

Magnetocaloric Effect in NiCl₂(bipy) at Low Temperatures

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Magnetothermal properties of the compound NiCl₂(bipy), where bipy = 4,4'-bipyridine, were studied. The single-ion anisotropy of Ni(II) ions was estimated and its influence on magnetocaloric effect in NiCl₂(bipy) was investigated. Above the metamagnetic transition a maximum in the isothermal change of the magnetic entropy is reached near 11 K at field change from 0 T to 7 T with peak value $-\Delta S = 6 \text{ J K}^{-1} \text{ kg}^{-1}$. The temperature dependence of ΔS above 7 K agrees with the assumed easy-axis type of single-ion anisotropy. The inverse magnetocaloric effect, typical for ordered antiferromagnets, was observed in the ordered state of NiCl₂(bipy) only for isothermal magnetization in small fields up to 2 T.

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1. Introduction

The magnetocaloric effect (MCE) is a magnetothermodynamic phenomenon based on the change of temperature caused when a material is exposed to an external magnetic field. The increased interest in the study of the MCE is mainly due to the possibility of applying this effect for magnetic refrigeration close to room temperature [1]. Until now, applications have been focused on cryogenic temperatures, employing paramagnetic salts [2]. Recently, molecular magnets and magnetic clusters, mainly based on rare-earth ions, have proven to be promising systems for cryogenic applications [3]. In addition, the MCE can be used to gain fundamental insight into the characteristics of excitation spectra and magnetic phase transitions. As a result of such studies, low-dimensional magnetic systems are considered good candidates for the observation of an enhanced MCE at low temperatures. The key prerequisites for observation of an enhanced MCE in such systems is a macroscopic degeneracy of the ground state with high residual entropy or a pronounced change of the magnetic entropy predicted close to the magnetic-field-induced quantum critical points [4, 5].

Herein, the magnetothermal properties of the $S = 1$ Heisenberg magnet NiCl₂(bipy), bipy is 4,4'-bipyridine (see the crystal structure in the inset of Fig. 1 [6]), are reported. While the dominant ferromagnetic (FM) exchange coupling exists along the $-\text{Ni}-\text{Cl}_2-\text{Ni}-$ chains (c -axis), an antiferromagnetic (AFM) long-range ordered state below 7 K was observed previously [7], also evidenced by a metamagnetic transition in field-dependence of the magnetization below the ordering temperature [8]. The orientation of ordered moments along the b -axis suggests it is an easy-axis of magnetization. Although, the dominant FM interaction estimated using Fisher's classi-

cal chain model is relatively weak (3.35 K) [9], the single-ion anisotropy of the Ni(II) ions as essential parameter for the description of the magnetic properties of Ni(II) complexes was not included in the previous analysis of magnetic properties of NiCl₂(bipy).

2. Results and discussion

Using a commercial Quantum Design SQUID magnetometer, the temperature dependence of susceptibility $\chi(T)$ of a nascent polycrystalline sample (determined as the ratio of the measured magnetic moment and the applied field of 100 mT) was measured in zero-field cooled regime in the temperature range from 2 K to 300 K (Fig. 1). A steep increase of the susceptibility at low temperatures, but above the ordering temperature, is evidence of the FM exchange coupling present in NiCl₂(bipy). A fit of the Curie-Weiss equation to the experimental data in the temperature range 50–300 K yields a Weiss temperature $\theta = 13.6$ K. Using a mean-field approximation for $S = 1$, the effective exchange coupling is calculated, neglecting the influence of single-ion anisotropy, as $zJ/k_B = 3\theta/2 = 20.4$ K with g -factor $g = 2$, where z is the number of the nearest neighbors [10]. For a FM chain with $z = 2$, the estimated exchange coupling is $J/k_B = 10.2$ K, which is higher than the reported value [9].

In order to estimate the single-ion anisotropy parameter D in NiCl₂(bipy), the results of magneto-structural correlation studies of octahedral Ni(II) complexes [11, 12] were used. Due to a very small rhombic distortion of the coordination octahedron, a possible rhombic parameter, E , was not included in the present analysis. The average Ni-Cl bond length necessary for the estimation of D was taken as an average value present in homoleptic Ni(II) complexes [13]. Our calculations yielded $D/k_B \approx -9$ K (with a deformation parameter $D_{str} = -7.1$ pm) and this value was used as a starting parameter for further analysis of the susceptibility and MCE. Assuming a strong easy-axis single-ion anisotropy as suggested from magneto-structural calculations, $\chi(T)$ can be analyzed by using

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$$\chi(T) = \frac{\chi_D(T)}{\left(1 - \frac{zJ}{N_A g^2 \mu_B^2} \chi_D(T)\right)}, \quad (1)$$

where N_A is the Avogadro constant, μ_B is the Bohr magneton, and the exchange coupling is introduced in terms of mean field theory [14, 15].

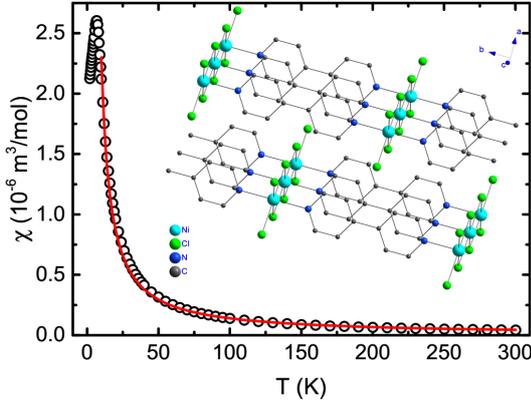


Fig. 1. Temperature dependence of susceptibility of NiCl₂(bipy) measured in an applied field of 100 mT after zero-field cooled protocol (open symbols). The solid line represents the fit to experimental data using Eq. (1). The inset shows the layered crystal structure of NiCl₂(bipy) (orthorhombic, space group $Cmmm$), layers are stacked along a -axis.

The susceptibility $\chi_D(T)$ representing the contribution of the single-ion anisotropy of Ni(II) ion was calculated for our polycrystalline sample as an average of the distribution of the magnetic-field vector over a triangular orientational grid using EasySpin package [16]. The fit of Eq. (1) to the experimental data yields $D/k_B = -21$ K, $zJ/k_B = 8.8$ K, and $g = 2.05$. It should be noted that the resulting exchange coupling $J/k_B = 4.4$ K ($z = 2$) is likely to be underestimated in comparison to the real one due to the influence of the AFM interchain exchange coupling.

Following the analysis of $\chi(T)$, the field dependence of magnetization was measured from 0 to 7 T at different temperatures from 2 to 30 K (as shown in the inset of Fig. 2) to evaluate the MCE response of NiCl₂(bipy). A pellet of NiCl₂(bipy) powder was used in the experiment to avoid possible re-orientation of the microcrystals in high magnetic fields due to the anisotropy. The field dependence of magnetization at each temperature was measured after cooling the sample in zero magnetic field from high enough temperature (15 K) to prevent the influence of a possible hysteresis in the ordered state. The MCE response, specifically the change of entropy during isothermal magnetization $\Delta S_M(T, B_{\text{final}}) = S(T, B_{\text{final}}) - S(T, 0)$, was then calculated using well known thermodynamic Maxwell equation. The temperature dependence of the calculated ΔS_M during isothermal magnetization from 0 T to B_{final} , where B_{final} changes from 1 T to 7 T in 1 T steps, is shown in Fig. 3. A maximum in the temperature dependence of $-\Delta S_M$ was observed at 11 K, positive values of $-\Delta S_M$ are expected for the normal MCE.

Well-developed inverse MCE typical for ordered Heisenberg AFM systems was observed in the ordered phase only close to 2 K and for isothermal magnetization up to 2 T (see Fig. 2), with the minimum $-\Delta S_M$ obtained at 1.25 T. This effect can be understood in connection with the observation of metamagnetic transition.

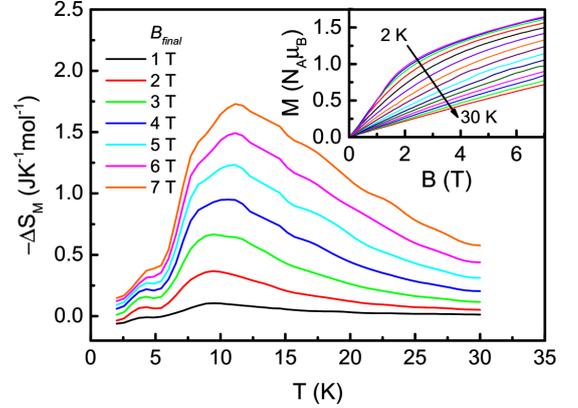


Fig. 2. Temperature dependence of the change of entropy $-\Delta S_M(T, B_{\text{final}})$ in NiCl₂(bipy) during isothermal magnetization from 0 T to different values of B_{final} calculated using Maxwell equation from magnetization curves shown in the inset.

Once the magnetic field is higher than the critical field of metamagnetic transition (slightly below 1 T) and the influence of AFM interchain exchange interaction is suppressed, normal MCE prevails and $-\Delta S_M$ increases and finally changes the sign for the magnetic fields above 2 T.

The influence of single-ion anisotropy and exchange coupling is to decrease the maximum value of $-\Delta S_M$. In the presence of a weak FM exchange coupling between magnetic ions, 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 $-\Delta S_M = 1.73$ J K⁻¹ mol⁻¹ for $B_{\text{final}} = 7$ T is much lower than a possible $-\Delta S_M = 9.13$ J K⁻¹ mol⁻¹ achievable at very low temperatures by a $S = 1$ paramagnet. Such reduction of maximum ΔS_M can be accounted to the influence of a strong single-ion anisotropy.

Figure 3 shows a simple comparison of $-\Delta S_M$ of powdered sample calculated for a $S = 1$ paramagnet, a $S = 1$ paramagnet including single-ion anisotropy, a $S = 1$ FM dimer including single-ion anisotropy. Parameters used for the simulation were obtained from the analysis of $\chi(T)$, namely $D/k_B = -21$ K, $J/k_B = 4.4$ K, and $g = 2.05$. Although, the maximum in $-\Delta S_M$ is shifted to lower temperatures in comparison with experimental results of NiCl₂(bipy), the simulation for a FM dimer displays similar features.

For a quantitative comparison of MCE performance of NiCl₂(bipy) with other complexes, the maximum value of $-\Delta S_M = 6$ J K⁻¹ kg⁻¹ for $B_{\text{final}} = 7$ T was calculated. It is not exceptionally high but is comparable to other 3d ion based systems, even including high-spin Mn(II)

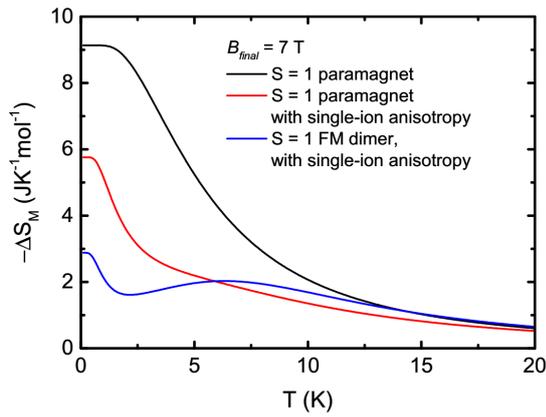


Fig. 3. Simulation of $-\Delta S_M(T, B_{\text{final}})$ where $B_{\text{final}} = 7$ T, for a $S = 1$ paramagnet (black line), a $S = 1$ paramagnet including single-ion anisotropy (red line), and a $S = 1$ FM dimer including single-ion anisotropy (blue line). Parameters used for the simulation are $D/k_B = -21$ K, $J/k_B = 4.4$ K, and $g = 2.05$.

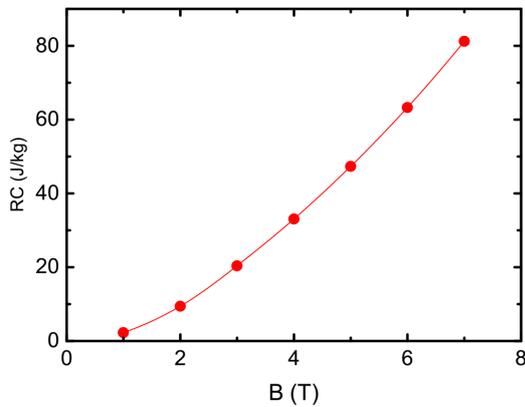


Fig. 4. The refrigerant capacity of $\text{NiCl}_2(\text{bipy})$ in a cooling cycle close to 11 K.

complexes [3]. Indeed, such a coolant could still be competitive because of a higher abundance of nickel (inexpensive, with simple preparation) in comparison with $4f$ ions based magnetic refrigerants. Another quantity for evaluation of MCE performance is the refrigerant capacity (RC), which can be calculated from ΔS_M using the formula

$$RC(\Delta B) = \int_{T_1}^{T_2} \Delta S_M(T, \Delta B) dT, \quad (2)$$

with ΔB as the difference between the minimum field (usually 0) and B_{final} , and T_1 and T_2 as the temperatures, where $-\Delta S_M$ reaches the half of the maximum value. The RC values obtained for $\text{NiCl}_2(\text{bipy})$ are shown in Fig. 4 with $RC = 81.2$ J/kg for $B_{\text{final}} = 7$ T.

3. Conclusions

Magnetothermal studies of the $S = 1$ Heisenberg magnet $\text{NiCl}_2(\text{bipy})$ show that strong easy-axis single-ion anisotropy needs to be taken into account to describe

the MCE observed in this compound. The maximum entropy change $-\Delta S_M = 6$ J K⁻¹ kg⁻¹ and refrigerant capacity $RC = 81.2$ J/kg during isothermal magnetization to $B_{\text{final}} = 7$ T can be possibly tuned by chemical design. The resulting reduction of single-ion anisotropy and/or decrease of ordering temperature could enhance the cooling performance and shift the working cycle to lower temperatures.

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