Critical behavior of the $\text{Mn}_2[\text{Nb}(\text{CN})_8]$ molecular magnet

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Complementary experimental methods such as μSR spectroscopy, ac magnetometry, and relaxation calorimetry have been employed as a probe of critical behavior of a unique ferrimagnetic molecular magnet $\{[\text{Mn}^{\text{II}}(\text{pydz})(\text{H}_2\text{O})_2][\text{Mn}^{\text{II}}(\text{H}_2\text{O})_2][\text{Nb}^{\text{IV}}(\text{CN})_8]\cdot 2\text{H}_2\text{O}\}_n$ with $T_c \approx 42$ K. A full set of critical exponents is determined. Static exponents α , β , γ , and the dynamic exponent w are extracted directly from the measurements. Further critical exponents ν , η , and z are derived on the basis of scaling or hyperscaling relations. The knowledge of the thermal dependence of the order parameter combined with the results of the calorimetric measurements allowed for the determination of two further static critical exponents κ and κ' . The system shows a close affinity to the three-dimensional (3D) Heisenberg model. Ferrimagnetism of the compound leads to a coexistence of typically ferro- and antiferromagnetic characteristics.

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I. INTRODUCTION

Molecular magnetism has been enjoying remarkable popularity both with chemists and physicists ever since the first successful synthesis of two ferro(ferri)magnetic molecular compounds in 1986.^{1,2} In contrast to conventional magnetic materials whose preparation requires high-temperature metallurgical routes, molecular magnets can be obtained at ambient temperature employing the self-assembly technique. Unceasing interest in this field is fostered by the fact that the properties of molecular magnets can be fine tuned by designing a case specific organic synthesis paths. To its most notable achievements belong among others single-molecule³ or single-chain magnets,^{4,6} room-temperature molecular magnets⁷ as well as molecular compounds showing technologically desirable multifunctionality, such as those exhibiting ferromagnetic behavior and second-order optical nonlinearity,⁸ magnetism in a mesoscopic phase,⁹ photoinduced magnetism,^{10–12} or magnetic spongelike behavior.^{13,14} Molecular magnets are formed through bridging paramagnetic cation centers with organic ligands. Among the wealth of ligands used in engineering new molecular magnets¹⁵ a prominent position is taken by the cyanide anions, which were demonstrated to lead to a rich variety of structures and functionalities.^{16–18}

An important feature of most molecule-based magnets is the fact that the constituent magnetic moments are well localized providing a natural testing ground for the predictions of existing spin models. The signatures of the nature and symmetry of magnetic interactions are known to be inscribed in the values of the corresponding critical exponents, which renders the studies of critical behavior a sound complementary method aimed at unravelling magnetic structure of a system as demonstrated, e.g., in Refs. 19 and 20. The present work reports a comprehensive analysis of the critical behavior of a novel molecular

magnet based on Mn^{II} and $[\text{Nb}^{\text{IV}}(\text{CN})_8]$.²¹ Its full chemical formula reads $\{[\text{Mn}^{\text{II}}(\text{pydz})(\text{H}_2\text{O})_2][\text{Mn}^{\text{II}}(\text{H}_2\text{O})_2][\text{Nb}^{\text{IV}}(\text{CN})_8]\cdot 2\text{H}_2\text{O}\}_n$, where “pydz” stands for pyridazine ($\text{C}_4\text{H}_4\text{N}_2$). Single crystal x-ray diffraction at room temperature was solved with the monoclinic system with space group $P2_1/c$ and with unit cell parameters: $a = 10.6052(1)$ Å, $b = 15.5751(2)$ Å, $c = 14.3869(2)$ Å, and $\beta = 108.285(1)^\circ$. The compound represents a three-dimensional (3D) cyanido-bridged framework composed of corrugated square-grid motifs parallel to the bc crystallographic plane and involving alternating arrangement of Mn^{II} and Nb^{IV} centers. These are linked at the Nb^{IV} centers by the ladder motifs running along the a crystallographic axis, see Fig. 1. There are two distinct Mn^{II} sites: the ones (Mn1) build the ladder motifs whereas the other (Mn2) are incorporated in the square-grid motifs. Mn1 is linked by cyanide bridges to three Nb^{IV} ions, while Mn2 to four Nb^{IV} centers. The lengths and dihedral angles of the Nb-C-N-Mn linkages are different in every case, indicating the presence of seven different exchange couplings. Each Nb^{IV} ion is surrounded by eight cyanide ligands of which one CN^- group is terminal and hydrogen-bonded to the oxygen atom of the aqua ligand coordinated to Mn1 . In the pyridazine ligand ($\text{C}_4\text{H}_4\text{N}_2$), one nitrogen atom is noncoordinating and hydrogen-bonded to the aqua ligand of Mn2 .²¹ Because of the lack of coordination for these two nitrogen atoms, we expect that their vicinities may host muon stopping sites.

The most striking physical property of this compound is a two-step shift of the ordering temperature toward higher temperatures observed upon dehydration.²¹ The first stage of dehydration involving the removal of the crystallization water and two aqua ligands enhances the intranetwork exchange interaction and triggers the increase of magnetic ordering temperature up to 68 K. Further dehydration leading to the removal of the remaining two water molecules affects the increase of the critical temperature up to 100 K. The

FIG. 1. (Color online) Crystal structure of $\text{Mn}_2[\text{Nb}(\text{CN})_8]$. Mn_2 sites together with Nb sites form corrugated square-grid motifs parallel to the bc crystallographic plane. The grids are cross linked by the ladder motifs formed by Mn1 sites resulting in a 3D extended network of coupled magnetic moments.

dehydration process is fully reversible, which places the compound among the technologically promising materials.

In the present contribution, we focus on the critical behavior of the as synthesized fully hydrated compound with transition temperature $T_c \approx 42$ K. To determine the corresponding critical exponents complementary experimental techniques have been used ranging from the magnetic ac susceptibility measurements, through calorimetric measurements up to μSR spectroscopy. This wide spectrum of experimental techniques enabled to determine a full set of critical exponents, both static (α , β , γ , ν , η) and dynamic (w , z). Apart from the standard exponents two further static exponents κ and κ' appearing in the combined scaling of excess entropy and order parameter are estimated.

The paper is organized as follows. In Sec. II, experimental details are provided. Section III deals with the critical behavior as revealed by the ac susceptibility measurement and provides the critical exponents β and γ . In Sec. IV, heat capacity measurements are reported yielding the critical exponent α . Further insight into the critical behavior is based on the versatile μSR spectroscopy technique. The ensuing values of the static critical exponents β and γ as well as the dynamic critical exponent w are determined and reported in Section V. The knowledge of the thermal dependence of the order parameter combined with the results of the calorimetric measurements allows for the determination of exponents κ and κ' , which is reported in Sec. VI. The findings of the work are summarized and discussed in the concluding Sec. VII.

II. EXPERIMENTAL

A powder sample of $\text{Mn}_2[\text{Nb}(\text{CN})_8]$ was obtained from aqueous solution of $\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$, pyridazine, and $\text{K}_4[\text{Nb}(\text{CN})_8] \cdot 2\text{H}_2\text{O}$ of ratio 5 : 50 : 1.²¹ Magnetic ac susceptibility measurement was carried out with the Lake Shore 7225 instrument in the temperature range of 4.2–250 K, in zero dc field, and with $H_{\text{ac}} = 5$ Oe for an array of frequencies $f = 10, 80, 625, 1000$ Hz. Magnetic measurements were carried out with MPMS SQUID magnetometer. Isothermal

magnetization curves recorded up to 5 T were measured at the temperatures ranging from 30 K up to 60 K. Close to T_c , the M - H data were collected at temperature intervals equal to 1 K. The heat capacity measurement was performed with the PPMS Quantum Design instrument by the relaxation calorimetry technique in the temperature range of 2–300 K. The μSR experiments were performed both at the ISIS Muon Facility in the UK and at the $S\mu\text{S}$ facility of the Paul Scherrer Institute, Switzerland using, respectively, ARGUS and GPS instruments. The latter instrument enabled the zero-field (ZF) precession studies of the magnetically ordered phase requiring fast time resolution. The pulsed nature of the muon source in the former instrument giving rise to temporal broadening by the 80-ns pulse width precluded the observation of the fast spin precession signals in the ordered phase. The output of the μSR experiments was analyzed with the help of WIMDA software²² and MATHEMATICA8.0 environment.

III. MAGNETIC PROPERTIES

Figure 2(a) shows temperature dependence of dc susceptibility detected at $H = 2$ kOe. It increases abruptly below approximately 50 K reaching the value of $24.84 \text{ cm}^3 \text{ mol}^{-1}$ at $T = 4.2$ K, which indicates a transition to a magnetically ordered phase. The isothermal magnetization, depicted in the insert of Fig. 2(a), saturates in the field of ≈ 5 kOe at the value of $9.51(1) \mu_B$. This is lower than the value of $11 \mu_B$ expected for all ferromagnetic couplings and slightly higher than that of $9 \mu_B$ expected for all antiferromagnetic couplings suggesting ferrimagnetic and weakly noncollinear arrangement of the constituent magnetic moments. The Nb-Mn1 and Nb-Mn2 distances range from ≈ 5.38 to $5.53 \text{ \AA}$, and from 5.44 to $5.60 \text{ \AA}$, respectively. Besides, the angles Mn-N-C are on average by $\approx 10^\circ$ higher for the linkages with Mn2 than for those with Mn1. These two facts indicate that the averaged molecular-field constant $|\lambda_{\text{Mn1Nb}}|$ may be larger than $|\lambda_{\text{Mn2Nb}}|$. Neglecting the coupling between sublattices Mn1 and Mn2 ($\lambda_{\text{Mn1Mn2}} = 0$) as there is no direct linkage between these ions, the molecular-field prediction for the susceptibility in the paramagnetic regime was calculated, see Appendix. On fixing the values of the spectroscopic factors at $g_{\text{Nb}} = g_{\text{Mn1}} = g_{\text{Mn2}} = 2.0$ it was fitted to the inverse susceptibility data in the temperature range of 68–170 K yielding for the molecular-field constants the negative values of $-41.9(1)$ and $-7.0(2) \text{ cm}^3 \text{ mol}^{-1}$. The experimental data with the best-fit curve are shown in Fig. 2(b). The higher absolute value should be assigned to molecular constant λ_{Mn1Nb} , whereas the lower one to λ_{Mn2Nb} . This is consistent with the inequivalence of the cyanido-bridges linking the Mn1 and Mn2 sublattices with the Nb sublattice. The average angle Mn1-N-C in the Mn1-NC-Nb linkages amounts to 153.6° and is less than its counterpart of 162.2° in the Mn2-NC-Nb linkages. This with the fact that significant deviations from linearity of the M -N-C angle (M is a metal) may lead to nonzero overlap between the underlying system of orbitals and introduce sizable antiferromagnetic contribution to the overall interaction^{23–26} seems to speak in support of this inequality $|\lambda_{\text{Mn1Nb}}| > |\lambda_{\text{Mn2Nb}}|$. In conclusion, the above findings indicate consistently that the coupling between the Nb sublattice and both the Mn sublattices is of antiferromagnetic character.

FIG. 2. (Color online) (a) Temperature dependence of the dc susceptibility of $\text{Mn}_2[\text{Nb}(\text{CN})_8]$ measured in $H = 2$ kOe. Below 50 K, an abrupt increase of the susceptibility values is observed marking the transition to a magnetically ordered phase. (Insert) Isothermal magnetization detected at $T = 4.37$ K. A rapid saturation at the value of $9.51(1) \mu_B$ is visible indicating a weakly noncollinear ferrimagnetic phase. (b) The inverse of the dc susceptibility signal. Solid line shows the best fit to the molecular field prediction in the high-temperature paramagnetic regime.

Temperature dependence of the ac susceptibility shows an unusually sharp anomaly at $T_c = 43$ K, see Fig. 3(a), revealing the transition to an ordered phase. Large values of the ac signal persisting below the transition temperature indicate that the compound can be classified as a soft magnet. The weak frequency dependence excludes the spin-glass-like behavior. To get insight into the critical behavior of the system, the static scaling analysis of χ_{ac} was performed using the classical scaling relation

$$\chi = c \left(\frac{T}{T_c} - 1 \right)^{-\gamma}. \quad (1)$$

Figure 3(b) shows the corresponding log-log scaling plot. The value of critical exponent $\gamma = 1.36(1)$ is found to be close to that corresponding to the three-dimensional (3D) Heisenberg model (≈ 1.4). It will be shown in what follows that it is

also consistent with the TF mode of the μSR experiment (see Sec. V).

Besides the critical analysis of the ac susceptibility signal, an independent approach was taken based on the dc measurements of the isothermal magnetization at temperatures covering the vicinity of the transition temperature. The critical exponents β and γ were determined by the Kouvel-Fisher (KF) method²⁷ using two quantities:

$$X(T) = \chi_0^{-1}(T) [d\chi_0^{-1}(T)/dT]^{-1} = \frac{T - T_c}{\gamma}, \quad (2)$$

$$Y(T) = M_s(T) [dM_s(T)/dT]^{-1} = \frac{T - T_c}{\beta}. \quad (3)$$

The method involves an iterative procedure in which a generalized Arrott-Noakes plot $[M^{1/\beta}]$ versus $(H/M)^{1/\gamma}$ is constructed. From it, the values of M_s are computed from the

FIG. 3. (Color online) (a) Temperature dependence of the real component of the ac susceptibility χ_{ac} for $\text{Mn}_2[\text{Nb}(\text{CN})_8]$. A sharp anomaly at $T_c \approx 43$ K marks the transition to a magnetically ordered phase. The weak frequency dependence excludes the spin-glass-like behavior. High levels of signal below the transition point imply magnetic softness of the compound. (b) Scaling plot of the ac susceptibility signal. The best-fit curve (solid line) was obtained by relaxing γ . The value of T_c was estimated from the μSR experiment and it was fixed at 42.08 K during the fitting procedure.

FIG. 4. (Color online) (a) Temperature dependence of quantities X and Y as obtained in the final step of the iterative Kouvel-Fisher procedure. The slopes of the straight solid lines yield the inverses of exponents β and γ , respectively. (b) Logarithmic scaling plot of $M|t|^{-\beta}$ vs $H|t|^{-(\beta+\gamma)}$ in the critical region evidence the validity of the critical exponents and the T_c value obtained from KF method. Inset: the same plot in a linear scale.

intercepts on the ordinate of the plot below T_c , whereas the values of χ_0 are calculated from the intercept on the abscissa of the plot for temperatures above T_c . These are subsequently used to determine $X(T)$ and $Y(T)$ in the critical region, which are linear functions of temperature with the slopes $1/\gamma$ and $1/\beta$, respectively [see Eqs. (2) and (3)], yielding newer values for β and γ . The procedure finishes when the desired convergence of the parameters is achieved. Figure 4(a) depicts the outcome of the final step of this procedure. The ensuing critical exponents and critical temperature are $\beta = 0.38(2)$, $\gamma = 1.35(5)$, and $T_c = 42.1(1)$ K. The reliability of the obtained exponents and temperature of magnetic ordering can be checked by comparison of the results with the prediction of the scaling hypothesis. For magnetic systems, the scaling equation of state can be written as

$$M(H, t) = t^\beta f_\pm \left(\frac{H}{t^{\beta+\gamma}} \right), \quad (4)$$

where f_+ for $T > T_c$, f_- for $T < T_c$ are smooth functions. Equation (4) indicates that $M|t|^{-\beta}$ plotted versus $H|t|^{-(\beta+\gamma)}$ should give two different curves: one for $T > T_c$ and another for $T < T_c$. Scaling plots presented in Fig. 4(b) corroborate the proper determination of critical exponents and the value of T_c for the studied compound.

IV. HEAT CAPACITY

The heat capacity measurement in zero applied field revealed a well-defined λ -shaped anomaly at 41.8 K (the peak position), see Fig. 5(a), bearing out the presence of a magnetic continuous phase transition. The peak temperature is slightly lower than the value found from the magnetic data (see Sec. III). To extract the magnetic excess heat capacity ΔC_p , the observed C_p values within the range 58–81 K above the transition temperature, can be expressed by the sum of the lattice heat capacity $C_p(\text{lattice})$ and the magnetic heat capacity

FIG. 5. (Color online) (a) Total heat capacity in zero magnetic field measured on powder sample. The λ -shaped anomaly signals the presence of a magnetic continuous phase transition. Solid line represents the baseline used to extract the magnetic contribution to the heat capacity. (b) Magnetic excess heat capacity. Solid lines represent the best fits to the scaling function. A negative value of critical exponent α is consistent with the 3D Heisenberg model.

contribution due to short-range order C_{mag} (short-range order). C_p (lattice) can be approximated by a polynomial function of temperature with cubic and higher-order terms, while C_{mag} (short-range order) is represented by a term proportional to T^{-2} . Thus the observed heat capacity within the range of 58–81 K can be described as

$$C_p = C_p(\text{lattice}) + C_{\text{mag}}(\text{short-range order}) \\ = \sum_{i=3}^n a_i T^i + b T^{-2}. \quad (5)$$

Fitting Eq. (5) with $n = 6$ to the experimental heat capacity values yielded $C_p(\text{lattice})/\text{JK}^{-1} \text{mol}^{-1} = 5.9998 \times 10^{-3} (T/\text{K})^3 - 1.5857 \times 10^{-4} (T/\text{K})^4 + 1.6265 \times 10^{-6} (T/\text{K})^5 - 6.0019 \times 10^{-9} (T/\text{K})^6$, and $b = 11.4766 \times 10^3 \text{ J K mol}^{-1}$. The lattice heat capacity $C_p(\text{lattice})$ thus determined extrapolated down to 0 K defined the baseline [solid curve in Fig. 5(a)]. The magnetic excess heat capacity ΔC_p was calculated by subtracting from the observed heat capacity the lattice heat capacity, see Fig. 5(b). To calculate the entropy change associated with the transition low temperature behavior of ΔC_p was additionally analyzed. Function fT^μ was fitted to the magnetic excess heat capacity in the range of 1.98–7.53 K. It corresponds to the low-temperature contribution from spin-wave excitations $C_{\text{SW}} \propto T^{d/n}$, where d denotes the dimensionality of the spin lattice and n is the exponent in the magnonic dispersion relation. The best fit yielded $f = 0.069(2) \text{ J K}^{-(1+\mu)} \text{ mol}^{-1}$ and $\mu = 2.16(1)$. The value of exponent μ is closer to the value of $3/2$ corresponding to the $T^{3/2}$ Bloch law expected for magnonic excitations in a 3D ferromagnet than to that of 3 expected for a 3D antiferromagnet. This best-fit function was next used to estimate the entropy contribution in the temperature range 0–1.98 K yielding $0.1 \text{ J K}^{-1} \text{ mol}^{-1}$. The entropic contribution in the temperature range 1.98–81 K was obtained by numerical integration of the area under the excess heat-capacity peak $S = \int \Delta C_p d \ln T$. It amounts to $33.6 \text{ J K}^{-1} \text{ mol}^{-1}$. Finally, the high temperature excess heat capacity bT^{-2} was used to estimate the entropic contribution above 81 K giving $0.9 \text{ J K}^{-1} \text{ mol}^{-1}$. The total entropy change thus amounts to $34.6 \text{ J K}^{-1} \text{ mol}^{-1}$ and is slightly lower than the value of $R \ln(6^2 \times 2) = 35.56 \text{ J K}^{-1} \text{ mol}^{-1}$ expected for one $1/2$ spin originating from the Nb^{IV} ion and two $5/2$ spins contributed by the Mn^{II} ions.

The scaling analysis of the magnetic excess capacity ΔC_p was performed by fitting the function

$$\Delta C_p = \frac{A}{\alpha} \left(\left| \frac{T - T_c}{T_c} \right|^{-\alpha} - 1 \right) \quad (6)$$

independently above T_c (for $T < 50 \text{ K}$) and below T_c (for $T > 20 \text{ K}$). To account for the elevated heat capacity shoulder for $T < T_c$, an additive constant B was introduced. The best fits [solid lines in Fig. 5(b)] yielded $A' = 4(1) \text{ J K}^{-1} \text{ mol}^{-1}$, $B' = 16(1) \text{ J K}^{-1} \text{ mol}^{-1}$, $\alpha' = -0.2(1)$, $A = 7.1(3) \text{ J K}^{-1} \text{ mol}^{-1}$, and $\alpha = -0.20(2)$, where primes refer to $T < T_c$. The result is consistent with the scaling prediction $\alpha = \alpha'$. The negative exponents imply that ΔC_p is finite at T_c with amplitudes equal to $B' - A'/\alpha' = 36(16) \text{ J K}^{-1} \text{ mol}^{-1}$ and $-A/\alpha = 35.5(6) \text{ J K}^{-1} \text{ mol}^{-1}$, respectively, which is in agreement with the continuous character of the transition.

The value of exponent α is close to that expected for the 3D Heisenberg model ($\alpha = -0.14$).²⁸

V. MUON SPIN ROTATION SPECTROSCOPY

Muons are ideally suited to studying the magnetic fluctuations and spin dynamics in the neighborhood of a phase transition. Hence the most straightforward application of the muon spin rotation/relaxation spectroscopy is the investigation of the critical behavior of a magnetic material. What is most important in this technique is that one does not need to subject the sample to external magnetic field to get a signal, which is impossible in other methods. Fully spin-polarized muons are precessing in the local field at the muon stopping site. The trajectory of that precession is traced by the positron emission and registered by the backward and forward detectors. The time evolution of the spin polarization of the implanted muons was detected by measuring the asymmetry function $A(t)$ given by

$$A(t) = \frac{N_B - N_F}{N_B + N_F}, \quad (7)$$

where N_F and N_B denote the numbers of decay positrons emitted forward and backward, respectively. It was demonstrated^{29–31} that, if only the critical region is reasonably broad, μSR provides a perfect means to extract a complete set of static and dynamic critical exponents. Firstly, the frequency shift in a small transverse field (TF) detected in the paramagnetic regime yields the γ exponent. Secondly, implanted muons in magnetically ordered phase precess in the local magnetic field with frequency directly proportional to the magnitude of that field, which enables one to obtain the β exponent determining the asymptotic behavior of order parameter near the transition point. And finally, the longitudinal muon spin relaxation is sensitive to the spin correlation time giving the exponent w describing the slowing down of critical fluctuations. The remaining exponents ν , η , and z can be estimated using a set of scaling relations.³²

A. transverse field (tf) mode

In the TF mode the sample is subject to the external magnetic field perpendicular to the direction of the muon beam. Due to that the magnetic moments of muons are precessing around the local magnetic field direction giving rise to the detected oscillations of the decay-positron signal. If the only component of the local field was the external magnetic field B_0 , the frequency of the oscillations would be proportional to that field, i.e., $f_0 = \gamma_\mu B_0/2\pi$, where $\gamma_\mu = 2\pi \times 135.5 \text{ MHz T}^{-1}$. As the TF field fixed during the measurement was equal to 20 G, the unperturbed frequency is $f_0 \approx 0.271 \text{ MHz}$. Such a situation would be probably encountered far away from the phase transition, in the paramagnetic state, where the dynamics of the constituent magnetic moments is highly uncorrelated. Yet, if one approaches the transition temperature from above, the spin fluctuations start to be more and more coherent resulting in building up an enhanced magnetic “polarizability” of the sample expressed in terms of the magnetic susceptibility χ . This, in turn, leads to the contribution B_{ind} to the local magnetic field induced by the presence of the external

magnetic field B_0 ; $B_{\text{ind}} \sim \chi B_0$. This contribution together with the external field results in the total field $B_{\text{total}} = B_0 + B_{\text{ind}}$ in the direction parallel with the external field B_0 if the sample can be assumed to be magnetically isotropic. It is this resultant field that is “felt” by the muons and that determines the observed frequency of the aforementioned oscillations. Phenomenologically, the field B_{ind} may be related to the magnetic susceptibility divergent at the transition, i.e.,

$$B_{\text{ind}} = b \left(1 - \frac{T}{T_c}\right)^{-\gamma}, \quad (8)$$

where $b \sim B_0$. Thus the observed “gross” frequency is given by the formula

$$f = \frac{\gamma_\mu B_{\text{total}}}{2\pi} = f_0 + \frac{\gamma_\mu b}{2\pi} \left(1 - \frac{T}{T_c}\right)^{-\gamma}. \quad (9)$$

The corresponding relative change of frequency due to approaching the phase transition then reads

$$\frac{f - f_0}{f_0} = \frac{\gamma_\mu b}{2\pi f_0} \left(1 - \frac{T}{T_c}\right)^{-\gamma}. \quad (10)$$

From the last Eq. (10), one can see that the relative value of the frequency shift may be used to determine the critical exponent γ . Figure 6(a) shows the frequency dependence detected in the TF mode as a function of temperature. It can be seen that the observed frequency lies always above the reference value f_0 corresponding to the external magnetic field $B_0 = 20$ G present during the measurement. However, the temperature dependence clearly fails to be a monotonic one. Far above the transition temperature of ~ 42 K the signal starts at an elevated level, then first slightly increases while temperature is lowered, then decreases below the initial level, and finally abruptly increases in the close proximity of the phase transition. While the steep increase of the frequency is consistent with the expected enhanced fluctuation level signaling the onset of the magnetic ordering, it is difficult to rationalize its thermal behavior further above the transition. We therefore concentrate

only on the analysis of the pretransitional effects with the view to obtaining an estimate of the exponent γ . The main difficulty of this task consists in the fact that one does not know the exact value of the reference frequency f_0 . This, in turn, is essential for a precise determination of γ . The other source of problem in this particular instance of the measurement is that there are not enough points to build up a reliable statistics. For these two major reasons we failed to determine unambiguously the value of the critical exponent γ , nevertheless, we are in the position to provide a consistency estimate of its value. Let us consider separately two subsets comprising two experimental points each, designated by full squares (lower subset) and triangles (upper subset) in Fig. 6(a). The subsets contain only two points as any threesome of them fails to reveal an accelerated increase with lowering temperature as formula in Eq. (10) suggests. For each subset, the following operations are performed. For the fixed values of the transition temperature T_c as well as the reference frequency f_0 , a straight line is drawn through the points in the log-log coordinates and the slope-related exponent γ is saved. The values of the parameters T_c and f_0 are taken from the intervals $(T_{\text{cmin}}, T_{\text{cmax}})$ and $(f_{0\text{min}}, f_{0\text{max}})$, respectively. Finally, the contour plots in the plane (f_0, T_c) are prepared. They are shown for the two subsets in Fig. 6(b). The minimal temperature for both subsets was set at $T_{\text{cmin}} = 41.5$ K. The maximal temperatures were, respectively, $T_{\text{cmax}} = 42.2$ and 42.02 K for the lower and upper subsets, and correspond to the minimal temperature attained in the given subset. The minimal value of the reference frequency was set at $f_{0\text{min}} = 0.271$ MHz, whereas the maximal values were assumed to be equal to $f_{0\text{max}} = 0.2726$ and 0.2753 MHz for the lower and upper subsets, respectively. They are chosen to correspond to the minimal frequency value attained in the given subset. The solid lines in Fig. 6(b) single out the contours corresponding to the value of $\gamma = 1.4$. It can be seen that for both subsets this value suggested by the findings of Sec. III is consistent for an array of T_c 's and f_0 's. However, only for the lower subset (solid line in the left upper corner), the corresponding interval of T_c lies closer to the value of 42.1 K revealed by the ac susceptibility measurements. In conclusion,

FIG. 6. (Color online) (a) Frequency of muon oscillations detected in the TF mode as a function of temperature. The solid line shows the reference level corresponding to the external magnetic field of $B_0 = 20$ G present during the measurement run. (b) Contour plots of the functions $\gamma = g(f_0, T_c)$ obtained on the basis of two subsets of points denoted in part (a) of the plot by squares and triangles. Thick solid lines show the contours corresponding to the value of $\gamma = 1.4$. See text for further details.

the above simple analysis shows that the value of $\gamma = 1.4$ is consistent with the μSR measurement in the TF mode, and the level of the true reference frequency may not exceed the lowest experimental point in Fig. 6(a). However, the increased values of frequencies observed far above the transition temperature still defy our understanding.

B. Zero-field (ZF) mode

Figure 7 shows the muon spin relaxation detected in the vicinity of the magnetic transition. Spontaneous oscillations observed in the time dependence of the asymmetry function $A(t)$ below 46 K indicate the presence of quasistatic local magnetic field causing a coherent precession of the spins of those muons with a spin component perpendicular to this local field. Their presence provides unambiguous evidence of the presence of long-range magnetic order in that temperature regime, in agreement with the ac susceptibility and heat capacity measurements. The frequency of these oscillations is related to the local field by $\nu_\mu = \gamma_\mu B/2\pi$. Four precession frequencies were observed in the measured asymmetry spectra implying several magnetically unique stopping sites in the material. To corroborate the presence of at least four different oscillatory components in the ZF signal we show the discrete Fourier transform of the asymmetry signal detected at 20.18 K, see Fig. 8. Four well separated peaks are apparent. Let us stress that on increasing the temperature the corresponding fields (frequencies) shift towards zero. This incurs the problem that the close lying frequencies may no longer be resolved while approaching the transition temperature from below. Unfortunately, this was the case in this study. We were able to obtain all four frequencies with acceptable resolution only at two lowest temperatures 20.18 and 35.44 K. At higher temperatures, only three frequencies denoted by f_1 through f_3 have been resolved. The temperature dependence of the

FIG. 7. (Color online) Time dependence of the ZF asymmetry function detected in the vicinity of the transition point. The onset of spontaneous oscillations in the relaxation signal below 46 K reveals the transition to a magnetically ordered phase. Solid line shows the fit to the sum of four damped oscillatory components.

FIG. 8. Discrete Fourier transform of the time dependence of the ZF asymmetry function detected at 20.18 K. The frequency scale has been expressed in terms of magnetic field strength. The spectrum is dominated by four resolved frequencies.

corresponding local magnetic fields is shown in Fig. 9. The three complete data sets of local fields were simultaneously fitted to the phenomenological form

$$B(T) = B(0) \left[1 - \left(\frac{T}{T_c} \right)^\sigma \right]^\beta, \quad (11)$$

where parameter σ pertains to the low-temperature properties governed by spin-wave excitations. While the exponent β determines the asymptotic behavior near the transition point. The best fit yields $\sigma = 1.55(5)$, $\beta = 0.38(1)$, $T_c = 42.08(3)$ K, and $B_1(0) = 399(12)$ G, $B_2(0) = 1312(20)$ G, $B_3(0) = 2312(38)$ G. The value of $B_4(0) = 1840(45)$ G was determined a posteriori by fixing the parameters T_c , σ , and β at the best-fit values. Let us note that the value of the exponent

FIG. 9. Temperature dependence of the local magnetic field as inferred from the μSR experiment. Solid line shows the fit to the phenomenological law $B(T) = B(0)[1 - (T/T_c)^\sigma]^\beta$. Four components of the internal field were found reflecting four possible muon stopping sites in the sample.

β falls very close to that predicted for the 3D Heisenberg model (≈ 0.38 , see Ref. 33), which is perfectly consistent with the findings of Sec. III, where bulk magnetic measurements were analysed. The parameter σ is consistent with the value of $3/2$ expected for ferromagnetic magnons, corroborating the findings of the heat capacity analysis. A comment on the value of σ would be in order here. For ferrimagnets in a bipartite lattice,^{34–36} the elementary magnetic excitations are known to split into two branches. One excitation branch, in accordance with the Goldstone theorem,³⁷ starts off at zero (gapless acoustic magnons), while the energy in the other branch remains finite for all values of the wave vector (gapped optical magnons). It is thus the acoustic modes that determine the thermal behavior of the total magnetization at low temperatures. Exhibiting a quadratic (ferromagnetic) dispersion relation in the long-wavelength limit, they lead to the $T^{3/2}$ Bloch-like dependence of the relative reduction of the total magnetization above 0 K. The above holds also for the reported compound, although its structure is more complex involving three nonequivalent sublattices with different coordination numbers and exchange integrals, as due to the Goldstone theorem one acoustic branch with ferromagnetic dispersion relation will always be present in addition to two optical branches.

To determine the approximate position of the muon stopping sites, the calculation of the dipole-field distribution was performed. We assumed antiparallel alignment of the Mn^{II} and Nb^{IV} magnetic moments and oriented them along the b crystallographic axis coinciding with the two-fold screw axis of the system. As the μSR experiment was performed on a polycrystalline sample it is difficult to take duly into account the demagnetizing field. Let us only mention that its maximal value in this compound can be estimated to amount to ≈ 1860 G and is expected to affect considerably lower local fields. What we calculated was the magnitude of the dipole field $|\mathbf{B}_{\text{dip}}(\mathbf{r})|$ corrected for the Lorentz spherical cavity field $B_{\text{Lor}} = 4\pi M/3$ aligned along the b axis. The contributions to the local field were summed over magnetic sites inside a sphere of radius ≈ 60 Å. Due to their uncompensated negative charge the terminal CN^- ligands are good candidates to capture the incident muons. Figure 10 shows the contour plot of $|\mathbf{B}_{\text{dip}}(\mathbf{r})|$ in the cross sections of the unit cell parallel to the crystallographic planes at the position of one out of four symmetry related N atoms. To reveal the orientation of the ligands the carbon atom is also shown. Besides, three nearest lying water molecules are shown. The contour lines corresponding to the values of $B_i(0)$ ($i = 1, \dots, 4$) found from the analysis of the ZF asymmetry signal run all close to the N atom confirming the possibility of muons stopping near the terminal cyanide ligands.

FIG. 10. Contour plot of the magnitude of the dipole field in the cross sections of the unit cell parallel to the crystallographic planes at the position hosting one out of four symmetry related N atoms of the terminal CN^- ligands. To reveal the orientation of the ligands the C atom is also shown. Besides, three nearest lying water molecules are shown. The contour lines corresponding to the values of $B_i(0)$ ($i = 1, \dots, 4$) found from the analysis of the ZF asymmetry signal run all close to the N atom confirming the possibility of muons stopping near the terminal cyanide ligands.

hydrogen N-H-O bonds. Yet this issue will be addressed elsewhere.

C. Longitudinal field (LF) mode

The temperature dependence of the muon longitudinal relaxation rate λ , originating from the muon-lattice interaction, reveals a sharp peak at ~ 42 K, which marks the transition to the long-range order state, see Fig. 12(a). In the fast fluctuation regime, it is directly proportional to the diverging spin correlation time $\tau \propto |T - T_c|^{-w}$ corresponding to the slowing down of critical fluctuations. The scaling analysis

FIG. 11. Contour plot of the magnitude of the dipole field in the cross sections of the unit cell parallel to the crystallographic planes at the position hosting the noncoordinated N atom of the pyridazine ligand. To reveal the vicinity of the atom, the whole ligand together with the nearest water molecule are depicted. The contour lines corresponding to the values of $B_i(0)$ ($i = 1, \dots, 4$) found from the analysis of the ZF asymmetry signal run all close to the N atom confirming the possibility of muons stopping near that position.

FIG. 12. (Color online) (a) Temperature dependence of the ZF muon longitudinal relaxation rate λ . (b) Scaling plot of λ for $T > T_c$ gives the dynamic critical exponent $w = 0.11(1)$.

of λ near T_c , depicted in Fig. 12(b), yields the value of the dynamic critical exponent $w = 0.11(1)$. In the fit the transition temperature $T_c = 42.08$ K found from the ZF mode was assumed, see Sec. VB. It will be shown in what follows to be consistent with the dynamical model of an isotropic antiferromagnet. Apart from the thermal dependence of the longitudinal relaxation rate, we also studied the field dependence of the nonprecessing longitudinal component of the polarization function. Figure 13 shows longitudinal polarization as a function of external magnetic field detected at two temperatures: 5 and 41.5 K. At the presence of an external magnetic field B parallel to the muon beam, in the case where the internal field seen by the muon takes the single value B_0 and for randomly oriented polycrystalline magnet, the longitudinal repolarization function A_z on appropriate orientational averaging takes the form³⁸

$$A_z(b) = \frac{3}{4} - \frac{1}{4b^2} + \frac{(b^2 - 1)^2}{8b^3} \ln \left| \frac{b+1}{b-1} \right|, \quad (12)$$

FIG. 13. (Color online) Longitudinal polarization as a function of external magnetic field detected at 5 and 41.5 K. In the legend, the corresponding values of the averaged local fields are listed.

where $b = B/B_0$. Fitting function $A A_z(B/B_0) + A_{bg}$ to the experimental results yields $B_0 = 1196(8)$ G and $B_0 = 525(6)$ G at $T = 5$ and 41.5 K, respectively. Although, the fitted formula in Eq. (12) corresponds to a single muon stopping site, while in the case under study, four such sites are anticipated, one can venture a rough consistency check with the results obtained in the analysis of ZF mode of Sec. VB. One can base the estimate of parameter $B_0(T)$, where its dependence on temperature is implied, on two major premises. The first one is the fact that the temperature dependence of the local field at each stopping site is given by the formula in Eq. (11). The other one is that the presence of several stopping sites can be roughly taken into account by appropriately weighing their contributions to $B_0(T)$. We propose here simple weighing factors using the amplitudes of the oscillating components of the asymmetry function A_i ($i = 1, \dots, 4$), i.e.,

$$w_i = \frac{A_i}{\sum_{i=1}^4 A_i}. \quad (13)$$

Then, the temperature dependence of parameter B_0 is given by the following formula

$$B_0(T) = \sum_{i=1}^4 w_i B_i(0 \text{ K}) \left[1 - \left(\frac{T}{T_c} \right)^\sigma \right]^\beta. \quad (14)$$

Employing the formula and using the amplitudes found at 35.44 K, $A_1 = 0.6(1)\%$, $A_2 = 1.7(6)\%$, $A_3 = 0.2(1)\%$, and $A_4 = 0.2(2)\%$, one obtains $B_0(T = 5 \text{ K}) = 1205$ G and $B_0(T = 41.5 \text{ K}) = 283$ G. The first value is perfectly consistent with the value found from the fit, whereas the other value disagrees with the fitted one by over 40%, yet a rough agreement is attained. The lack of the precise correspondence may be due to the fact that a more elaborate approach should be taken where several values of the local field are to be considered.

FIG. 14. (Color online) (a) $\Delta S/Q^2$ versus $(T_c - T)/T_c$ in log-log plot for $\text{Mn}_2[\text{Nb}(\text{CN})_8]$. The experimental points tend to align while approaching the transition temperature, which signals the algebraic scaling behavior. Solid line shows the corresponding linear fit yielding the exponent κ . The arrow shows the temperature of ≈ 29 K, at which a crossover to the scaling regime takes place. (b) Log-log plot of the excess entropy ΔS as a function of the square of order parameter Q^2 . The alignment of the data while approaching the transition temperature is apparent. The linear fit (solid line) gives the exponent κ' . The arrow is the same as in (a).

VI. COMBINED SCALING OF EXCESS ENTROPY AND ORDER PARAMETER

The main advantage of the ZF μSR spectroscopy is the direct insight into the thermal behavior of the order parameter related to the nonvanishing internal fields marking unambiguously the onset of the transition to an ordered phase. This crucial information can be combined with that gleaned from the complementary calorimetric measurement to further characterize the critical behavior. The critical laws for specific heat and order parameter imply the validity of a combined scaling of excess entropy and the square of order parameter²⁸ below the transition point T_c :

$$\frac{\Delta S}{Q^2} \propto \left(1 - \frac{T}{T_c}\right)^\kappa, \quad (15)$$

where κ is the corresponding critical exponent related to critical exponents α and β ,

$$\kappa = \begin{cases} 1 - \alpha - 2\beta & \alpha > 0, \\ 1 - 2\beta & \alpha \leq 0. \end{cases} \quad (16)$$

Equivalently, this scaling relation between both quantities can be also expressed by the following law:

$$\Delta S \propto Q^{2\kappa'}, \quad (17)$$

where

$$\kappa' = \begin{cases} (1 - \alpha)/2\beta & \alpha > 0, \\ 1/2\beta & \alpha \leq 0. \end{cases} \quad (18)$$

The excess entropy was calculated numerically from the excess heat capacity data,

$$\Delta S = \int_0^\epsilon \frac{\Delta C_p}{1 - \epsilon'} d\epsilon', \quad (19)$$

where $\epsilon = 1 - T/T_c$. As the multiplicative factors are irrelevant in the scaling analysis, the thermal dependence of the order parameter was replaced by that of the local field obtained from the μSR experiment, cf. Fig. 9. Figures 14(a)

and 14(b) show that the experimental points tend to align while approaching the transition temperature. The ensuing asymptotic linear behavior yields the following values of the exponents: $\kappa = 0.219(3)$ and $\kappa' = 1.294(4)$. These values are close to 0.26 and 1.31, respectively, predicted for the 3D Heisenberg model.²⁸ Using Eqs. (16) and (18) for $\alpha < 0$ and the value of $\beta = 0.38(1)$ found in μSR experiment, one obtains $\kappa = 0.24(2)$ and $\kappa' = 1.32(3)$, which are both consistent with the values determined from the scaling analysis.

VII. CONCLUSIONS

Table I recapitulates those critical exponents that have been found in this work by applying complementary experimental methods. For comparison, the static critical exponents for two model systems: the mean-field and the 3D Heisenberg models, have been listed. It can be seen that the 3D Heisenberg universality class satisfactorily matches the critical behavior of the studied compound. Let us also note that the exponents α , β , and γ found from the corresponding scaling laws reproduce well the Rushbrooke scaling relation, yielding $\alpha + 2\beta + \gamma = 1.9(2)$, which agrees with the expected value of 2. Using the hyperscaling relations $\nu = (2 - \alpha)/d$ and $\eta = 2 - \gamma/\nu$, where $d = 3$ is the spatial dimension, one can calculate the remaining static critical exponents. For ν , one obtains 0.73(3), which is close to the value of 0.71(2) expected for

TABLE I. Critical exponents determined in this work for $\text{Mn}_2[\text{Nb}(\text{CN})_8]$ (3) and for three model systems: the mean-field model (1) and the 3D Heisenberg model (2).²⁸ The values of exponents κ and κ' were calculated for the first two entries using the relations given by Eqs. (16) and (18).

	α	β	γ	κ	κ'	w
(1)	0	0.5	1	0	1	...
(2)	-0.14(8)	0.37	1.38	0.26	1.31	...
(3)	-0.2(1)	0.38(1)	1.35(5)	0.219(3)	1.294(4)	0.11(1)

the 3D Heisenberg model.³³ For η , one arrives at the positive value of 0.2(1) as expected for a continuous transition.³² It is known that the exponent η governs the asymptotic behavior of the correlation function at the critical point, $G(r) \propto r^{-(d-2+\eta)}$. Hence, its enhanced value corresponding to a stronger falloff of spatial correlations may be related with the short-range character of the exchange interactions in the system under study. Finally, the exponent w is related to the dynamic exponent z and two static exponents by $w = \nu(z + 2 - d - \eta)$.³⁹ To derive the z exponent from the measured exponents, let us combine the last formula with the hyperscaling relations to obtain $z = d(2 + w - \gamma - \alpha)/(2 - \alpha) = 1.3(3)$. This estimate is consistent with the value of $d/2 = 1.5$ expected for dynamical model G of isotropic antiferromagnet.³⁹

In conclusion, the full set of static and dynamic critical exponents for the cyanido-bridged molecular magnet $\text{Mn}_2[\text{Nb}(\text{CN})_8]$ has been determined using complementary experimental methods. The resultant exponents are consistent with the universality class of the 3D Heisenberg model. It has been demonstrated that for a ferrimagnetic material, like this studied here, both ferromagnetic (the $T^{3/2}$ Bloch law, the low-temperature magnetic heat capacity) and antiferromagnetic (the dynamical z exponent) hallmarks may coexist. Further studies of molecular magnetic materials are bound to further verify or discover the rules governing condensed matter at criticality.

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APPENDIX: MOLECULAR-FIELD PREDICTION

Let us consider three magnetically coupled sublattices. The magnetizations of these sublattices in the paramagnetic regime

are proportional to the local magnetic field,

$$M_i = \chi_i H_i, \quad (\text{A1})$$

where $i = 1, 2, 3$, and χ_i is the susceptibility of the i th sublattice. The local fields can be written as follows:

$$H_i = H + \sum_{j \neq i} \lambda_{ij} M_j, \quad (\text{A2})$$

where H is the external magnetic field and $\lambda_{ij} = \lambda_{ji} (\neq 0 \text{ for } i \neq j)$ are the molecular-field constants. Inserting Eq. (A2) into Eq. (A1), one arrives at Cramer's system of linear equations, which is readily solved for M_i yielding

$$\chi = \frac{M_1 + M_2 + M_3}{H} = \frac{N}{D}, \quad (\text{A3})$$

where

$$\begin{aligned} N &= \chi_1 + \chi_2 + \chi_3 \\ &+ 2(\lambda_{12}\chi_1\chi_2 + \lambda_{13}\chi_1\chi_3 + \lambda_{23}\chi_2\chi_3) \\ &- (\lambda_{12}^2 + \lambda_{13}^2 + \lambda_{23}^2)\chi_1\chi_2\chi_3 \\ &+ 2(\lambda_{12}\lambda_{23} + \lambda_{13}\lambda_{23} + \lambda_{12}\lambda_{13})\chi_1\chi_2\chi_3 \end{aligned} \quad (\text{A4})$$

and

$$D = 1 - \lambda_{12}^2\chi_1\chi_2 - \lambda_{13}^2\chi_1\chi_3 - \lambda_{23}^2\chi_2\chi_3 - 2\lambda_{12}\lambda_{13}\lambda_{23}\chi_1\chi_2\chi_3. \quad (\text{A5})$$

The susceptibilities of the sublattices are given by the Curie paramagnetic law $\chi_i = C_i/T$ with

$$C_i = \frac{N_A g_i^2 S_i(S_i + 1)}{3k_B}, \quad (\text{A6})$$

where N_A is the Avogadro number, g_i is the Landé spectroscopic factor, S_i is the spin quantum number, and k_B is the Boltzmann constant. The molecular-field constants are related to the exchange coupling constants J_{ij} ,

$$\lambda_{ij} = \frac{z J_{ij}}{N_A \mu_B^2 g_{\text{avg}}^2}, \quad (\text{A7})$$

where z is the number of the nearest neighbors and $g_{\text{avg}} = \sqrt{g_i g_j}$ is the mean spectroscopic factor.

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