220 (1937).
- ³K. I. Kugel and D. I. Khomskii, Sov. Phys. Usp. **25**, 2312 (1982).
- ⁴L. F. Feiner, A. M. Oleś, and J. Zaanen, Phys. Rev. Lett. **78**, 2799 (1997).
- ⁵V. Fritsch, J. Hemberger, N. Büttgen, E.-W. Scheidt, H.-A. Krug von Nidda, A. Loidl, and V. Tsurkan, Phys. Rev. Lett. **92**, 116401 (2004).
- ⁶N. Büttgen, J. Hemberger, V. Fritsch, A. Krimmel, M. Mücksch, H.-A. Krug von Nidda, P. Lunkenheimer, R. Fichtl, V. Tsurkan, and A. Loidl, New J. Phys. **6**, 191 (2004).
- ⁷R. Fichtl, V. Tsurkan, P. Lunkenheimer, J. Hemberger, V. Fritsch, H.-A. Krug von Nidda, E.-W. Scheidt, and A. Loidl, Phys. Rev. Lett. **94**, 027601 (2005).
- ⁸R. V. Pound, Phys. Rev. **79**, 685 (1950).
- ⁹T. Kiyama and M. Itoh, Phys. Rev. Lett. **91**, 167202 (2003); R. M. Eremina, M. V. Eremin, S. V. Iglamov, J. Hemberger, H.-A. Krug von Nidda, F. Lichtenberg, and A. Loidl, Phys. Rev. B **70**, 224428 (2004).
- ¹⁰S. Giri, H. Nakamura, and T. Kohara, Phys. Rev. B **72**, 132404 (2005). This work appeared while we worked out the revised version of our manuscript.
- ¹¹D. E. MacLaughlin and H. Alloul, Phys. Rev. Lett. **36**, 1158 (1976); W. Trinkl, N. Büttgen, H. Kaps, A. Loidl, M. Klemm, and S. Horn, Phys. Rev. B **62**, 1793 (2000).
- ¹²N. J. Curro, P. C. Hammel, B. J. Suh, M. Hücker, B. Büchner, U. Ammerahl, and A. Revcolevschi, Phys. Rev. Lett. **85**, 642 (2000).
- ¹³P. Mendels, A. Keren, L. Limot, M. Mekata, G. Collin, and M. Horvatić, Phys. Rev. Lett. **85**, 3496 (2000).
- ¹⁴M. Itoh, I. Yamada, K. Ubukoshi, K. Hirakawa, and H. Yasuoka, J. Phys. Soc. Jpn. **55**, 2125 (1986).
- ¹⁵D. Bono, P. Mendels, G. Collin, and N. Blanchard, Phys. Rev. Lett. **92**, 217202 (2004).
- ¹⁶L. E. Drain, Proc. Phys. Soc. London **80**, 1380 (1962).
- ¹⁷L. Brossard, H. Oudet, and P. Gibart, J. Phys. (Paris), Colloq. **C6**, C6-23 (1976).
- ¹⁸T. Moriya, Prog. Theor. Phys. **28**, 371 (1962).
- ¹⁹H. Benner and J. P. Boucher, in *Magnetic Properties of Layered Transition Metal Compounds*, edited by L. J. de Jongh (Kluwer Academic Publishers, Dordrecht, 1990), p. 358.
- ²⁰A. Krimmel, M. Mücksch, V. Tsurkan, M. M. Koza, H. Mutka, and A. Loidl, Phys. Rev. Lett. **94**, 237402 (2005).
- ²¹T. Moriya, Prog. Theor. Phys. **16**, 23 (1956).
- ²²E. Berg, E. Altman, and A. Auerbach, Phys. Rev. Lett. **90**, 147204 (2003).