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Magnetocaloric effect in M–pyrazole– [Nb(CN)₈] (M = Ni, Mn) molecular compounds

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Abstract

We report a study of magnetocaloric effect (MCE) in cyanido-bridged $\{[M^{II}(pyrazole)_4]_2[Nb^{IV}(CN)_8]\cdot 4H_2O\}_n$ molecular compounds where M = Ni, Mn, pyrazole = $C_3H_4N_2$. The substances show a sharp phase transition to a long range magnetically ordered state, with ferromagnetic coupling between M and Nb sublattices in the case of the Ni-based sample 1 ($T_c = 13.4$ K) and ferrimagnetic coupling for the Mn-based sample 2 ($T_c = 23.8$ K). The magnetic entropy change ΔS due to applied field change ΔH as a function of temperature was determined by the magnetization and heat capacity measurements. The maximum value of ΔS at $\mu_0 \Delta H = 5$ T is 6.1 J mol⁻¹ K⁻¹ $(5.9 \text{ J kg}^{-1} \text{ K}^{-1})$ for **1** at T = 14 K and 6.7 $\text{ J mol}^{-1} \text{ K}^{-1}$ (6.5 $\text{ J kg}^{-1} \text{ K}^{-1}$) for **2** at T = 25 K. MCE data at different applied fields have been presented as one universal curve, which confirms magnetic transitions in 1 and 2 to be of second order. The temperature dependences of the *n* exponent characterizing the dependence of ΔS on ΔH have been obtained. The $n(T_c)$ values, consistent with the shape of the magnetization curves, pointed to the 3D Heisenberg behaviour for 2 and some anisotropy, probably of the XY type, for 1. The $(H/T_c)^{2/3}$ dependence of the maximum entropy change has been tested in the ferrimagnetic $Mn_2-L-[Nb(CN)_8]$ (L = C₃H₄N₂, C₄H₄N₂) series.

(Some figures may appear in colour only in the online journal)

1. Introduction

High interest in the study of the magnetocaloric effect (MCE) is motivated mostly by the search for materials which could be used for refrigeration. As is known, a measure of MCE is an isothermal magnetic entropy change ΔS or/and an adiabatic change of temperature, ΔT_{ad} , on withdrawing or applying the magnetic field ΔH . Previously, the effect was used for reaching temperatures lower than that of liquid helium by means of demagnetization of paramagnetic salts. The discovery of the giant magnetocaloric effect in Gd₅Si₂Ge₂ has been a turning point in a possible application of the effect in magnetic refrigeration near room temperature. The value

of ΔS found in that compound is 27 J kg⁻¹ K⁻¹ at 272 K for 2 T [1]. Now, the highest value of ΔS is observed for the MnAs material, which undergoes a combined structural and ferro-paramagnetic transition of the first order with ΔS reaching 32 J kg⁻¹ K⁻¹ at 2 T [2].

MCE is an intrinsic thermodynamic property of any magnetic solid. Besides para- or ferromagnets a sizeable MCE also occurs for ferrimagnets [3] or for antiferromagnets at the field induced metamagnetic transition [4]. The value of the effect depends on the temperature derivative of magnetization, thus ΔS achieves a maximum at the magnetic ordering temperature T_c . MCE at first order magnetic transitions may be in this respect more promising, but

thermal and magnetic hysteresis losses related to this type of transition may adversely affect the practical applications. Consequently, large attention is also paid to materials showing the second order magnetic phase transition. Investigations of magnetocaloric effect are also important from the fundamental point of view, because the dependence of ΔS on temperature and on magnetic field ΔH , as well as its value at T_c , are correlated to the magnetic characteristics of the material and to its critical behaviour. Several papers presenting the phenomenological description or the microscopic theory of the MCE have been published [5–8].

MCE in molecular materials has been relatively less explored. It has been investigated most of all for molecular nanomagnets, that is slowly relaxing molecules with large spin, named single molecule magnets (SMMs) [9]. Due to the large ground-state spin s of SMMs, the entropy associated with the magnetic degrees of freedom, $S_{\rm m} = R \ln(2s + 1)$ (R is the gas constant), should be substantial. It turned out that molecular anisotropy, crucial for the long relaxation time and blocking temperature, hinders spin polarization and depolarization, thus yielding a lower MCE [10]. However, thanks to the fact that advanced synthesis methods enable the rational design of molecular materials, a record MCE value, similar to that of MnAs in the room temperature range, has been recently obtained for a Gd^{3+} dimer with weak ferromagnetic intramolecular interaction [11]. The maximum entropy change observed at T = 1.8 K at the field change of 7 T is 42 J kg⁻¹ K⁻¹ (\approx 32 J kg⁻¹ K⁻¹ for 2 T) [11]. Due to the large drop in temperature, ΔT_{ad} , equal to 3 K at $\mu_0 \Delta H$ of 1 T, this substance may be an efficient cooler below liquid helium temperatures.

In general, magnetocaloric investigations in molecular compounds are of interest. MCE studies are able to deliver insightful information on the magnetic behaviour of this new type of material. Molecular magnets have properties difficult to meet in inorganic materials, such as low density, transparency and recyclability. Moreover, their properties can be changed due to external stimuli (light, pressure, temperature and guest molecules). First investigations of the MCE driven by long range magnetic order in molecule-based materials refer to Prussian blue analogues: ferromagnetic $C_{sNi}[Cr(CN)_6]H_2O$ with $T_c = 90$ K and ferrimagnetic $Cr_3[Cr(CN)_6]_2 \cdot 12H_2O$ with $T_c = 230$ K [12], ferromagnetic $Ru_{0.2}Ni_{2.7}[Cr(CN)_6]_2 \cdot zH_2O$ with $T_c = 62$ K [13] and $Cu_{0.73}Mn_{0.77}[Fe(CN)_6] \cdot zH_2O$, in which the magnetic pole reversal observed at low fields (≤ 1 kOe) brings about the bipolar switching of MCE [14].

Recently, we published the first study of the magnetocaloric effect in a molecular magnet, which is an example of a magnetic sponge, as it changes, in a reversible way, the ordering temperature T_c and the coercive field H_c upon hydration/dehydration [15]. The material belongs to the family of compounds based on the octacyanido building block $[M(CN)_8]^{n-}$ (M = Nb^{IV}, Mo^V and W^V), forming the M^{II}-L-[Nb(CN)_8] networks, where M = Mn, Fe, Ni and L is a nonmagnetic organic ligand which significantly affects the overall behaviour of the material. The unique {[Mn(pydz)(H₂O)₂][Mn(H₂O)₂][Nb(CN)_8]·2H₂O}_n



Figure 1. Crystal structure of 1 and 2 viewed along the c axis; pyrazole ligands, coordinated to 3d metal centres, are helically arranged along the c axis.

(pydz = pyridazine, the six-membered C₄H₄N₂ ring ligand), upon dehydration, undergoes two-step structural transformation, associated with large shifts in T_c [16]. The maximum entropy changes ΔS_{max} determined for this compound at $\mu_0\Delta H = 5$ T were equal to 5.36 J mol⁻¹ K⁻¹ at T = 43 K for the primary sample, 3.33 J mol⁻¹ K⁻¹ at 68 K for the dehydrated sample and 3.38 J mol⁻¹ K⁻¹ at 98 K for the anhydrous compound. The field dependence of MCE at T_c was consistent with the values of critical exponents derived from magnetization data [15].

Herein, we present a study of MCE in two related bimetallic { $[M^{II}(pyrazole)_4]_2[Nb^{IV}(CN)_8] \cdot 4H_2O\}_n$ compounds, where M = Ni, Mn, and pyrazole is the fivemembered C₃H₄N₂ ring ligand. { $[Ni(pyrazole)_4]_2[Nb(CN)_8] \cdot$ 4H₂O}_n (1) and { $[Mn(pyrazole)_4]_2[Nb(CN)_8] \cdot$ 4H₂O}_n (2) crystallize in the same tetragonal space group $I4_1/a$ and are isomorphous [17]. The structure of both systems consists of a 3D cyanido-bridged M^{II}–NC–Nb^{IV} skeleton comprised of two sets of oppositely corrugated square grids, interconnected in half of the Nb centres. The channels between square grids are filled with pyrazole ligands coordinated to 3d metal centres, helically arranged along the *c* axis. Figure 1 shows a section of the structure perpendicular to the *c* axis.

As will be shown below, despite the same structure, the two compounds differ in respect of mutual orientation of the M and Nb sublattices, which is ferromagnetic in case of the Ni-based sample and ferrimagnetic for the Mn-based one. It seemed therefore interesting to compare the magnetocaloric effect in the two structure-related, ferro- and ferrimagnetic, molecular systems.

2. Experimental details

The synthesis of the compound and the structural data have been already reported elsewhere [17]. DC magnetic measurements were carried out for powder samples placed in a gel capsule, using the MPMS5-XL SQUID magnetometer. Isothermal magnetization curves recorded up to 5 T were measured at temperatures ranging from 3 up to 32 K for



Figure 2. Temperature dependence of the in-phase ac susceptibility for 1 and 2. Inset: isothermal M(H) curves measured for 1 and 2 at T = 4.23 K.

1 and from 13 up to 48 K for **2**. The measurements of AC susceptibility were performed with a Lake Shore 7225 AC susceptometer/DC magnetometer. The real component of χ_{AC} was measured with a frequency f = 120 Hz and an amplitude of the oscillating field of $H_{AC} = 3$ Oe for **1** and with f = 125 Hz and $H_{AC} = 5$ Oe for **2**. Heat capacity measurements were carried out by means of a Physical Property Measurement System (PPMS).

3. Results and discussion

3.1. Magnetic properties

Magnetic measurements reveal different types of magnetic ordering of the examined compounds. The real component of AC susceptibility for both samples shows a sharp increase upon cooling, which indicates transition to the long range ordered state (figure 2). The critical temperatures determined from the minimum of the $d\chi'/dT$ derivative are $T_c = 13.4$ K and 23.8 K for 1 and 2 respectively. The magnetization value in the field of 56 kOe measured at 4.3 K for 1 reaches the value of 5.31 $\mu_{\rm B}$. This value is close to that expected for ferromagnetic coupling of Ni and Nb sublattices, with spins $S_{\rm Ni} = 1$ and $S_{\rm Nb} = 1/2$ and Landé factors g = 2.18 and 2, respectively [17]. The magnetization measured for 2 at T = 4.3 K increases rapidly and reaches the saturation value of 8.95 $\mu_{\rm B}$ at 56 kOe, very close to the value expected for antiferromagnetic coupling between Mn and Nb sublattices $(S_{Mn} = 5/2, g_{Mn} = 2)$. This confirms that **2** is a ferrimagnet with magnetic moment of the Nb ion oriented antiparallel to the moments of the two Mn ions. The slower magnetization M(H) increase of 1 indicates a weak magnetic anisotropy in our Ni-based ferromagnet. In both cases the hysteresis loops measured at liquid helium temperature (not shown) are extremely narrow, with coercive field $H_{\rm C} \leq 10$ Oe.

Analysis of the high-temperature susceptibility using the molecular field approach, performed in [17], has allowed for an estimation of the magnetic coupling energies. Magnetic

interaction M^{II} –NC–Nb^{IV} pathways in **1** and **2** are equivalent, thus only one exchange coupling between the nearest neighbours, J_{MNb} , was assumed.

3.2. Magnetocaloric effect

MCE for 1 and 2 has been determined from magnetic measurements. The magnetic entropy change ΔS was calculated from the isothermal magnetization data using the integrated Maxwell relation $\Delta S(T) = \int_{H_0}^{H_1} \partial M(T, H) / \partial T \, dH.$ Isothermal magnetization curves were recorded in applied field up to 50 kOe in a wide temperature range (figures 3(a), (b)). Close to T_c , the M(H) data were collected at small temperature intervals to exactly identify the temperature at which ΔS maximizes. The results were transformed to $(M-T)_H$ data and then to $(dM/dT)_H$ plots at different T values. Integrating $(dM/dT)_H$ plots from H = 0 up to the desired field value yielded the entropy change of the sample due to a field change ΔH as a function of temperature. Figures 3(c) and (d) show the $\Delta S(T)$ dependences for 1 and **2** for the field change $\mu_0 \Delta H = 1-5$ T. Both samples exhibit a maximum value of ΔS at temperatures corresponding to $T_{\rm c}$. ΔS increases with increased value of ΔH . A slightly higher value of ΔS is observed for **2**: at T = 25 K, $\mu_0 \Delta H = 5$ T is $\Delta S = 6.7 \text{ J mol}^{-1} \text{ K}^{-1}$ (6.5 J kg⁻¹ K⁻¹). The value of ΔS calculated for 1 at T = 14 K, $\mu_0 \Delta H = 5$ T is $\Delta S =$ $6.1 \text{ J mol}^{-1} \text{ K}^{-1} (5.9 \text{ J kg}^{-1} \text{ K}^{-1}).$

The magnetocaloric effect of a material can be also evaluated from specific heat measurements. The heat capacity of **1** was measured first in zero applied field and then in 1, 5 and 9 T applied field. The temperature dependence of C(T)/Tis presented in the inset of figure 4(a). It can be seen clearly that at T = 13 K a well defined λ -shaped anomaly occurs. Based on the C(T)/T data, the magnetic entropy change may be calculated according to

$$\Delta S = \int_0^T \frac{C_p(T)_{H_0} - C_p(T)_{H_i}}{T} \, \mathrm{d}T.$$

As the heat capacity measurements were carried out not from T = 0 but from T = 3 K, in order to account for the (0, 3 K) interval we have numerically extrapolated the heat capacity values down to T = 0 K and calculated the associated entropy content. The function $f(T, H) = a(H)T^3 + b(H)T^{3/2}$ was used, where the first term accounts for the lattice contribution to the specific heat and the second one is due to the low-temperature ferromagnetic spin wave contribution. The corresponding ΔS corrections for the (0, 3 K) interval were equal to 0.08 J K⁻¹ mol⁻¹, 0.61 J K⁻¹ mol⁻¹ and 1.15 J K⁻¹ mol⁻¹ for 1 T, 5 T and 9 T, respectively.

The results obtained for ΔS are displayed in figure 4(a). The bars indicate the ΔS values without considered extrapolation. The values of ΔS obtained with $T \rightarrow 0$ K extrapolation of the experimental heat capacity are presented as filled circles and can be considered as an upper bound. Again the largest changes are seen near T_c , where for $\mu_0 \Delta H = 9$ T we get $\Delta S = 8.9$ J mol⁻¹ K⁻¹ (8.6 J kg⁻¹ K⁻¹). Moreover, ΔS obtained for $\mu_0 \Delta H = 1$ and 5 T is in good agreement with the previous estimation inferred from M(H, T) data.



Figure 3. Magnetization versus field isotherms for different temperatures measured for 1 (a) and 2 (b). Temperature dependence of the magnetic entropy change of 1 (c) and 2 (d) determined for $\mu_0 \Delta H = 1-5$ T. The insets of (c) and (d) show the temperature dependences of the exponent characterizing the field dependences of ΔS_m for 1 and 2, respectively.

The extrapolation also allowed us to calculate the adiabatic temperature change using the formula $\Delta T_{ad} = T(S, H) - T(S, H = 0)$ [18]. The results obtained are displayed in figure 4(b). The maximum of ΔT_{ad} is 2.9 K for $\mu_0 \Delta H =$ 9 T (2.0 K for 5 T). Even though the value of ΔT_{ad} is smaller than those reported for conventional inorganic magnetocaloric materials [19], it is still larger than those obtained for hexacyanochromate Prussian blue analogues [12] and for Mn₂-pydz-[Nb(CN)₈] [15].

An important parameter, which provides a measure of the efficiency of magnetocaloric material, is the relative cooling power (RCP), defined as

$$\text{RCP} = |\Delta S|^{\text{max}} \delta_{\text{FWHM}},$$

where δ_{FWHM} is the full width at half maximum of the magnetic entropy change $\Delta S(T)_H$. The calculated values of RCP under the magnetic field variation of 5 T are 75.6 J mol⁻¹ (73.1 J kg⁻¹) for **1** and 136.9 J mol⁻¹ (132.9 J kg⁻¹) for **2**, which are five times less than the RCP value of the gadolinium magnetocaloric standard [20].

3.3. Analysis of the magnetocaloric effect: master curve, dependence on magnetic field, dependence on the critical temperature in the Mn_2 –L– $[Nb(CN)_8]$ (L = pyrazole, pyridazine) series

It was interesting to check whether for the ferrimagnet magnetic entropy changes at different applied fields may be presented as one universal curve, as is the case for ferromagnets. As demonstrated in [21], a universal behaviour of $\Delta S(T)$ curves at different applied fields is a hallmark of magnetic compounds with second order phase transition, while for those with first order phase transition, the breakdown of the universal curve is expected. Such a phenomenological universal curve is constructed in a two-step process [21]. At first, all $\Delta S(T)$ curves are normalized to their maximum value ΔS^{max} . In the second step the temperature axis below and above the critical temperature is rescaled and a new variable θ is defined by the following expression:

$$\theta = \begin{cases} -(T - T_{\rm c})/(T_{\rm r1} - T_{\rm c}) & T \le T_{\rm c}, \\ (T - T_{\rm c})/(T_{\rm r2} - T_{\rm c}) & T > T_{\rm c}, \end{cases}$$
$$\Delta S(T_{\rm r1})/\Delta S^{\rm max} = \Delta S(T_{\rm r2})/\Delta S^{\rm max} = h,$$

where T_{r1} , T_{r2} are the temperatures of two reference points and *h* is a level of reference, here taken as h = 0.6 for both compounds. The normalized entropy change curves as a function of the rescaled temperature for compounds **1** and **2** are shown in figures 5(a) and (b). It appears that for both materials $\Delta S(T)/\Delta S(T)^{\text{max}}$ curves collapse onto a single curve; therefore, we also deal with the MCE universal behaviour for the ferrimagnet and the transitions are of the second order.

The order of the magnetic phase transition can also be tested by an analysis of the Arrott plots. According to the Banerjee criterion [22], a positive slope of the M^2 versus H/M curves indicates a magnetic phase transition to be of the second order, while a negative slope corresponds to a first order transition. The positive slope of the curves presented



Figure 4. (a) Magnetic entropy change ΔS of **1** as a function of temperature for 1, 5 and 9 T obtained from magnetic (triangles) and thermal measurements (filled circles and bars). Inset: temperature dependence of $C_p(T)/T$ of **1** at different applied magnetic fields (for clarity only three curves are shown). (b) The temperature dependence of the adiabatic temperature change of **1** obtained from thermal measurements for $\mu_0 \Delta H = 1, 5$ and 9 T.

in figures 5(c) and (d) confirms the validity of the results obtained by scaling of the $\Delta S(T)$ curves.

The MCE in the vicinity of the ferro- or ferrimagnetic transition should reflect the critical behaviour of the system. Using the MCE data from figures 3(c) and (d) we determine the exponent *n* which describes the ΔS dependence on the applied magnetic field for materials with a second order phase transition according to the relation

$\Delta S(T, H) \propto H^n$.

From the mean field approach, one gets that n = 1 at temperatures well below T_c and n = 2 well above T_c , while at T_c n = 2/3 [21, 23]. The temperature dependences of n obtained for 1 and 2, depicted in insets of figures 3(c) and (d), have a similar character, but the minimum values at transition temperatures are different and equal to n = 0.59 for 1 and n = 0.64 for 2. The constant offset term appearing when fitting data to the $\Delta S(T, H) \propto H^n$ relation, which reflects the distribution of local T_c-points [24], was negligible. It was shown in [21] that the *n* exponent at T_c is dependent on critical exponents β and γ through the relation $n(T_c) = 1 + \frac{\beta - 1}{\beta + \gamma}$. The *n* value obtained for **1** agrees with $n(T_c)$ calculated using β and γ adequate for a 3D magnet with XY anisotropy, which may be associated with some anisotropy visible in the magnetization curve of 1 (see figure 2 inset). On the other hand, the *n* value determined for **2** is equal to that expected for a 3D Heisenberg magnet, which conforms to the shape of the magnetization curve of **2** (see figure 2 inset). In this way, investigation of the MCE has been helpful in probing the details of magnetic interactions in the spin system. One should also note that a close affinity of **2** to the 3D Heisenberg model has been recently proved by us with a study of critical behaviour using μ SR spectroscopy, ac magnetometry and relaxation calorimetry [25].

Theoretical calculations aimed to study the MCE dependence on critical temperature, spin value and magnetic field change have justified the $(H/T_c)^{2/3}$ dependence of the maximum entropy change, with a proportionality factor that is a function of spin [7]. Because of different spin values and two magnetic sublattices in 1 and 2, it is not possible to check these suppositions. However, one can check whether the $\Delta S^{\text{max}} \propto T_c^{-2/3}$ relation is valid for the Mn₂–L–[Nb(CN)₈] compounds, with the same spins, of two Mn ions and one Nb ion, but with different bridging ligands. Figure 6(a) shows the temperature dependence of the magnetic entropy change recorded in applied field of 1, 3 and 5 T for sample 2 $(Mn_2-pyrazole-[Nb(CN)_8])$ together with that for the three phases of the above mentioned magnetic sponge $Mn_2-L-[Nb(CN)_8]$ (L = pyridazine) (3). The transition temperature for the as-synthesized **3** is 43 K; $T_{\rm c}$ for the partially dehydrated sample is 68 K, while for the fully anhydrous one it is 98 K. Reduction of ΔS^{max} value is observed with increasing T_c along the series. The maximum entropy change ΔS^{max} detected at $\mu_0 \Delta H = 5$ T for **2** is equal to 6.7 J mol¹ K⁻¹ at 25 K and then ΔS^{max} is decreasing, reaching 5.36 J mol⁻¹ K⁻¹ at T = 43 K for the as-synthesized sample **3** and 3.38 J mol⁻¹ K⁻¹ at 98 K for the anhydrous compound 3anh. The slightly incompatible reduction of ΔS^{max} observed for the dehydrated sample 3deh ($\Delta S^{\text{max}} =$ 3.33 J mol⁻¹ K⁻¹ at 68 K) can be explained by the sample instability. Hence, the linear dependence of ΔS^{max} values plotted in figure 6(b) as a function of $T_c^{-2/3}$ confirms the ΔS^{max} proportionality to $T_c^{-2/3}$ for the Mn₂-L-[Nb(CN)₈] molecular materials.

Conclusions

In conclusion, we have investigated the magnetocaloric effect in two structure-related molecular magnets [MII(pyrazole)₄]₂ $[Nb^{IV}(CN)_8] \cdot 4H_2O (M = Ni, Mn)$, showing different stype of magnetic order: ferromagnetic for the Ni-based compound (1) and ferrimagnetic for the Mn-based one (2). The maximum entropy change ΔS^{max} obtained at $\mu_0 \Delta H = 5$ T for **1** at T = 14 K is equals to 6.1 J mol⁻¹ K⁻¹, while that for 2 at T = 25 K is 6.7 J mol⁻¹ K⁻¹. For both compounds magnetic entropy changes at different applied fields could be presented as one universal curve, which confirms magnetic transitions in 1 and 2 to be of the second order. Temperature dependences of the *n* exponent characterizing the dependence of ΔS on the applied field have been obtained. The $n(T_c)$ values, consistent with the shape of the magnetization curves, pointed to the 3D Heisenberg behaviour of 2 and some anisotropy, probably of the XY type, in 1. The $(H/T_c)^{2/3}$ dependence of the maximum entropy change has been justified in



Figure 5. Normalized entropy change for different applied magnetic fields as a function of the rescaled temperature θ for **1** (a) and **2** (b). Arrott plots: M^2 versus H/M isotherms obtained for **1** (c) and **2** (d).



Figure 6. (a) Temperature dependence of the magnetic entropy change for a Mn_2 -L-[Nb(CN)₈] (L = pyrazole, pyridazine) series undergoing a second order phase transition. (b) ΔS^{max} values obtained for applied field 1, 3 and 5 T as a function of $T_c^{-2/3}$.

the ferrimagnetic Mn_2 -L-[Nb(CN)₈] series (L = pyrazole, pyridazine). Investigation of MCE appeared to be a valuable method for probing the details of magnetic interactions in the spin systems.

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