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The Magnetocaloric Effect in $\{[Cu(bapa)]_3[Cr(CN)_6]_2\}_n \cdot 6nH_2O$ at Low Temperatures

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The crystals of $\{[Cu(bapa)]_3[Cr(CN)_6]_2\}_n \cdot 6nH_2O$ (bapa = bis(3-aminopropyl)amine) are formed by infinite Cu(II)–Cr(III) antiparallel chains, which are connected into the third direction by additive [Cu(bapa)] moieties. The onset of long-range magnetic order at 3.2 K was observed by AC susceptibility. The study of the magnetocaloric effect from magnetization measurements yields a large entropy change $-\Delta S_M = 13.65\ \mathrm{J\,K^{-1}mol^{-1}}$ ($-\Delta S_M = 12.25\ \mathrm{J\,kg^{-1}K^{-1}}$) at the field change from 0 T to 3 T at temperature 4 K. The analysis of the critical behavior of $-\Delta S_M$ suggests the value of critical exponent $n = 0.577$ at the ordering temperature characteristic for three-dimensional magnets with Ising anisotropy.

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1. Introduction

Magnetic refrigeration is a potential application, based on the magnetocaloric effect (MCE), that has aroused great interest recently. In the magnetic refrigeration cycle, a change in the magnetic entropy (ΔS_M) of the refrigerant upon removing the magnetic field (under adiabatic conditions) leads to the cooling of the system. Thus, MCE can be characterized as the adiabatic temperature change or the isothermal entropy change of materials when varying the external magnetic field. Both the sign and the extent of the temperature or entropy change between the initial and final state of the material depend on numerous intrinsic and extrinsic factors. The great number of materials with the significant MCE was found in recent years and their applicability temperature range is usually related to the occurrence of magnetic transitions [1]. For cryogenic applications, molecular magnets and magnetic clusters, mainly based on rare-earth ions, have proven to be promising systems [2]. In addition, the MCE can be used to gain fundamental insight into the characteristics of excitation spectra and magnetic phase transitions of studied materials.

Herein, the magnetothermal properties of a three-dimensional (3D) alternating spin system $\{[Cu(bapa)]_3[Cr(CN)_6]_2\}_n \cdot 6nH_2O$ (**1**), bapa is bis(3-aminopropyl)amine, are reported. A ferromagnetic (FM) long-range ordering (LRO) appears at $T_C = 3.2$ K and the analysis of susceptibility confirmed the presence of a strong FM exchange interaction [3]. Further AC susceptibility studies confirm the ordering temperature and the MCE close to T_C yields quite high entropy change $-\Delta S_M = 12.25\ \mathrm{J\,kg^{-1}K^{-1}}$ at field change from 0 to 3 T only. It is suggested from the analysis of field dependence of $-\Delta S_M$ at the ordering temperature that (**1**) represents a 3D FM system with Ising anisotropy.

2. Experimental details

The crystal structure of $\{[Cu(bapa)]_3[Cr(CN)_6]_2\}_n \cdot 6nH_2O$ (bapa = bis(3-aminopropyl)amine) is formed by infinite Cu(II)–Cr(III) antiparallel chains, which are connected by additional [Cu(bapa)] moieties into the 3D network (Fig. 1). The structural network yields an 1/2-3/2 spin alternation along the chains and in the third dimension also. Magnetic measurements were performed in a Quantum Design MPMS3 SQUID-VSM magnetometer on nascent polycrystalline sample with mass of 4.52 mg fixed in a polypropylene capsule held by a brass sample holder. Temperature dependences of the in-phase (χ') and out-of-phase (χ'') components of the AC susceptibility in zero static field was measured with the excitation alternating field 0.1 mT and frequency varying from 0.1 to 1000 Hz. The field dependence of magnetization from 0 to 3 T at each temperature between 1.8 and 5 K (with $\Delta T = 0.2$ K up to 4.4 K, then $\Delta T = 0.3$ K up to 5 K) was measured after cooling the sample in zero magnetic field from high enough temperature to prevent the possible preferential orientation of magnetic moments.

3. Results and discussion

AC magnetic measurements have been performed on (**1**) in the frequency range from 0.1 to 1000 Hz using the excitation field with excitation amplitude 0.1 mT in the temperature range from 1.8 to 4 K in order to confirm the presence of magnetic ordering are shown in Fig. 2. Temperature dependences of χ' and χ'' components of the AC susceptibility measured at different excitation frequencies shows a steep increase at $T_C = 3.2$ K. The frequency independent position of the peaks in χ' and

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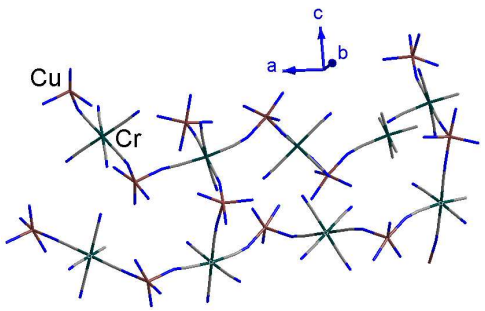

Fig. 1. Part of the 3D network formed by alternating Cu(II)–Cr(III) moieties in the crystal structure of (**1**). Cr, Cu, N, and C atoms only shown for clarity. For details of the crystal structure see Ref. [3].

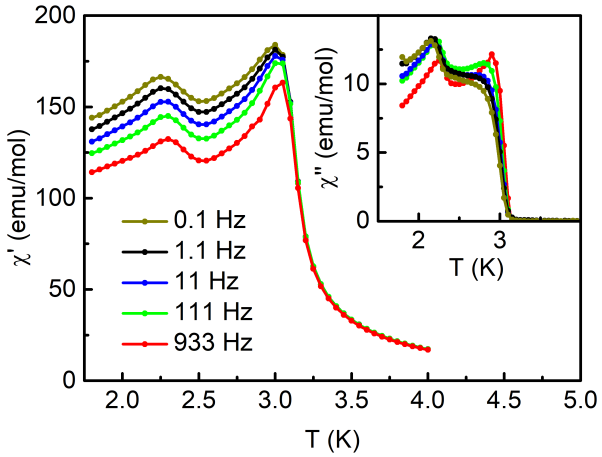

Fig. 2. Temperature dependence of χ' and χ'' (inset) at different frequencies of the excitation field.

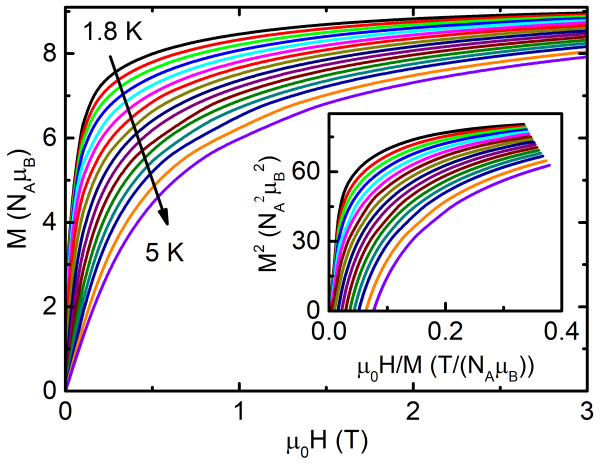

Fig. 3. Isothermal magnetization curves and Arrott plot (inset) of (**1**) in the temperature range from 1.8 to 5 K.

χ'' close to the ordering temperature confirms LRO. The order of the magnetic phase transition can be evidenced from the Arrott plots [4], constructed from the field dependence of isothermal magnetization (Fig. 3). The positive slope of renormalized curves $M^2 \propto H/M$ shown in the inset of Fig. 3 indicates the presence of the second-order phase transition in (**1**). On the other hand, a maximum observed in the temperature dependence of AC susceptibility below the LRO at 2.25 K is weakly frequency dependent.

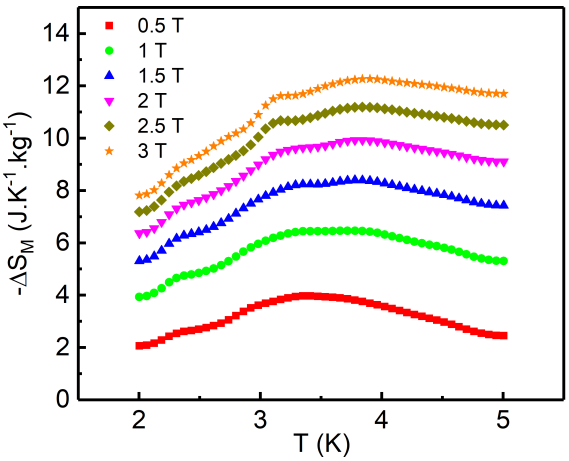

Fig. 4. Temperature dependence of the change of entropy $-\Delta S_M$ in (**1**) during isothermal magnetization from 0 T to different values of final field from 0.5 T to 3 T calculated using Maxwell equation from magnetization curves shown in Fig. 3.

The shift of the peak temperature T_P with the frequency $\omega$of the applied excitation field in χ', analyzed using Mydosh criterion [5], is $\Delta T_P/(T_P \Delta(\log\omega)) \approx 0.004$ which is a typical value for insulating spin glasses. The spin-glass behavior below the LRO temperature was also observed in Prussian-blue analogues [6] due to a structural disorder. One can speculate that in (**1**) the complicated structure consisting of interwoven chains [3] may lead to the presence of additional frustrating exchange couplings. This would result in the appearance of glassy state below the LRO temperature.

Following the analysis of magnetic ordering, the MCE response of (**1**) close to T_C was evaluated from the field dependence of magnetization (Fig. 3). The MCE response, specifically the change of entropy during isothermal magnetization $\Delta S_M = S_M(T, \mu_0 H_{final}) - S_M(T, 0)$, was calculated using well known thermodynamic Maxwell equation. The temperature dependence of the calculated ΔS_M during isothermal magnetization from 0 T to the final magnetic field $\mu_0 H_{final}$ (from 0.5 T to 3 T in 0.5 T steps), is shown in Fig. 4. A maximum in the temperature dependence of $-\Delta S_M$ was observed at 4 K, which is above the observed LRO temperature, with $-\Delta S_M = 12.25\ \mathrm{J\,kg^{-1}K^{-1}}$ ($-\Delta S_M = 13.65\ \mathrm{J\,K^{-1}mol^{-1}}$). Only a small bump with a slightly lower value of $-\Delta S_M$ was observed at T_C. Positive val-

ues of $-\Delta S_M$ are expected for the normal MCE. In the presence of a FM exchange coupling between magnetic ions in coordination complexes the maximum value of $-\Delta S_M$ is reduced, but it is possible to enhance the magnetic cooling performance at higher temperatures and in small fields in comparison with paramagnetic system [3]. The maximum value $-\Delta S_M = 13.65\ \mathrm{J\,K^{-1}mol^{-1}}$ for $\mu_0 H_{final} = 3$ T is much lower than a possible $-\Delta S_M = R\,(3\ln(2S_1+1) + 2\ln(2S_2+1)) = 40.34\ \mathrm{J\,K^{-1}mol^{-1}}$ achievable at very low temperatures by a paramagnet consisting from three $S_1 = 1/2$ and two $S_2 = 3/2$ ions per molecular unit as contained in the crystal structure of (**1**).

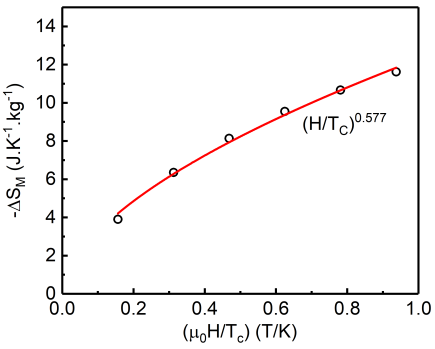

Fig. 5. The reduced-field dependence of $-\Delta S_M$ at constant temperature (at $T_C = 3.2$ K) extracted from Fig. 4 (open symbols) including a fit to the Eq. 1 (solid line) yielding critical exponent $n = 0.577$.

Probably due to a strong FM correlations most of the entropy is removed in a wide temperature range above the ordering temperature and the LRO occurs with a small entropy removal. For a quantitative comparison of MCE performance of (**1**) with other complexes, the maximum value of $-\Delta S_M = 12.25\ \mathrm{J\,kg^{-1}K^{-1}}$ for $\mu_0 H_{final} = 3$ T is important. It is not exceptionally high but with $\mu_0 H_{final} = 3$ T only is comparable or even higher than $-\Delta S_M$ obtained in other $3d$ ion based systems, including high-spin Mn(II) complexes [2].

The MCE close to the FM transition reflects the critical behavior of the spin system From the field dependence of isothermal $-\Delta S_M$ one can determine the exponent n describing $-\Delta S_M$ for materials with a second-order phase transition as

$$-\Delta S_M \propto (H/T_C)^n. \qquad (1)$$

In the Fig. 5 the extracted field dependence of $-\Delta S_M$ at T_C is shown including the fit of the Eq. 1 to experimental data yielding $n = 0.577$. The mean-field theory predicts that in the vicinity of a second-order phase transitions $n = 2/3$ [7, 8]. On the other hand, the n exponent at T_C is dependent on critical exponents β and γ through the relation $n\,(T_C) = 1 + \frac{\beta-1}{\beta+\gamma}$ [9, 10]. The value $n = 0.577$ obtained for (**1**) agrees well with the one calculated from β and γ corresponding to a 3D magnet with Ising anisotropy [11–13] and this approach was also applied to some similar 3D ferrimagnets [14, 15]. In the case of title compound the underlying anisotropy may originate from the single-ion anisotropy of Cr(III) ions.

4. Conclusions

Magnetothermal studies of alternating spin magnet $\{[\mathrm{Cu(bapa)}]_3[\mathrm{Cr(CN)_6}]_2\}_n \cdot 6n\mathrm{H_2O}$ revealed a large entropy change $-\Delta S_M = 12.25\ \mathrm{J\,kg^{-1}K^{-1}}$ at the field change from 0 to 3 T close to the magnetic ordering temperature, comparable even to some high-spin Mn(II) complexes. The analysis of the critical behavior of MCE suggests that the title compound can be characterized as a 3D magnet with Ising anisotropy with critical exponent $n = 0.577$.

Acknowledgments

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