Ground state and low-energy magnetic dynamics in the frustrated magnet CoAl_2O_4 as revealed by local spin probes

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(Received 3 February 2015; published 24 April 2015)

We report a combined experimental study of magnetic properties of a single crystal of the frustrated diamond lattice antiferromagnet CoAl_2O_4 with Co^{2+} electron spin resonance, ^{27}Al nuclear magnetic resonance, and muon spin rotation/relaxation techniques. With our local probes, we show that the frustration of spin interactions and the Co/Al site disorder strongly affect the spin dynamics. The experimental results evidence inhomogeneous and slow magnetic fluctuations and the occurrence of short-range electron spin correlations far above a characteristic temperature $T^* = 8$ K at which the spin system turns into a quasistatic state. Our data indicate that this spin order is likely short range and unconventional with spin fluctuations persistent even at $T \ll T^*$. The results of three spectroscopy techniques highlight a nontrivial role of structural disorder for the magnetism of a frustrated diamond spin lattice at the proximity to the critical point.

DOI: 10.1103/PhysRevB.91.144419

PACS number(s): 75.30.-m, 76.30.-v, 76.60.-k, 76.75.+i

I. INTRODUCTION

Frustration of magnetic interactions in correlated transition-metal and rare-earth oxide antiferromagnets (AFM) continues to be a hot research topic in magnetism over the past two decades (see, e.g., [1]). The interest in spin systems, where frustration resulting from a specific topology of the lattice or competing exchange interactions inhibits conventional AFM Néel order, is largely stimulated by the quest for new magnetic ground states and exotic excitations which may emerge instead. Spin-spiral structures, spin liquid phases, and fractional monopole excitations are widely discussed in this context (see, e.g., [2–5]).

One class of oxide materials in which the phenomenon of magnetic frustration has been extensively studied experimentally are spinels AB_2O_4 , where either A or B, or both metal cations can be magnetic ions. The B-site cations form a strongly geometrically frustrated pyrochlore lattice. In contrast, the A sublattice has a diamond structure which is not frustrated geometrically. A substantial spin frustration can nevertheless occur due to a sizable next-nearest-neighbor AFM exchange interaction J_2 compared to the nearest neighbor exchange J_1 . Indeed, several A-site magnetic spinels have been classified as strongly frustrated magnets, among those CoAl_2O_4 has attracted a lot of attention [6–13].

It has been pointed out theoretically that for the overcritical ratio of the exchange couplings $J_2/J_1 > 1/8$ the diamond spin lattice develops a massively degenerate set of coplanar spirals forming kind of a spiral spin liquid [14]. Yet, theory predicts an entropy driven so-called “order by disorder” mechanism in which thermal disorder lifts the spiral degeneracy and yields an ordered ground state. The spin structure of this ground state is, however, very different from the collinear AFM Néel order expected for the undercritical ratio $J_2/J_1 < 1/8$. According to the inelastic neutron scattering data, this ratio in CoAl_2O_4 amounts to $J_2/J_1 \approx 0.11$ [9], i.e., close to the critical point which separates collinear and noncollinear phases.

Apparently the proximity of CoAl_2O_4 to the critical point makes its ground state prone to perturbations. In particular, experimental magnetic studies reveal an important role of the A-B site inversion that takes place in CoAl_2O_4 . The intermixing of Al and Co sites is quantified by the inversion parameter x which is defined as $[\text{Co}_{1-x}\text{Al}_x][\text{Al}_{2-x}\text{Co}_x]\text{O}_4$. Recent dc and ac susceptibility measurements on polycrystalline samples with tunable intermixing in the range $0.0467 \leq x \leq 0.153$ revealed signatures of the spin liquid state for x up to 0.0643 which crosses over to a spin glass state for $x \geq 0.101$ [11]. A collinear order for small inversion $x < 0.06$ was reported in Refs. [10,12].

On the theoretical side, there has been a recent proposal of the ordering mechanism referred as “order by quenched disorder” [15]. It addresses the breaking of degeneracy of the spin liquid by quenched random impurities on the diamond lattice and acts in addition to the aforementioned order by disorder mechanism. Such impurities, arising, e.g., due to the site inversion, locally deform spin spirals and favor a specific spiral wave vector for the ordered phase. However, regarding CoAl_2O_4 , it was conjectured that, given its proximity to the critical point where the spin stiffness vanishes, fluctuations of the wave vector make magnetic order unstable and instead a disordered ground state may be realized.

In this work we address the role of disorder for the magnetism of CoAl_2O_4 by a combination of three local dynamic spin probe techniques, electron spin resonance (ESR), nuclear magnetic resonance (NMR), and muon spin rotation/relaxation (μSR) spectroscopies. To our knowledge, such experiments have not been performed so far on single crystals of CoAl_2O_4 . For our study we have chosen a single crystal of CoAl_2O_4 with the inversion parameter $x \approx 8\%$. Part of this crystal was studied before by neutron scattering (NS) and thermodynamic techniques [9,13]. Bulk magnetic measurements agree very well with the polycrystalline results in Ref. [11] for the same x , classifying this sample to

the spin liquid regime [13]. NS data were interpreted in terms of the occurrence of spiral spin liquid correlations at elevated temperatures and of an unconventional static short-range collinear AFM order emerging below a characteristic temperature $T^* = 8$ K [9]. In our local probe experiments we observe pronounced slow inhomogeneous dynamics of Co spins which sets in at temperatures substantially higher than T^* . This signals an extended spin correlated regime at elevated temperatures which is followed by a crossover to a quasistatic state below T^* . Remarkably we find that the low frequency magnetic fluctuations are still appreciable even at $T \ll T^*$ at odds with the expected behavior of a conventional long-range ordered AFM. A combined discussion of the data reveals a special role of impurities for the magnetism of the frustrated diamond spin lattice antiferromagnet near the critical point.

The paper is organized as follows. In Sec. II sample particulars and details on the experimental setups are given. Experimental data and their primary analysis are presented in Sec. III, followed by their discussion in Sec. IV. Finally, major conclusions are summarized in Sec. V.

II. EXPERIMENTAL DETAILS

The CoAl_2O_4 single crystal with $x \approx 8\%$ [9,13] was grown and primarily characterized in Ref. [16] and then was further investigated by neutron scattering and thermodynamic methods in Refs. [9,13]. Static magnetization data of this single crystal used for the analysis of the NMR results in the present work were taken from Ref. [13].

NMR measurements were performed with a Tecmag solid-state pulsed spectrometer and a superconducting magnet (0–9.2 T) from Magnex Scientific at a fixed frequency $\nu = 85.42$ MHz. The spectra were collected by step-by-step sweeping the field and integrating the echo signal obtained by the standard Hahn echo pulse sequence at each field step. The longitudinal nuclear spin relaxation rate T_1^{-1} was measured with inversion recovery and stimulated echo pulse protocols [17]. μSR measurements were performed using the GPS spectrometer located at the πM3 beamline of the Swiss Muon Source at the Paul Scherrer Institut, Switzerland in a temperature range from 1.7 to 300 K using a He flow cryostat. The data were analyzed using the MUSRFIT package [18]. ESR spectra were measured with a homemade multifrequency high-field ESR (HF-ESR) spectrometer at magnetic fields up to 16 T and at frequencies ν up to 400 GHz [19]. For the generation and detection of the microwave radiation millimeter wave backward oscillators and an InSb bolometer from QMC Instruments Ltd., as well as a millimeter wave network analyzer from AB Millimetre, have been used. dc magnetic fields have been obtained with a solenoid superconducting magnet from Oxford Instruments.

III. EXPERIMENTAL RESULTS

A. Nuclear magnetic resonance

NMR measurements on the single crystal of CoAl_2O_4 were performed on the ^{27}Al nuclei (natural abundance 100%) which possess a spin $I = 5/2$, the quadrupole moment $Q = 0.149$ barns, and the gyromagnetic ratio $\gamma_n = 11.094$ MHz/T. Characteristic NMR spectra at room temperature for different orientations of the external magnetic field $\mathbf{H}$ with respect to the

FIG. 1. Room temperature ^{27}Al NMR spectra for various directions of the applied magnetic field $\mathbf{H}$ obtained by rotating $\mathbf{H}$ about the crystallographic [010] axis in the (010) plane. The angles which the field vector makes with the [100] axis are indicated in the plot.

crystallographic axes are shown in Fig. 1. The spectra consist of a main line and satellites which positions change depending on the field direction. The spectrum collapses in a single line when $\mathbf{H}$ approaches approximately the [101] axis. This can be also clearly seen in the angular dependence of the width of the spectrum shown in Fig. 2.

The satellites in the spectrum arise due to the quadrupole splitting of the nuclear Zeeman levels in the presence of electrical field gradient (EFG) as described by the following Hamiltonian [20]:

$$\mathcal{H} = -\gamma_n H_0 \hbar m_z + \frac{e^2 q Q}{4I(2I-1)} \frac{3 \cos^2 \theta - 1}{2} \left[3m_z^2 - I(I+1) + \frac{1}{2} \eta (m_+^2 + m_-^2) \right]. \quad (1)$$

FIG. 2. (Color online) Width of the room temperature ^{27}Al NMR spectra taken at 10% of the height as a function of angle α between the magnetic field $\mathbf{H}$ and the [001] axis when the sample is rotated about the [010] axis. The solid line is a guide for the eye.

Here m_z and $m_{\pm}$ are projections of the nuclear spin I on the z -quantization axis given by the external magnetic field $\mathbf{H}$ and perpendicular to it, respectively, e is the elementary charge, q is the gradient of the electrical field, θ is the angle between $\mathbf{H}$ and the principal axis of the EFG tensor, and η is the asymmetry parameter of the EFG. For $I = 5/2$ the quadrupole shift ν_{Qi} of the four satellites ($i = 1, \dots, 4$) from the main central line at $\nu_0 = \gamma_n H_0$ corresponding to the transition $\langle m_z \leftrightarrow m_z - 1 \rangle = \langle +1/2 \leftrightarrow -1/2 \rangle$ can be derived from Eq. (1). For the two outermost satellites $i = 1$ ($\langle -5/2 \leftrightarrow -3/2 \rangle$) and $i = 4$ ($\langle +5/2 \leftrightarrow +3/2 \rangle$), and the two innermost satellites $i = 2$ ($\langle -3/2 \leftrightarrow -1/2 \rangle$) and $i = 3$ ($\langle +3/2 \leftrightarrow +1/2 \rangle$) it reads

$$\begin{aligned} \nu_{Qi} &= \pm[2\nu_Q + \delta_{Qi}(\eta)]f, & i = 1, 4, \\ \nu_{Qi} &= \pm[\nu_Q + \delta_{Qi}(\eta)]f, & i = 2, 3. \end{aligned} \quad (2)$$

Here the plus sign corresponds to $i = 1, 2$ and the minus sign corresponds to $i = 3, 4$, respectively, $\nu_Q = 3e^2qQ/h2I(2I - 1)$ is the quadrupole frequency for $\eta = 0$, $\delta_{Qi}(\eta)$ are corrections to the shift in the presence of the asymmetry ($\eta \neq 0$) [21], and $f = (3 \cos^2 \theta - 1)/2$ is the angular factor. The satellites merge with the central line for $\theta = 54.74^\circ$ when $f = 0$. Experimentally the narrowing of the spectrum is maximal for the direction of the magnetic field approximately along the [101] axis (Figs. 1 and 2). This implies that the EFG axis is oriented close to the edge of the cubic unit cell deviating from it most likely by about 4.5° as suggested by the local symmetry of the oxygen ligands surrounding the aluminum atom. For further NMR experiments two orientations, [001] the most resolved and [101] collapsed, have been chosen.

A closer inspection of the quadrupole split ^{27}Al NMR spectrum reveals that its successful modeling can be achieved only by addition of a second contribution with different ν_0 with the weight of $\sim 10\%$. This is exemplified in Fig. 3 where the most resolved spectrum for $\mathbf{H} \parallel [001]$ is analyzed. The spectrum can be reasonably well modeled as a sum of the quadrupole split spectrum with quadrupole frequencies $[\nu_{Q1}, \nu_{Q2}, \nu_{Q3}, \nu_{Q4}] = [0.632, 0.332, 0.521, 0.798]$ MHz and with the asymmetry parameter $\eta = 0.253$, and of an additional weak line without

FIG. 3. (Color online) ^{27}Al NMR spectrum at $T = 240$ K for the direction of the magnetic field $\mathbf{H}$ parallel to the [001] axis (full squares). The modeled spectrum assuming two contributions (dashed and dot-dashed lines) is shown by the thick solid line. a and b denote positions at which the nuclear relaxation rate $1/T_1$ was measured (for details see the text).

quadrupole satellites. Here the η was estimated using the point charge model. The quadrupole frequencies appear similar to the polycrystalline result in Ref. [12]. A nonuniformity of the quadrupole shifts is due to corrections arising from the asymmetry of the EFG [Eq. (2)] and some misalignment of the measured single crystal. Considering the relative weights of the two components it is natural to assign the minor contribution to the aluminum nuclei residing in an inverted (i.e., Co lattice site) position, which in the studied single crystal amounts to $\sim 8\%$ (see Sec. II). The ^{27}Al nucleus in the inverted site resides in the center of a regular tetrahedron of oxygen ligands where the EFG q is zero. This explains the absence of the quadrupole structure for the minor contribution.

At $T < 100$ K the ^{27}Al NMR spectra exhibit substantial transformation for both resolved [001] and collapsed [101] orientations of the single crystal. The spectra strongly broaden and in particular for $\mathbf{H} \parallel [101]$ acquire a Gaussian-like shape without any visible structure (Fig. 4). Remarkably the structure does not reappear below $T^* = 8$ K as it is usually the case in the long-range commensurate AFM ordered state where a narrowing and splitting of the lines due to the staggered magnetization is observed.

For the [001] orientation the spectra were fit at each temperature as a sum of two contributions with the relative weights of about 9 : 1 as depicted in Fig. 3. The individual width of the quadrupole lines for the major component and the width of the line for the minor component were the fit parameters. We note that in the temperature dependent measurement shown in Fig. 4(left) the sample was slightly tilted off from the most resolved orientation shown in Figs. 1 and 3 which did not affect the quality of the fit.

For the collapsed [101] orientation the NMR signal can be fitted in principle with two Gaussians corresponding to the contributions from regular and inverted Al sites. However, the uncertainty of the two-line fit does not enable an accurate estimate of the parameters for the weak “inverted” line. Therefore, for this orientation only parameters of the main

FIG. 4. (Color online) ^{27}Al NMR spectra at selected temperatures $T \leq 100$ K for the direction of the magnetic field $\mathbf{H} \parallel [001]$ (left) and $\mathbf{H} \parallel [101]$ (right). Note substantial broadening and loss of the structure with decreasing T for both orientations.

line were determined by fitting the spectrum with a single Gaussian.

From the modeling of the spectra the Knight shift K has been determined. The local averaged magnetization causes the shift of the ^{27}Al NMR line from the Larmor frequency ν_0 , $\nu = \nu_0(1 + K)$. A linear relation $K = K_{\text{orb}} + A\chi$ holds over an extended temperature range as exemplified in Fig. 5 for field geometries $\mathbf{H} \parallel [001]$ and $\mathbf{H} \parallel [101]$. Here K_{orb} is the T -independent orbital contribution to the shift and A is the hyperfine coupling constant. The hyperfine constants appear different in the magnitude for the regular and inverted Al sites and slightly anisotropic, $A_{\text{reg}}^{[001]} = -0.95$ kOe/ μ_B , $A_{\text{reg}}^{[101]} = -0.89$ kOe/ μ_B , and $A_{\text{invert}}^{[001]} = -0.55$ kOe/ μ_B , respectively. Below $T \sim 22$ K, the Knight shift $K(T)$ substantially deviates from linearity indicating that in the short-range spin correlated regime which sets in at these temperatures the local magnetization seen by the ^{27}Al nuclei deviates from the bulk magnetization (see below). The larger value of A_{reg} is naturally expected since Al at the regular site sits closer to magnetic Co ions compared to the Al in the inverted, i.e., Co site.

Insights into the dynamics of the Co spin system in CoAl_2O_4 were obtained by measurements of the ^{27}Al $1/T_1$ relaxation rates. A decay of the spin echo intensity at the central line (position a in the spectrum, Fig. 3) as a function

FIG. 5. (Color online) Relation between the Knight shift K and the static susceptibility χ for regular and inverted Al sites with temperature as an implicit parameter. The linear slope of the dependence is given by the hyperfine constant A (see the text).

of the time delay t between the exciting and detecting pulses in the respective pulse protocols can be well described by the following equation for the transition $\pm 1/2$ of the nuclear spin $I = 5/2$ [22]:

$$m_a(t) = n_0 + 0.029 \exp\left(\frac{-t}{T_{1r}}\right)^\beta + 0.18 \exp\left(\frac{-6t}{T_{1r}}\right)^\beta + 0.79 \exp\left(\frac{-15t}{T_{1r}}\right)^\beta. \quad (3)$$

Here n_0 accounts for the noise level, $1/T_{1r}$ is the relaxation rate of Al nuclei at the regular site, and β is the stretching exponent. The signal on position b of the spectrum in Fig. 3 consists of two contributions, that of the main line of the regular Al spectrum and that of the unsplit line arising from the inverted Al positions. As a consequence, in the echo decay, a second contribution arises in addition to the main one [Eq. (3)], and the total nuclear magnetization at position b reads

$$m_b(t) = A_r m_a(t) + A_i \exp\left(\frac{-t}{T_{1i}}\right)^\beta. \quad (4)$$

Here $1/T_{1i}$ is the relaxation rate of Al nuclei at the inverted site and A_r and A_i are the respective weights of the two contributions. The experimentally observed rounded steplike $m(t)$ dependence at position b of the total spectrum can be very well fitted by Eq. (4) (Fig. 6). Here the free parameters are A_r , A_i , and $1/T_{1i}$, whereas the rate $1/T_{1r}$ was determined from the magnetization decay at position a of the spectrum at each respective temperature. For the collapsed orientation $\mathbf{H} \parallel [101]$ the spin echo decay at the peak of the signal was fitted according to Eq. (3) since the nuclei at the inverted Al site do not contribute to the spin echo decay at this field position.

The fit for the $[001]$ orientation yields a practically temperature independent ratio $A_r/A_i = 0.85/0.15$ which changes slightly around T^* . Indeed, the ratio of the two contributions to the nuclear magnetization decay is consistent with the ratio of the regular and inverted Al sites in the studied single crystal, thus confirming the assignment of $1/T_{1r}$ and $1/T_{1i}$ to these two sites, respectively.

FIG. 6. (Color online) Time dependence of the ^{27}Al stimulated spin echo decay for $\mathbf{H} \parallel [001]$ at $T = 40$ K at position b of the spectrum in Fig. 3. The solid line is a fit to Eq. (4).

The T dependence of the relaxation rates $1/T_{1r}$ and $1/T_{1i}$ are plotted in Fig. 7 for two magnetic field geometries. In magnetic substances the nuclear T_1 relaxation is dominated by fluctuating fields at the nuclear site produced by electron

FIG. 7. Temperature dependence of the ^{27}Al $1/T_1$ relaxation rates for the regular and inverted Al sites, circles and triangles, respectively, for $\mathbf{H} \parallel [001]$ (closed symbols) and $\mathbf{H} \parallel [101]$ (open symbols). Solid lines are guides for the eye. Inset shows the low-temperature behavior of $1/T_1$ on an enlarged scale.

spins. If electron spin fluctuations are fast, which is usually the case in the noncorrelated paramagnetic regime at high temperatures, the rate $1/T_1 \sim T\chi$ depends only weakly on T , since $\chi \sim 1/T$ [20]. This situation is obviously relevant for CoAl_2O_4 at temperatures above ~ 30 K (Fig. 7). Here the ratio of the relaxation rates T_{1r}^{-1}/T_{1i}^{-1} for $\mathbf{H} \parallel [001]$ and of the rates $T_{1r[001]}^{-1}/T_{1r[101]}^{-1}$ for field directions $[001]$ and $[101]$ corresponds approximately to the square ratio of the respective HF constants (Fig. 5), as expected. The increase of $1/T_1$ at lower T indicates an enhancement of electron spin correlations. In this regime the stretching exponent β decreases from 1 to ~ 0.8 indicating a distribution of fluctuation times of electron spins. A broad peak at $T^* = 8$ K is a characteristic of the onset of the static spin correlations on the NMR time scale.

B. Muon spin relaxation

In the μSR setup the single crystal of CoAl_2O_4 was mounted in the cryostat on a fork holder with the $[110]$ direction parallel to the muon beam and the muon spin tilted to the upward direction by 45° .

In Fig. 8 zero field μSR spectra are shown for selected temperatures. At all temperatures a fast relaxing component of about 30% of the total polarization is visible at early times. The occurrence of such a component with different weights appears as a generic feature of A-site spinels AAI_2O_4 [23] and is most likely not related to bulk magnetic properties. In the following we focus on the temperature behavior of the majority of the polarization at longer times (70%) which is specific to the bulk magnetism of CoAl_2O_4 .

At high temperatures the spectra are characterized by weak Gauss-Kubo-Toyabe depolarization typical for the presence of a magnetic field distribution at the muon site due to static nuclear moments. At temperatures below ~ 30 K electronic magnetism sets in as seen by an increasingly stronger relaxation of the μSR spectra with decreasing T . The shape of the relaxation function changes from Gaussian-like to exponential and finally to stretching exponential with decreasing temperatures. Below about $T^* = 8$ K a much

FIG. 8. (Color online) Zero field μSR spectra of CoAl_2O_4 at selected temperatures (for details see the text).

stronger transverse relaxation sets in indicating the static magnetic order of the system. Notably, below T^* overdamped oscillations are visible (Fig. 8, inset). This indicates static order with a large number of magnetically inequivalent muon sites in the magnetic structure, e.g., incommensurate order.

The time-dependent muon spin polarization $P(t)$ has been analyzed with the following function:

$$P(t) = 0.3P_{\text{HT}}(t) + 0.7[(1 - f)P_{\text{NM}}(t) + fP_{\text{Mag}}(t)]. \quad (5)$$

The first term describes the fast relaxing high temperature (HT) minority component (see above) and has the following form:

$$P_{\text{HT}}(t) = e^{-\lambda_{\text{HT}} t}. \quad (6)$$

The second term in (5) describes the major part of the polarization signal which probes intrinsic magnetism of CoAl_2O_4 . It is composed of the polarization P_{NM} coming from muons which see nonordered (or nonmagnetic, NM) environment and of the polarization P_{Mag} from muons in the (quasistatic) magnetic environment, and f is the weight of this magnetic fraction.

The nonmagnetic polarization function is given by

$$P_{\text{NM}}(t) = \left[\frac{1}{3} + \frac{2}{3}(1 - \sigma^2 t^2) e^{-\frac{1}{2}\sigma^2 t^2} \right] e^{-(\lambda_L t)^\beta}. \quad (7)$$

It is a multiplication of a static Gauss-Kubo-Toyabe function (in square brackets) due to a static field distribution originating from the present nuclear moment with the dynamic relaxation function representing the effect of the slowing down of the electronic moments. The corresponding relaxation rates are σ and λ_L , respectively, and β is the stretching exponent.

Since the μSR spectra at $T < T^*$ indicate multiple magnetically inequivalent sites (see above), the magnetic polarization function is defined as

$$P_{\text{Mag}}(t) = \frac{2}{3} j_0(t) e^{-\frac{1}{2}\sigma_{\text{Mag}}^2 t^2} + \frac{1}{3} e^{-(\lambda_L t)^\beta}, \quad (8)$$

where $j_0(t)$ is the first order Bessel function usually used to describe incommensurate magnetic structures and σ_{Mag} is a relatively large additional damping due to disorder and/or multiple muon sites.

In Fig. 9 the important fit parameters are shown on a logarithmic temperature scale. The uppermost graph shows the onset of quasistatic magnetic fraction below approximately $T^* = 8$ K and a corresponding development of the muon spin rotation frequency (inset). The latter agrees very well with the intensity of the magnetic Bragg peak that appears in the neutron diffraction pattern at T^* [9] which is shown in the upper inset for comparison. The lower two graphs characterize the spin dynamics. The dynamic relaxation rate λ_L peaks at T^* . The stretching exponent β falls below 1. This indicates, similar to NMR, a broad distribution of fluctuation times characteristic of an inhomogeneous spin dynamics which continuously slows down by approaching T^* . Notably, below the transition the dynamic relaxation rate λ_L is still relatively large ($0.4 \mu\text{s}^{-1}$) suggestive of a quasistatic low temperature order only.

C. Electron spin resonance

Measurements of HF-ESR have been carried out for two field geometries $\mathbf{H} \parallel [001]$ and $\mathbf{H} \parallel [101]$ yielding very similar results irrespective of the field orientation. In the following most of the data will be shown for the $[101]$ field direction.

FIG. 9. (Color online) Results of the fit of the zero field μSR spectra (Fig. 8) according to Eqs. (5), (6), (7), and (8). Top: Quasistatic magnetic fraction and muon rotation frequency compared with the intensity of the magnetic Bragg peak [9] (inset). Middle: Longitudinal muon relaxation rate λ_L and its comparison with the ^{27}Al NMR relaxation rate (inset). Bottom: Stretching exponent β illustrating an increase of the distribution of electron spin fluctuation times ($\beta < 1$) below 100 K (for details see the text).

The HF-ESR spectrum of CoAl_2O_4 comprises a single Lorentzian-shaped line in the whole temperature range of the study (Fig. 10). Frequency dependent measurements at a high temperature of 270 K yield a linear relation between the frequency ν and the resonance field H_{res} , $\nu = (h/\mu_B)gH_{\text{res}}$, as expected for a paramagnetic resonance (Fig. 11). Here h and μ_B are the Planck constant and Bohr magneton, respectively. From the slope of this dependence the g factor can be accurately determined. Its value $g = 2.25$ represents a textbook example of the g factor of Co^{2+} ion in a tetrahedral ligand coordination [24]. Note that Co^{2+} in this coordination has a spin $S = 3/2$ and possesses no orbital angular momentum in the ground state. The g factor is therefore isotropic and its

FIG. 10. (Color online) HF-ESR spectra at a selected frequency $\nu = 166$ GHz at various temperatures. Vertical dashed line marks the resonance field at high temperatures. Inclined dashed line visualizes the shift of the signal below $T \sim 30$ K.

deviation from the pure spin value of 2 is due to higher order spin-orbit coupling effects [24].

The ESR line is very broad already at high temperatures, where the linewidth amounts to $\Delta H \sim 3$ T. In exchange coupled electron spin systems the ESR linewidth in the high temperature limit $T \gg J$ is mainly determined by the anisotropic contributions to the Heisenberg superexchange of the magnitude $A < J$ arising due to the spin-orbit coupling. In the strong exchange limit $J > g\mu_B H_{\text{res}} > g\mu_B \Delta H$, the so-called exchange narrowed Lorentzian-shaped ESR line has a width $\Delta H = (10/3)(\hbar^2/g\mu_B)(A^2/J)$ [25]. With $\max(|J_1|, |J_2|) = 0.92$ meV [9] and $\Delta H \sim 3$ T one obtains an order of magnitude estimate of $A \sim 0.3$ meV.

FIG. 11. (Color online) Frequency ν vs resonance field H_{res} branch at a high ($T = 270$ K) and low ($T = 5$ and 20 K) temperatures (symbols). Solid lines are fits to the paramagnetic and AFM resonance dependence. Dashed line is the estimated dependence $\nu(H_{\text{res}})$ at $T = 20$ K (see the text).

FIG. 12. Temperature dependence of the ESR linewidth ΔH at $\nu = 166$ GHz. Dashed line shows the value of ΔH in the high temperature limit.

Below ~ 100 K, which corresponds approximately to the Curie-Weiss temperature $\Theta = -85$ K, the ESR signal begins to broaden strongly and reaches the width of 12 T at the lowest temperature (Fig. 12) [26,27]. Furthermore, below $T \sim 30$ K the signal begins to shift continuously to lower fields (Figs. 10 and 13).

Remarkably the $\nu(H)$ dependence of the HF-ESR signal at $T = 5$ K substantially deviates from the high temperature linear dependence reminiscent of the AFM resonance branch of a two-sublattice antiferromagnet in the “hard” direction [28] and reveals a gap at $H = 0$ for the resonance excitation (Fig. 11). A fit to the simple relation $h\nu = \sqrt{\Delta(H=0)^2 + (g\mu_B H)^2}$ [28] yields the gap value $\Delta(H=0) = 118 \pm 16$ GHz or 0.48 meV.

FIG. 13. (Color online) Temperature dependence of the resonance field H_{res} at $\nu = 166$ GHz. Dashed line shows the value of H_{res} in the high temperature limit corresponding to the g factor $g = 2.25$. The low temperature behavior of $H_{\text{res}}(T)$ on the enlarged scale is shown in the inset. Deviation of the data points from the horizontal dashed line below ~ 40 K indicates the temperature regime of the quasistatic spin correlations on the time scale of ESR.

Small deviation from the high temperature linear dependence of $\nu(H)$ is noticeable even at $20\text{ K} \gg T^*$ (Fig. 11) which is reflected in the T -dependent shift of the resonance field measured at a constant ν (Fig. 13). The excitation gap Δ is given by the product of the exchange energy and anisotropy energy $\Delta \sim \sqrt{JA}$ [28]. Despite the crudeness of the approximations, the estimated geometrical mean $\sim \sqrt{JA} \sim 0.5\text{ meV}$ is surprisingly close to the value of the experimentally determined gap.

IV. DISCUSSION

As already mentioned in the Introduction, the consequences of magnetic frustration for the ground state and excitations of the diamond spin lattice have been recently studied theoretically [14,15]. For the overcritical ratio of the AFM next-nearest-neighbor (J_2) and nearest-neighbor (J_1) exchange constants $J_2/J_1 > 1/8$ a broad spiral spin liquid regime due to the massive degeneracy of coplanar spin spirals with different propagation vectors has been identified at higher temperatures which is eventually followed by noncollinear spin order at lower temperature. The order is due to entropy driven splitting of the degenerate ground states, referred to as order by disorder mechanism [14], as well as due to random quenched impurities that induce order by quenched disorder [15]. A simple collinear AFM Néel order is found for undercritical $J_2/J_1 < 1/8$.

The role of the disorder due to the Co-Al site inversion x in $[\text{Co}_{1-x}\text{Al}_x][\text{Al}_{2-x}\text{Co}_x]\text{O}_4$ has been extensively addressed experimentally (see, e.g., [6–13]). The ratio $J_2/J_1 \approx 0.1 < 1/8$ in CoAl_2O_4 , as revealed by inelastic NS [9,10], is undercritical, locating this material on the collinear order side of the phase diagram. Indeed, in the case of small disorder ($x < 0.06$) a collinear ground state was observed [10,12], whereas for $x \gtrsim 0.1$ a spin glass state was found, as is generally expected in the case of strong disorder [6,8,11].

A situation becomes much more interesting for a moderate amount of disorder $x < 0.1$, for which signatures of an extended spin liquid regime were reported [11]. In particular, for the single crystal of CoAl_2O_4 with $x \approx 0.08$ studied in the present work a previous NS work [9] has concluded on an unconventional collinear type order below $T^* = 8\text{ K}$ with the correlation length of just a few lattice spacings, whereas the low lying excitations are spiral states persisting down to low temperatures $T \ll T^*$. Considering the proximity of CoAl_2O_4 to the critical point $J_2/J_1 = 1/8$ where the spin system gets particularly prone to perturbations, one can conjecture a special role of a moderate disorder for the phase diagram in Refs. [14,15] which was not addressed so far theoretically. In the following we discuss how our results of the local spin probe techniques contribute to the understanding of this picture.

Slow electron spin dynamics and growth of spin correlations make major contributions over a broad temperature range to the μSR and ^{27}Al NMR relaxation rates as well as to the shift and broadening of the NMR and Co^{2+} ESR lines. Low-frequency electron spin fluctuations yield progressively stronger damping of the muon polarization below 30 K (Fig. 8). The longitudinal relaxation rate λ_L enhances strongly towards the peak value at T^* and persists unusually large even at $T \ll T^*$. Consistently with NMR results, the μSR data evidence a broad temperature interval above T^* characterized

by a gradual increase of the muon relaxation rate associated with inhomogeneous slow dynamics of electron spins in CoAl_2O_4 which eventually turns into a complex quasordered state below T^* . One should note that the peak in the NMR rate $1/T_1$ at T^* is apparently broader as compared with the μSR peak (see inset in the middle panel in Fig. 9). This can be attributed to the effect of the NMR magnetic field of almost 8 T and resembles the broadening of the spin excitation spectrum in INS under the application of magnetic field of a similar strength [9].

In NMR, according to the Redfield's theory [20], the longitudinal nuclear spin relaxation rate T_1^{-1} is determined by the magnitude of the transferred field H_x and H_y and the correlation time τ_0 of the electron spins:

$$T_1^{-1} = \gamma_n^2 [\overline{H_x^2} + \overline{H_y^2}] \tau_0 / (1 + \omega_n^2 \tau_0^2). \quad (9)$$

By increasing τ_0 the relaxation gets faster until the T_1^{-1} reaches a maximum when $1/\tau_0$ approaches the NMR frequency window ω_n ($\omega_n \tau_0 \sim 1$) and finally decreases again. Such a correlation peak is clearly seen in the ^{27}Al NMR $T_1^{-1}(T)$ data shown in Fig. 7 for both Al sites. Notably, one can see in the inset of this figure that the peak is centered around $T^* \sim 8\text{ K}$ and is very round and broad suggesting rather a crossover to the quasistatic regime than a true second order magnetic phase transition. With the aid of Eq. (9) one can extract the temperature dependence of the correlation time τ_0 which is shown in Fig. 14. τ_0 begins to increase strongly below $T \sim 13\text{ K}$ and continuously grows down to the lowest temperature. Though magnetic correlations appear anisotropic in magnetic field, as seen by neutron diffraction at $T \ll T^*$ [13], τ_0 is practically independent of the field direction and of the particular nuclear site suggesting a continuous slowing down of the three-dimensional spin dynamics in CoAl_2O_4 across T^* . One should note that the strong increase of τ_0 occurs concomitantly with the broadening of the NMR linewidth (Fig. 15) and both obviously have a common origin.

The temperature dependence of the NMR linewidth for the regular Al site obtained from the modeling of the ^{27}Al NMR

FIG. 14. (Color online) Temperature dependence of the correlation time of electron spins τ_0 seen by NMR for the regular and inverted Al sites, circles and triangles, respectively, for $\mathbf{H} \parallel [001]$ (closed symbols) and $\mathbf{H} \parallel [101]$ (open symbols). Solid lines are guides for the eye (see the text).

FIG. 15. (Color online) T dependence of the width of the NMR signal for the regular Al site at $\mathbf{H} \parallel [001]$ and $\mathbf{H} \parallel [101]$ (inset). Solid lines are guides for the eye. Dashed line is the scaled T dependence of the susceptibility $w = w_0 + c\chi H$. Triangles and squares are intensities of the magnetic Bragg peak and of the diffusive streak, respectively, from Ref. [9] (see the text).

spectra (Fig. 4) is shown in Fig. 15. The linewidth gradually increases in the whole temperature range. The dependence for $\mathbf{H} \parallel [101]$ exhibits an inflection point around $T \sim 13$ K where a substantially steeper increase of the linewidth sets in (Fig. 15, inset).

An inhomogeneous broadening of an NMR line in paramagnets is due to the distribution of local fields which is proportional to the magnetization $M = \chi H$ and which gives a T -dependent contribution to the total width $w = w_0 + c\chi H$. This relation, after choosing appropriate scaling parameters w_0 and c for the experimental susceptibility data, is plotted in the inset of Fig. 15 by the dashed line. The NMR data for the [101] direction follow closely this dependence at higher temperatures but substantially deviate upon approaching T^* . This additional inhomogeneous contribution is obviously due to the spin correlations which continue to develop down to the lowest temperature. The steep increase of the linewidth at low temperatures corresponds closely to the growth of the magnetic Bragg peak at the commensurate position in the NS experiment (Fig. 3 in Ref. [9]). Its intensity is plotted in the inset of Fig. 15 for comparison. Such similarity suggests that an additional NMR line broadening is due to the onset of the static (short-range) order at T^* . For the [001] direction the linewidth deviates much earlier from the χH dependence and the low temperature increase is more gradual (Fig. 15, main panel). Interestingly, the growth of the NMR linewidth in this direction follows closely the growth of the intensity of the diffusive streaks in the neutron diffraction pattern which connect magnetic Bragg peaks (Figs. 4 and 5 in Ref. [9]). As discussed above, these streaks have been associated with the thermal population of the incommensurate low-energy coplanar spiral states in CoAl_2O_4 [9] which apparently give an anisotropic contribution to the NMR linewidth.

The above discussion of the NMR data validates the conclusion of the occurrence of two regimes in CoAl_2O_4 . The dynamic regime in an extended temperature range above T^* is characterized by slow dynamics of correlated spins

due to the frustration driven fluctuations within the multitude of quasidegenerate, possibly spiral-like, energy states. This regime is followed by a crossover to an inhomogeneous static magnetic state where the spins are short-range ordered on a complex pattern [29].

It should be further noted that the broadening of the ^{27}Al NMR line bears a remarkable similarity with the broadening of the Co^{2+} ESR signal. A strong growth of the ESR linewidth ΔH gives evidence that the time scale of electronic spin-spin correlations in CoAl_2O_4 slows down below 100 K to the characteristic ESR time window. The shift of H_{res} from its high temperature value $H_{\text{res}}(T = 270 \text{ K}) = h\nu/g\mu_B$ determined by the g factor is also suggestive of the onset of the short-range quasistatic correlations on the time scale of ESR far above the ordering temperature $T^* = 8 \text{ K}$.

In ESR one measures spin excitation modes at zero wave vector q . Therefore, the observed gap at $T < T^*$ (Fig. 11) obviously corresponds to the spin wave gap in the magnetic zone center ($q = 0$) which arises due to magnetic anisotropy in an antiferromagnet, and as such it agrees very well with the magnitude of the gap observed in the inelastic NS (INS) experiment on the same crystal [9].

The shift of the HF-ESR signal to low fields in the temperature dependent measurements can be obviously attributed to the opening of the gap in the excitation spectrum. Remarkably, this shift can be traced up to the temperatures substantially higher than T^* (Figs. 10 and 13), suggesting a persistence of the gap in the low frequency dynamic spin-correlated regime. In the INS measurements the gap at $q = 0$ vanishes at T^* . A strong broadening of the signal precludes ESR measurements below $\sim 150 \text{ GHz}$. Nevertheless, the HF-ESR frequency dependent data at $T = 20 \text{ K}$ enable a rough estimate of the gap value of about $60 \text{ GHz} = 0.25 \text{ meV}$ at this temperature (intercept of the dashed line in Fig. 11 with the frequency axis). A peak at such energy is not seen in the INS spectrum at $q = 0$ (see Fig. 9 in Ref. [9]). Remarkably, at the magnetic zone boundary $q = \pi$ which is not accessible for ESR, the spin wave excitation disperses to higher energies and a quasielastic peak in INS is clearly visible up to 90 K [9].

The above discussion of the HF-ESR data completes the picture of the low temperature magnetism of the studied single crystal of CoAl_2O_4 . In conventional nonfrustrated three-dimensional antiferromagnets the critical broadening of the ESR line usually occurs very close to the phase transition temperature T_N . Switching on the magnetic frustration extends this critical regime to temperatures well above T_N where the fluctuations within the multitude of degenerate spin states gradually develop. In this context, a continuous strong broadening of the Co^{2+} ESR signal and its shift incipient far above T^* strongly support the scenario of a frustrated spin system in CoAl_2O_4 with multiple quasidegenerate low-energy states which exhibit a slow spin dynamics at elevated temperatures and evolve some kind of static order below T^* . Note that there is no anomaly in the ESR measurables at $T^* = 8 \text{ K}$, usually associated with a magnetic phase transition to a long-range ordered state of a conventional three-dimensional antiferromagnet. An enormous width of the signal $\Delta H \sim 12 \text{ T}$ at $T = 5 \text{ K}$ suggests a broad distribution of internal fields in the ground state characteristic of only a short-range order. This is consistent with a continuous

broadening of the ^{27}Al NMR signal across T^* and down to $T \ll T^*$. The spectrum remains broad and structureless even at the lowest temperature, whereas a long-range collinear AFM order should generally give rise to the narrowing and structuring of the single-crystalline NMR spectrum. The T^* can be therefore considered rather as a crossover temperature and not as a phase transition point. This is particularly clear for the measurements in the magnetic field, though in the zero field μSR the strongly damped muon spin rotation frequency indicating a rather inhomogeneous magnetic system develops rather sharp as a function of temperature and follows closely the intensity of the magnetic Bragg peak (Fig. 9, top inset).

Obviously the disorder due to the site inversion turns out to be optimally tuned in the studied single crystal of CoAl_2O_4 to obtain insights onto its implications for the properties of the phase diagram of the diamond spin lattice at the proximity to the critical point $J_2/J_1 = 1/8$ from the collinear side. It appears that quenched impurities smear the boundary between the two phases possibly due to local modulation of exchange constants J_1 and J_2 . Also, as conjectured in Ref. [15], owing to the proximity of CoAl_2O_4 to the critical point where the spin stiffness vanishes, fluctuations of the spiral wave vector may become large. As a result, there maybe a competition of collinear and noncollinear ground states with the low lying spiral excitations responsible for an inhomogeneous spin dynamics as revealed by our local spin probes. This calls for a theoretical study of this interesting regime.

V. CONCLUSIONS

We have addressed the low-energy spin dynamics and the ground state properties of the CoAl_2O_4 single crystal [16] with a moderate Al/Co site inversion parameter $x \approx 0.08$ with three local spin probes, ESR, NMR, and μSR spectroscopies. Given the degree of the site disorder and the proximity of CoAl_2O_4 to the critical exchange constant ratio $J_2/J_1 = 1/8$ which separates the collinear and noncollinear AFM phases, it

offers an opportunity to study the special role of impurities for the magnetism of frustrated antiferromagnets on the diamond lattice near the critical point. All three techniques provide clear indications of an inhomogeneous slow spin dynamics at elevated temperatures followed by a gradual crossover to a quasistatic state at $T \leq T^* = 8$ K. The ordering is most likely short range with spin fluctuations persistent even at $T \ll T^*$.

The data analysis unravels an interesting regime in the phase diagram where tunable disorder has a nontrivial impact on the magnetism of a frustrated diamond spin lattice antiferromagnet. Strong disorder is well known to have a conventional effect of inducing a spin glass state, whereas small disorder in spin lattices with small frustration usually simply lowers the ordering temperature, e.g., due to spin dilution. It appears that increasing disorder can give an unusual effect beyond these two limiting cases especially if the spin lattice is close to a critical instability as in CoAl_2O_4 . Though the exact mechanism is yet to be elucidated, it is conceivable that moderate disorder may facilitate coexistence of phases separated by the critical point and boost low-energy spin fluctuations, e.g., due to local modulation of competing exchange interactions that smears the phase boundary. It is appealing to address this problem theoretically.

ACKNOWLEDGMENTS

This work has been supported in part by the Deutsche Forschungsgemeinschaft (DFG) through project KA 1694/8-1, projects B01 and C2 of SFB 1143, and by the Russian Foundation for Basic Research through project RFBR 14-02-01194. S.W. acknowledges funding by DFG with Emmy Noether project WU 595/3-1. M.I. acknowledges support of the Russian Government Program of Competitive Growth of Kazan Federal University. Part of this work was performed at the Swiss Muon Source, Paul Scherrer Institut, Villigen, Switzerland.

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