

# Magnetocaloric Effect in $\text{CsDy}(\text{MoO}_4)_2$

R. TARASENKO<sup>a,\*</sup>, V. TKÁČ<sup>a</sup>, A. ORENDÁČOVÁ<sup>a</sup>, M. ORENDÁČ<sup>a</sup>, V. SECHOVSKÝ<sup>b</sup>, A. FEHER<sup>a</sup>  
<sup>a</sup>Institute of Physics, Faculty of Science, P.J. Šafárik University, Park Angelinum 9, 041 54 Košice, Slovak Republic

<sup>b</sup>Department of Condensed Matter Physics, Faculty of Mathematics and Physics, Charles University, Ke Karlovu 5, CZ-12116 Prague 2, Czech Republic

$\text{CsDy}(\text{MoO}_4)_2$  belongs to the family of binary alkaline rare-earth molybdates, with detectable low-temperature structural phase transitions, caused by the cooperative Jahn-Teller effect. Magnetocaloric studies of a single crystal of  $\text{CsDy}(\text{MoO}_4)_2$  have been performed in the temperature range from 2 K to 18 K in magnetic fields up to 7 T applied along the crystallographic  $a$  axis. The maximum value of the isothermal entropy change is about 8 J/(kgK) and was achieved already in the fields above 2 T. The observed results suggest that the studied system can be used as a magnetic refrigerant at helium temperatures.

DOI: [10.12693/APhysPolA.133.414](https://doi.org/10.12693/APhysPolA.133.414)

PACS/topics: 75.30.Sg, 75.30.Gw, 71.70.Ej

## 1. Introduction

Magnetic cooling based on magnetocaloric effect (MCE) has become a focus of interest in recent years due to using of environmentally friendly materials, higher efficiency and promising application in future cryogenic technique [1–5]. Large MCE close to room temperature can be useful for household and several technological applications [6] while large MCE in low-temperature region can be utilized, e. g. in the process of liquefaction of helium for cryogenics, or hydrogen in fuel industry [7]. MCE is determined by the isothermal magnetic entropy change ( $\Delta S_M$ ) and the adiabatic temperature change ( $\Delta T_{ad}$ ) induced by the change of the external field [8–9].

The title compound  $\text{CsDy}(\text{MoO}_4)_2$  belongs to a large group of binary molybdates  $M\text{RE}(\text{MoO}_4)_2$  with chain-layered structure, where  $M$  stands for alkali metal and RE for rare earth. The spontaneous cooperative Jahn-Teller effect, caused by a strong coupling between the rare-earth electron and phonon system, is responsible for the presence of low-temperature structural phase transitions. The low-symmetry crystal field splits the ground multiplet of  $\text{Dy}^{3+}$  ion,  ${}^6\text{H}_{15/2}$ , into 8 doublets. The lowest excited states are 110 and 250  $\text{cm}^{-1}$  above the ground doublet [10]. Considering the crystal symmetry and sufficiently low temperatures, the system approximates an Ising system with the effective spin 1/2 and the easy magnetization corresponding to the crystallographic  $a$  axis. Previous specific heat studies performed in zero magnetic field indicated a magnetic phase transition at  $T_c = 1.3$  K, described within a 2d Ising model [11].

In this paper we present the magnetocaloric response of a single crystal of  $\text{CsDy}(\text{MoO}_4)_2$ , investigated at temperatures above the magnetic phase transition in the magnetic field applied along the easy axis.

## 2. Experimental details

The single crystals of  $\text{CsDy}(\text{MoO}_4)_2$  were obtained by means of a flux growth method at the Institute of Low Temperature Physics in Kharkov [12]. As already mentioned,  $\text{CsDy}(\text{MoO}_4)_2$  undergoes two structural phase transitions [13, 14]. While at room temperature, the crystal structure is monoclinic (space group  $P2_1/c$ ) with the lattice parameters  $a = 5.05$  Å,  $b = 9.49$  Å,  $c = 7.97$  Å and  $\beta = 88.4^\circ$ , at temperatures below the structural transition occurring at  $\approx 120$  K, the system enters the orthorhombic phase (space group  $Pcca$ ) with the lattice parameters  $a = 5.013$  Å,  $b = 18.76$  Å,  $c = 7.92$  Å, determined at 50 K. Another structural transition appears at about 40 K, below which the system returns to the monoclinic symmetry (space group  $P2_1/c$ ). The lattice parameters  $a = 10.05$  Å,  $b = 18.86$  Å,  $c = 7.78$  Å and  $\beta = 86.6^\circ$  correspond to the temperature of 15 K (Fig. 1).

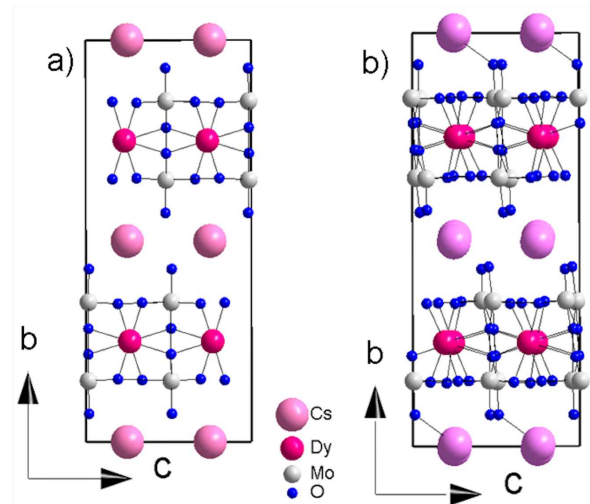


Fig. 1. The crystal structure of  $\text{CsDy}(\text{MoO}_4)_2$  projected to the  $bc$  plane (a) in the orthorhombic phase at 50 K (b) in the monoclinic phase at 15 K.

\*corresponding author; e-mail: [robert.tarasenko@upjs.sk](mailto:robert.tarasenko@upjs.sk)

Magnetocaloric studies of a single crystal of  $\text{CsDy}(\text{MoO}_4)_2$  have been performed in the magnetic field up to 7 T applied along the crystallographic  $a$  axis in the temperature range from 2 K to 18 K. The isothermal magnetization curves have been measured in a commercial Quantum Design SQUID magnetometer MPMS 7 T.

### 3. Results and discussion

The isothermal magnetization curves are shown in Fig. 2. Since no hysteresis was observed over the entire temperature and magnetic field intervals, a reversible MCE can be expected. It should be noted that the magnetization at 2 K achieves nearly saturated values already in magnetic fields above 2 T.

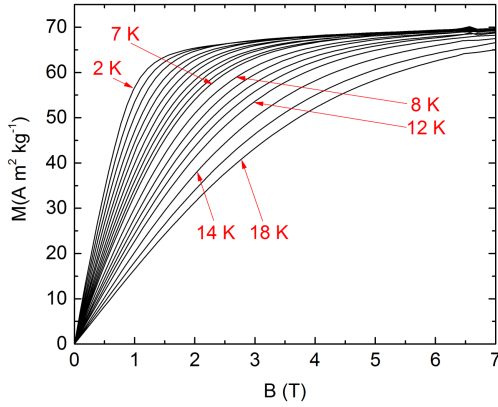


Fig. 2. Isothermal magnetization curves of  $\text{CsDy}(\text{MoO}_4)_2$ , temperature step  $\Delta T = 0.5$  K, 1 K, and 2 K for the interval 2–7, 8–12, and 14–18 K, respectively.

The isothermal magnetic entropy change  $\Delta S_M$  has been calculated using the Maxwell relation [6]

$$\Delta S_M(T, \Delta B) = \int_{B_i}^{B_f} \frac{\partial M(T, B)}{\partial T} dB, \quad (1)$$

where  $B_i$  and  $B_f$  represent the initial and final magnetic field, respectively.

The temperature dependences of  $-\Delta S_M$  derived from experimental magnetization data for  $B_i = 0$  and several values of  $B_f$  are shown in Fig. 3. As can be seen, the isothermal entropy change of about 8 J/(kg K) has been achieved already for the magnetic field of 2 T. While further increase of magnetic field did not enhance  $-\Delta S_M$  values significantly, it widened the temperature interval with large  $-\Delta S_M$ , forming a plateau; the higher field, the longer plateau. The absence of significant enhancement of  $-\Delta S_M$  above 2 T at lowest temperatures can be ascribed to the inaccuracy in  $dM/dT$  values calculated in the saturation region. Consequently, error bars were added to  $-\Delta S_M$  values for the fields above 2 T at lowest temperatures (Fig. 3). For comparison with other refrigerant, recently reported  $-\Delta S_M$  of  $\text{KEr}(\text{MoO}_4)_2$  was 14

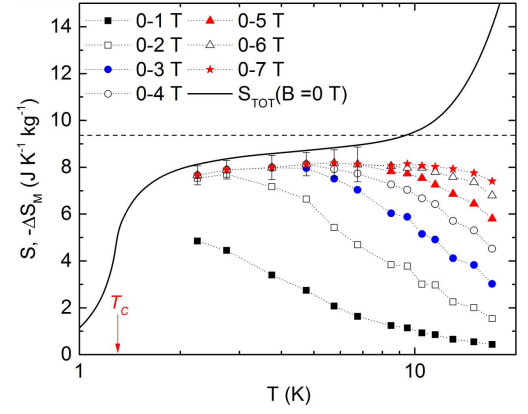


Fig. 3. Temperature dependence of the entropy and isothermal entropy change in  $\text{CsDy}(\text{MoO}_4)_2$  for different intervals of magnetic field change. Symbols represent  $-\Delta S_M$  values obtained from experimental magnetization curves; a thick line represents total entropy (lattice and magnetic contribution) calculated from the experimental specific heat data in zero field taken from refs.11 and 16. The dashed line represents the maximum theoretical entropy for the spin 1/2.

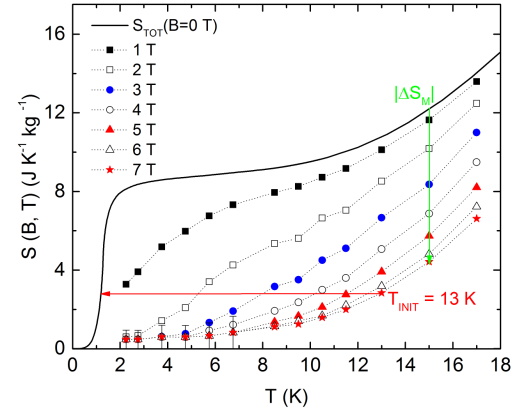


Fig. 4. Temperature dependence of the entropy in  $\text{CsDy}(\text{MoO}_4)_2$ . A thick line has the same meaning as in Fig. 3. Symbols represent the entropies in magnetic field. For illustration, the horizontal arrow shows how much the sample is cooled from the initial temperature,  $T_{init}$  during adiabatic demagnetizing from magnetic field of 7 T, while the vertical arrow shows the isothermal entropy change during magnetizing to the magnetic field of 7 T.

J/(kg K) for 5 T [15]. To use  $\text{CsDy}(\text{MoO}_4)_2$  as a potential magnetic refrigerant, the refrigerant capacity (RC) has been calculated using relation [6]

$$RC = \int_{T_{cold}}^{T_{hot}} \Delta S_M(T) dT, \quad (2)$$

where  $T_{cold}$  and  $T_{hot}$  denote the working temperature interval of the refrigerant (Fig. 5, inset). We used  $T_{cold} = 2$  K and  $T_{hot} = 17$  K. It can be seen that RC

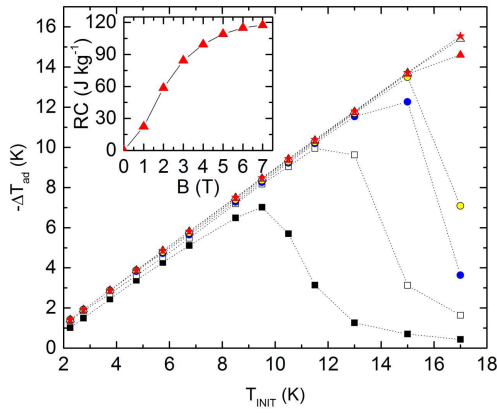


Fig. 5. Temperature change in  $\text{CsDy}(\text{MoO}_4)_2$  as a function of initial temperature during adiabatic demagnetizing from magnetic field of 1 T (solid black square), 2 T (open square), 3 T (solid blue circle), 4 T (solid yellow circle), 5 T (solid red triangle), 6 T (open triangle) and 7 T (red star). Inset: Field dependence of the refrigerant capacity in  $\text{CsDy}(\text{MoO}_4)_2$ .

of the studied sample is larger than 90 J/kg for magnetic fields above 3 T. Apparently, the obtained RC values are highly underestimated due to the lack of data below 2 K.

Temperature dependence of the entropy  $S(B, T)$  shown in Fig. 4, was obtained using a relation  $S(B, T) = S_{tot}(B = 0) - |\Delta S_M(B, T)|$  [15]. The expressions  $S_{tot}(B = 0)$  and  $|\Delta S_M(B, T)|$  denote the total (lattice and magnetic) entropy, calculated from the experimental specific heat in  $B = 0$  T [11, 16] and the absolute values of isothermal entropy change in applied external magnetic field, respectively. Applying the procedure depicted in Fig. 4, the adiabatic temperature change,  $-\Delta T_{ad}$ , was calculated as a function of initial temperature during the isentropic change from nonzero initial magnetic field,  $B_i$ , to zero  $B_f$  (Fig. 5). The resulting dependencies  $-\Delta T_{ad}$  vs. initial temperature are characterized by quasi-linear behaviour for the adiabatic demagnetization from the initial magnetic field  $B_i > 2$  T. The linear curves for different values of  $B_i$  merge to a universal curve at low  $T_{init}$  as a result of the vicinity of the magnetic phase transition.

#### 4. Conclusions

In conclusion, we studied magnetocaloric properties of a single crystal of  $\text{CsDy}(\text{MoO}_4)_2$  in magnetic fields applied along the easy axis. The maximum value of the isothermal entropy change was about 8 J/(kgK) and was achieved already in the fields above 2 T.

Since  $\text{CsDy}(\text{MoO}_4)_2$  is characterized by large magnetic anisotropy, the rotational MCE [15] will be investigated in future to find which kind (conventional or rotational) MCE is more appropriate for the utilizing the material as a cryo-refrigerant.

#### Acknowledgments

This work has been supported by the projects APVV-14-0073, VEGA 1/0269/17, ERDF EU project No. ITMS 26220120047. Experiments were performed in the Czech Research Infrastructure MGML (see: <https://mgml.eu/>).

#### References

- [1] R. Sessoli, *Angew. Chem. Int. Ed.* **51**, 43 (2012).
- [2] Yu.I. Spichkin, A.K. Zvezdin, S.P. Gubin, A.S. Mishchenko, A.M. Tishin, *J. Phys. D* **34**, 1162 (2001).
- [3] J.W. Sharples, D. Collison, *Polyhedron* **54**, 91 (2013).
- [4] A.M. Tishin, Y.I. Spichkin, *The Magnetocaloric Effect, its Applications*, Institute of Physics Publishing, Bristol, Philadelphia 2003).
- [5] O. Tegus, E. Bruck, K.H.J. Buschow, F.R. de Boer, *Nature (London)* **415**, 150 (2002).
- [6] K.A. Gschneider, Jr., V.K. Pecharsky, A.O. Tsokol, *Rep. Prog. Phys.* **68**, 1479 (2005).
- [7] A. Midya, S.N. Das, P. Mandal, S. Pandya, V. Ganesan, *Phys. Rev. B* **84** (2011) 235127.
- [8] V.K. Pecharsky, K.A. Gschneider Jr., *J. Magn. Magn. Mater.* **200**, 44 (1999).
- [9] A.M. Tishin, Y.I. Spichkin, *The Magnetocaloric Effect, its Applications* Institute of Physics Publishing, Bristol, 2003.
- [10] Ch.D. Elchaninova, A.I. Zvyagin, *Fiz. Nizkikh Temp.* **9**, 1200 (1983).
- [11] P. Stefányi, A. Orendáčová, A. Feher, *Phys. Stat. Sol. (b)* **150**, K63 (1988).
- [12] V.A. Vinokurov, P.V. Klevtsov, *Kristallografiya* **17**, 127 (1972).
- [13] E.N. Khatsko, A. Zheludev, J.M. Tranquada, W.T. Klooster, A.M. Knigavko, R. C. Srivastava, *Low Temp. Phys.* **30**, 184 (2004).
- [14] S.M. Poperezhai, N.S. Bondar, V.I. Kut'ko, A.S. Kovalev, *Low Temp. Phys.* **40**, 854 (2014).
- [15] V. Tkáč, A. Orendáčová, E. Čížmár, M. Orendáč, A. Feher, A. G. Anders, *Phys. Rev. B* **92**, 024406 (2015).
- [16] E.E. Anders, A.I. Zvyagin, L.S. Shestachenko, *Ferroelectrics* **48**, 93 (1983).