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Studies on magnetic properties of unique molecular magnet $\{[Fe^{II}(pyrazole)_4]_2[Nb^{IV}(CN)_8]\cdot 4H_2O\}_n$

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Abstract. In this paper magnetic properties of hybrid inorganic-organic compound $\{[Fe^{II}(pyrazole)_4]_2[Nb^{IV}(CN)_8]\cdot 4H_2O\}_n$ are presented. This is a three dimensional molecular magnet with well localized magnetic moments, which make it a suitable candidate for testing magnetic models. In order to characterize the magnetic properties of the above compound we performed the AC/DC magnetometry in the range 0-5 T. The special attention was paid to the phase transition at 7.9 K. The study in magnetic field supports magnetic ordering below 7.9 K.

1 Introduction

The family of molecular magnets differs from classical magnetic materials because of specific properties of these compounds. What is characteristic of them is that their physicochemical behaviour can be designed at the stage of the process of synthesis. Molecular magnets have complex structure and features of both organic and inorganic materials. This unique properties are the reason why molecular magnets are of great interest from the point of view of chemistry and condensed matter physics.

2 Experimental

The self-assembly of $[Nb^{IV}(CN)_8]^{4-}$ with iron center in aqueous solution and an excess of pyrazole resulted in the formation of 3D network $\{[Fe^{II}(pyrazole)_4]_2[Nb^{IV}(CN)_8]\cdot 4H_2O\}_n$. It crystallizes in the $I4_1/a$ space group and shows cyanido-bridged structure decorated with pyrazole molecules coordinated to Fe^{II} centers [1]. It is a unique structure with one type of Fe^{II}-NC-Nb^{IV} linkage with negligible interaction between Fe ions. In this arrangement Nb is bridged by four CN to Fe and Fe is bridged to two Nb ions.

The ac magnetic susceptibility measurements were performed with Lake Shore 7225. The results presented here refer mainly to the value of Hac=5 Oe. Static susceptibility was measured by means of the Cahn RG electrobalance in the temperature range 4.2-300 K with 1 kOe applied field. DC magnetization as a function of applied field up to 55 kOe was performed for zero-field-cooled samples with the use of Lake Shore 7225.

3 Results

The magnetization as a function of applied field is presented in figure 1. The coercivity is on the order of single Oe's which indicates a soft magnetic character of the compound. Although 55 kOe magnetic field was applied, saturation was not observed. To extract the saturation magnetization (M_S), a polynomial formula:

$$M\left(\frac{1}{H}\right) = M_S + B\left(\frac{1}{H}\right) + C\left(\frac{1}{H}\right)^2 + D\left(\frac{1}{H}\right)^3 + E\left(\frac{1}{H}\right)^4 + \cdots \tag{1}$$

was fitted to isothermal magnetization. The obtained value was about $M_S \approx 8.0\ \mu_B$.

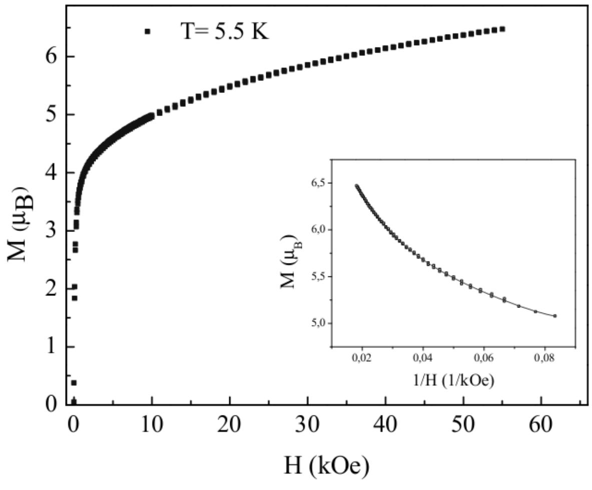

Fig. 1. Magnetization as a function of applied field in T=5.5 K. Insert, inverse magnetization as a function of inverse magnetic field with polynomial fit for saturation magnetization.

The temperature dependence of inverse dc susceptibility χ_{dc} measured in 1000 Oe field is presented in figure 2. It was analyzed with the use of the Curie-Weiss law in the form:

$$\chi = \frac{C}{T-\theta} + \chi_0 \qquad (2)$$

which resulted in values C=6.24·10^{-3} K·cm^3/g, μ_{eff}=7.17 μ_B/f.u., χ_0=1.62·10^{-5} cm^3/g and Θ=13.4 K. The positive value of Θ indicates a ferromagnetic coupling.

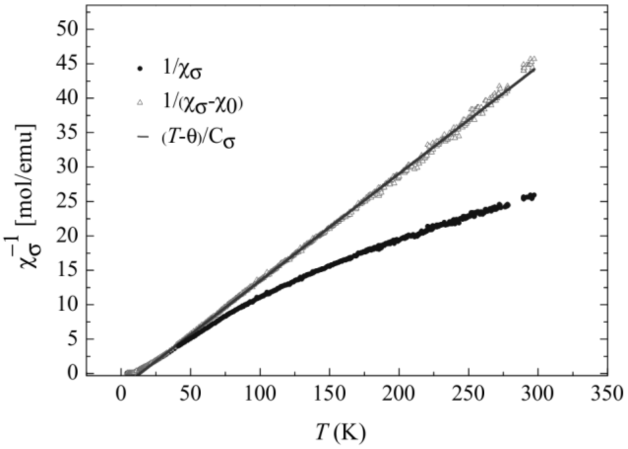

Fig. 2. Inverse susceptibility versus temperature with Curie-Weiss fit (solid curve).

The results of the ac susceptibility measurements are presented in figure 3. The temperature of the peak of χ' at T≈7.8 K is considered to be the critical temperature, below which the system orders magnetically. The spin glass is excluded because the frequency dependence is negligible. Both the high value of χ_{ac} and the low coercivity confirm the soft magnet behaviour. Classical scaling relation in the form:

$$\chi = c\left(\frac{T}{T_c} - 1\right)^{-\gamma} \qquad (3)$$

was used to extract critical exponent γ from the ac susceptibility, figure 4. The obtained value of γ=1.42±0.07.

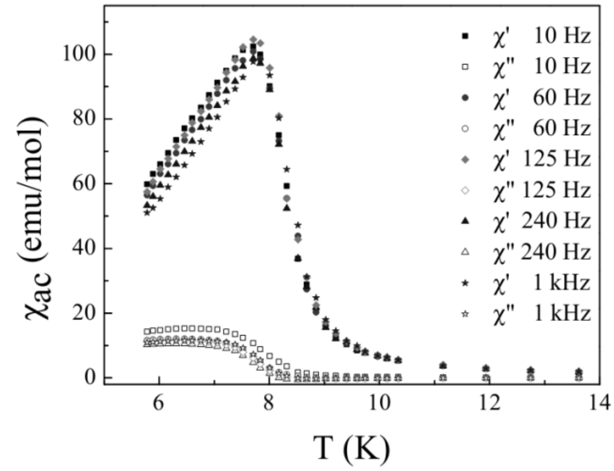

Fig. 3. AC susceptibility (both real and imaginary part) as a function of temperature with H_{ac}=5 Oe and f=10, 60, 125, 240, 1000 Hz.

To compare the value of the critical exponent γ from the classical scaling of χ_{ac} the Kouvel-Fisher method for the dc susceptibility (χ_σ) was used [2], with the defining formula:

$$X(T) = \chi_\sigma^{-1}(T)\left[\frac{d\chi_\sigma^{-1}(T)}{dT}\right]^{-1} = \frac{T-T_C}{\gamma} \qquad (4)$$

Figure 5 presents the X(T) as a function of temperature. The inverse of the slope of the best-fit line gives the value of γ = 1.45±0.06 consistent with the output of the classical scaling.

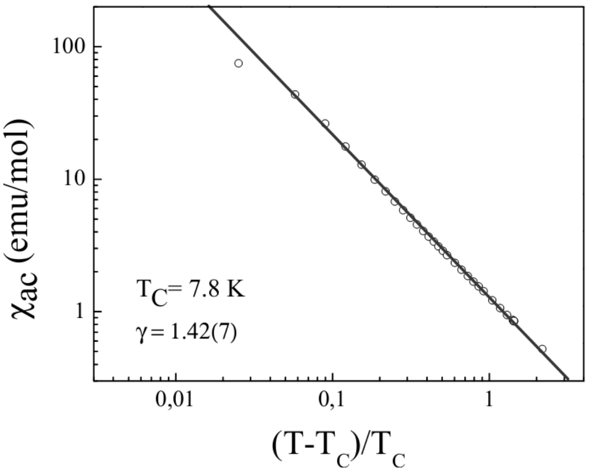

Fig. 4. Scaling plot of ac susceptibility. Solid line represents the best fit. T_c was determined by the maximum of χ_{ac}', which allowed to obtain the value of γ = 1.42(7).

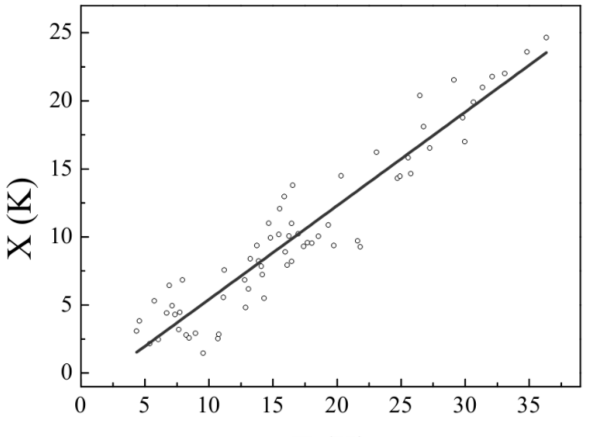

Fig. 5. Temperature dependence of X(T) from the Kouvel-Fisher method.

4 Conclusions

The positive value of Θ obtained from the Curie-Weiss analysis indicates a ferromagnetic coupling in which case all magnetic moments being parallel should result in the saturation value of the magnetization of ≈9.6 μ_B. However the extrapolated value of the magnetization saturation is ≈8.0 μ_B. This value is on the other hand slightly higher than 7.6 μ_B expected in the case of all the moments coupled antiferromagnetically. The value of the effective magnetic moment μ_{eff} and the saturation value M_S which both were found between the limiting values for antiferromagnetic and ferromagnetic arrangement, may be explained by a non-collinear magnetic system.

The value of γ=1.42±0.07 from the classical scaling agrees well with the 3D Heisenberg model (≈1.4 [3]). Also the result of the Kouvel-Fisher method points to this behaviour (γ=1.45±0.06). Moreover, the inequality of the effective magnetic moment and the magnetization saturation value M_S confirms a quantum model of magnetism in this sample. Nevertheless, further research will be carried out in the near future in order to clarify magnetic behavior of the compound.

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