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Scaling analysis of $[Fe(pyrazole)_4]_2[Nb(CN)_8]$ molecular magnet

P. Konieczny [a,*], R. Pełka [a], P.M. Zieliński [a], F.L. Pratt [b], D. Pinkowicz [c], B. Sieklucka [c], T. Wasiutyński [a]

[a] Institute of Nuclear Physics, Polish Academy of Sciences, Radzikowskiego 152, 31-342 Kraków, Poland
[b] ISIS Facility, Rutherford Appleton Laboratory, Chilton, Oxfordshire OX11 0QX, United Kingdom
[c] Department of Chemistry, Jagiellonian University, Ingardena 3, 30-060 Krakow, Poland

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ABSTRACT

The critical behaviour of the three dimensional (3D) molecular magnet $\{[Fe^{II}(pirazol)_4]_2[Nb^{IV}(CN)_8]\cdot 4H_2O\}_n$ has been studied with the use of experimental techniques such as ac magnetometry and zero field μSR spectroscopy. The sample orders magnetically below $T_c = 7.8$ K. The measurements allowed to determine static exponents β, γ, and the dynamic exponent w. The resulting exponent values indicate that the studied system belongs to the universality class of the 3D Heisenberg model.

1. Introduction

Molecular magnets are of great interest from the viewpoint of chemistry and condensed matter physics because their properties can be designed by a careful selection of building blocks in the chemical process. The possibility of a rational design of the physicochemical properties of molecular magnets at the synthesis stage is their major advantage over classical magnetic materials. One of the possible criteria that can be used to classify these compounds is the dimensionality of their coordination network [1–4].

In the present paper we focus on the critical behaviour of molecular magnet $\{[Fe^{II}(pyrazole)_4]_2[Nb^{IV}(CN)_8]\cdot 4H_2O\}_n$. The experimental results were analyzed using the scaling laws to describe the sample in the critical region and extract the critical exponents. This investigation allowed us to compare the behaviour of the sample with existing magnetic models.

The sample under study, is a 3D coordination polymer. This compound was formed as a result of the self-assembly of $[Nb^{IV}(CN)_8]^{4-}$ with a Fe^{II} centre in aqueous solution with a high concentration of pyrazole ($C_3H_3N_2H$). This molecular magnet crystallizes in tetragonal $I4_1/a$ space group where Nb^{IV} and Fe^{II} ions are coordinated to each other through cyanide bridges and decorated with pyrazole molecules [5]. It is a unique 3D structure with one type of Fe^{II}–NC–Nb^{IV} linkage where interactions between Fe^{II} ions can be neglected (see Fig. 1). In this arrangement Nb^{IV} ions are linked to four Fe^{II} ions through CN bridges. At the same time, Fe^{II} centres are connected with only two nearest neighbour Nb^{IV} ions through CN links. The remaining four coordination sites of Fe^{II} are filled with pyrazole ligands. There are no direct connections between Fe^{II} ions. The coordination spheres of Fe^{II} centres have slightly distorted octahedral geometry. Eight C atoms of cyanide ligands are included in the coordination spheres of Nb^{IV}. Their geometry is that of a slightly distorted dodecahedron.

In the previous report on hybrid molecular magnets of general formula $\{[M^{II}(pyrazole)_4]_2[Nb^{IV}(CN)_8]\cdot 4H_2O\}_n$ (M^{II} = Fe, Co, Ni and Mn), a general characteristics of the magnetic properties of this family of compounds was presented [5]. On the mere basis of the dc magnetic measurements it was put forward that in the sample with M^{II} = Fe ($S_{Fe} = 2$, $g_{Fe} = 2.163(2)$, $S_{Nb} = 1/2$, $g_{Nb} = 2$) antiferromagnetic superexchange interactions through CN bridges with $J_{Fe-Nb} = -3.1(2)\,cm^{-1}$ leads to an ordered phase [5]. The value of J_{Fe-Nb} was estimated with the use of the molecular field model.

2. Experimental

The polycrystalline samples of the $\{[Fe^{II}(pyrazole)_4]_2[Nb^{IV}(CN)_8]\cdot 4H_2O\}_n$ were synthesized according to the methods reported in [5]. The X-ray powder diffraction pattern was obtained using the X'PERT PRO Pananalytical Diffractometer in order to ascertain that the sample contained a single phase. The ac magnetic susceptibility χ_{ac}

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[*] Corresponding author. Tel.: +48 12 662 8000.
E-mail address: piotr.konieczny@ifj.edu.pl (P. Konieczny).

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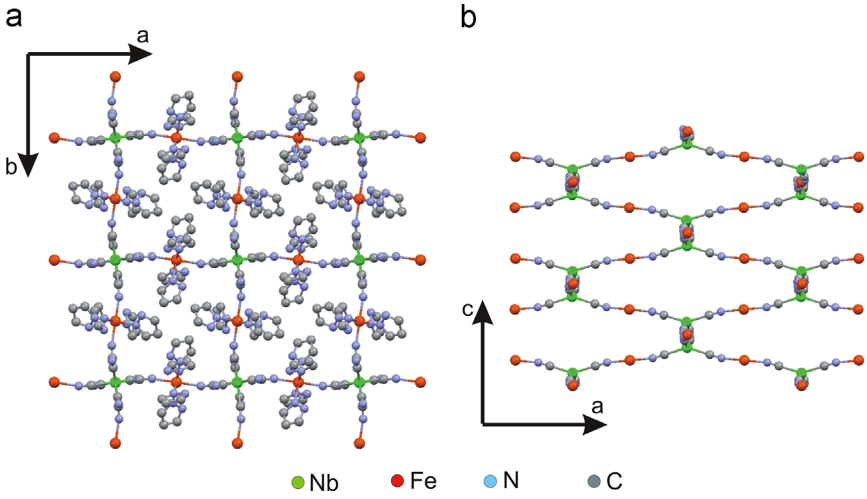

Fig. 1. Structure of $\{[Fe^{II}(pyrazole)_4]_2[Nb^{IV}(CN)_8]\cdot 4H_2O\}_n$. (a) View of the structure along the *c* crystallographic axis. The water molecules and hydrogen atoms are not shown for clarity. (b) View of the structure along the *b* crystallographic axis. All nonbridging cyanido ligands and the pyrazole ligands have been removed for clarity.

was obtained with the 7225 Lake Shore instrument in the temperature range 4.5–25 K in zero dc field with $H_{ac}=1$ Oe for an array of frequencies $f=10$, 60, 240, and 1000 Hz. The μSR zero-field (ZF) precession measurements were performed at the ISIS Muon Facility in the UK using ARGUS instrument. A powder sample was inserted into an envelope made of silver foil and mounted on a silver holder. Data from the μSR experiments were analyzed with WIMDA software [6].

3. Measurements and analysis

3.1. AC magnetometry

The results of the ac susceptibility measurements are presented in Fig. 2(a). A sharp peak of χ' at $T_c=7.8$ K is observed accompanied by the onset of the χ'' signal coming from the presence of a net magnetic moment in the ordered phase. Since the frequency dependence of the peak position is negligible the spin-glass state may be excluded. The classical scaling relation, which is applicable to 3D molecular magnets as systems of localized spin densities, in the form

$$\chi = c\left(\frac{T}{T_c}-1\right)^{-\gamma} \quad \text{where } T>T_c \qquad (1)$$

was used in the fitting region $|(T_c-T)/T_c|<0.2$ to extract the critical exponent γ from the high-temperature wing of the ac susceptibility, see Fig. 2(b). The obtained value of $\gamma=1.38(8)$ agrees well with the 3D Heisenberg model ($\gamma\approx1.4$ [7]).

3.2. Muon spin rotation

Positive muon spin rotation (μSR) measurements were used to get insight into the internal magnetic field in the compound, quasistatic on the microsecond scale and reflecting the temperature dependence of the order parameter. In this technique, positive spin-polarized muon (μ^+) beam hits a target sample. The muons rapidly lose their energy and usually end up in an interstitial position. μ^+ possesses its own magnetic moment, and when it is under the influence of local magnetic field it precesses with frequency proportional to that field, which makes it an excellent micro magnetic probe to investigate even very small magnetic fields (down to ~10^{-5} T) [8]. Information about the local magnetic field *B* at the muon site is obtained from the time evolution of the muon spin polarization, which is proportional to the asymmetry

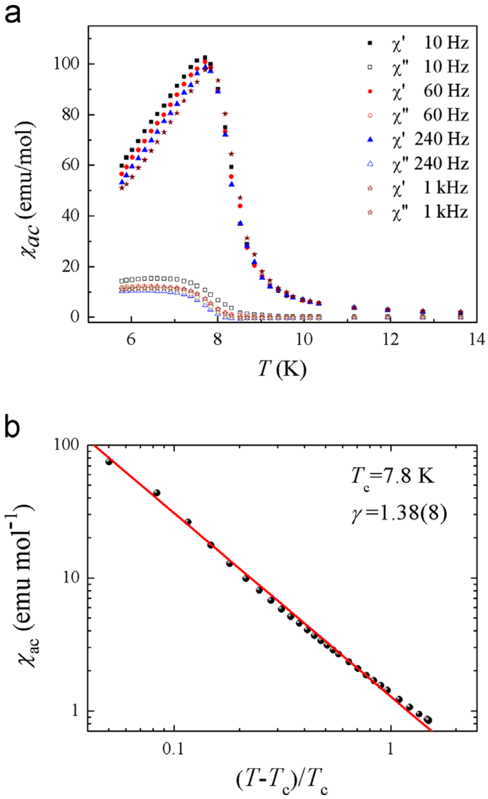

Fig. 2. (a) ac Susceptibility (both real and imaginary part) as a function of temperature with $H_{ac}=1$ Oe and $f=10$, 60, 240, and 1000 Hz. (b) Scaling log—log plot of ac susceptibility. T_c was determined by the maximum of χ'_{ac}. Solid line represents the best fit and implies the value of $\gamma=1.38(8)$.

function [8]. One of the applications of μSR is to follow the temperature dependence of the internal field without applying external field (zero field mode—ZF), which allows to extract the β critical exponent [9]. The value of β determines the temperature behaviour of the order parameter near the transition temperature. Furthermore, an extended analysis of damping of asymmetry oscillations provides an insight into the dynamical properties of the studied system by allowing one to determine the dynamic critical exponent *w*.

Fig. 4 shows several examples of ZF μSR spectra detected for a sample of $\{[Fe^{II}(pirazol)_4]_2[Nb^{IV}(CN)_8]\cdot 4H_2O\}_n$. The characteristic