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Magnetocaloric effect and slow magnetic relaxation in $CsGd(MoO_4)_2$ induced by crystal-field anisotropy

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ABSTRACT

The experimental and theoretical study of magnetocaloric effect and magnetic relaxation of the powder sample of $CsGd(MoO_4)_2$ were performed. The large conventional magnetocaloric effect was found around 2 K with $-\Delta S_{max} \approx 26.5$ J/(kg K) for $B = 7$ T. AC susceptibility measurement revealed multiple-time scale magnetic relaxation effects on different time scales. Slowest relaxation effect was attributed to the direct process with a bottleneck effect and two faster relaxation processes are effectively temperature independent, probably as a result of averaging in the powder sample.

1. Introduction

The magnetocaloric effect (MCE) represents a promising alternative to the classical refrigerator based on isothermal compression of gas. Searching for MCE materials with better properties is an effort spanning decades [1]. In this endeavor, Gd based materials have a dominant position [2–4] with potential applications at room temperatures [5] as well as low temperatures [6]. The latter is stimulated by recent liquid helium crisis [7,8].

$CsGd(MoO_4)_2$ belongs to the rare-earth double molybdates $MR(MoO_4)_2$, where M^+ stands for alkali-metal and R^{3+} represents a rare earth ion. While these materials are widely investigated for their optical applications at room temperatures [9–11], they have also interesting magnetic properties at low temperatures [12,13]. Previous studies [14,15] of $CsGd(MoO_4)_2$ indicated a phase transition to magnetic long range order at $T_C = 0.45$ K.

Recently, theoretical simulations [16] of magnetocaloric properties of $CsGd(MoO_4)_2$ were performed, considering only crystal electric field effects. This approach can provide relevant results in the paramagnetic phase, at sufficiently high temperatures above T_C. The calculations revealed that in high magnetic fields, $B \gtrsim 4$ T, relative independence of MCE on the orientation of magnetic field can be expected; a maximum magnetic entropy change was predicted to occur at about 2 K with the values $-\Delta S_{max} \approx 26.8$ J/kg K in $B \| a$ and $-\Delta S_{max} \approx 26.4$ J/kg K in $B \| c$ for the field 7 T. This result allows a use of powder or randomly oriented compact magnetocaloric medium for high magnetic field magnetocaloric applications with superconducting coils.

Different situation occurs in smaller magnetic fields below 1 T, the region for classical magnetic coils or permanent magnet applications, where rather strong anisotropy of MCE can be expected; in the field 1 T, the values $-\Delta S_{max} \approx 19.2$ J/kg K in $B \| a$ and $-\Delta S_{max} \approx 10.5$ J/kg K in $B \| c$ were predicted, which is almost 50 % reduction of $-\Delta S_{max}$.

The theoretical predictions motivated the present work, which is focused on the investigation of magnetocaloric properties of a powder sample in a wide region of magnetic fields ranging from zero up to 5 T. The studies are completed by ac susceptibility measurements to obtain information about magnetic relaxation phenomena which are important for the possible application of $CsGd(MoO_4)_2$ as cryo-refrigerant at helium temperatures.

2. Experimental details

$CsGd(MoO_4)_2$ crystallizes in the orthorhombic system *Pccm* (D_{2h}^3) with the unit cell parameters $a = 5.07$ Å, $b = 9.25$ Å and $c = 8.05$ Å with $z = 2$ [17,18]. This material is characterized by a layered crystal structure; *ac* layers built of $[Gd(MoO_4)_2]^-$ units are separated by Cs^+ ions. The coupling between the layers is weak due to electrostatic nature of the bonding. Gd^{3+} ions create chains along the *c* axis, with the shortest distance $c/2$ between Gd^{3+} ions. The local surrounding of Gd^{3+} ions consists of eight oxygen atoms creating a slightly distorted square antiprism producing crystal electric field (CEF) with uniaxial symmetry. Corresponding magnetic anisotropy can be described by the CEF parameter $B_2^0 = -0.0557$ K [16].

Isothermal magnetisation curves have been investigated in the temperature range from 2 to 25 K and magnetic fields from 0 to 5 T. AC susceptibility measurement has been performed in the magnetic

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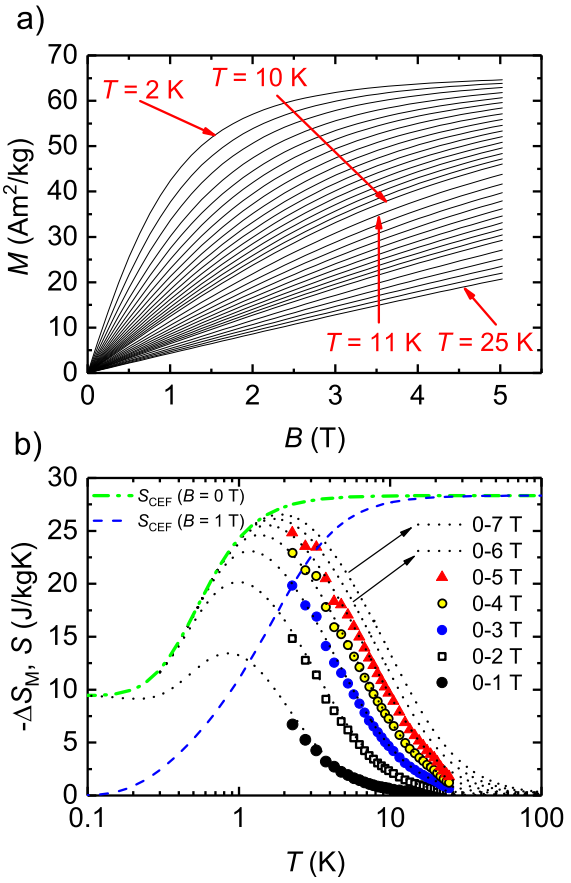

Fig. 1. (a) Isothermal magnetization curves of $CsGd(MoO_4)_2$ powder sample measured with the temperature step 0.5 K and 1 K for the temperature interval 2–10 K and 11–25 K, respectively. (b) Temperature dependence of the entropy and isothermal entropy change in $CsGd(MoO_4)_2$ powder sample in different magnetic fields. Symbols represent $-\Delta S_M$ values obtained from experimental magnetization curves, dotted lines represent $-\Delta S_M$ values calculated from the CEF energies corresponding to $B_2^0 = -0.0557$ K. For more details, see text. Dashed-dotted and short-dashed line represent magnetic entropy in zero field and 1 T, respectively, calculated from the CEF energies corresponding to $B_2^0 = -0.0557$ K.

field of 1 T at frequencies from 0.1 Hz up to nominally 1 kHz in the commercial Quantum Design SQUID magnetometer. The powder sample with mass about 40.6 mg was used for the measurements.

3. Results and discussion

3.1. Magnetocaloric effect

Experimental isothermal magnetization curves (Fig. 1a) were used for the calculation of the isothermal magnetic entropy change, ΔS_M. For this purpose, standard Maxwell relation [1] was applied

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

where $\Delta B = B_f - B_i$, B_i and B_f represent initial and final magnetic field, respectively. Temperature dependence of $-\Delta S_M$ obtained from the experimental magnetization data for $B_i = 0$ and $B_f = 1 - 5$ T is shown in Fig. 1b. Apparently, no maximum is achieved in the experimental temperature range. To explore MCE properties of $CsGd(MoO_4)_2$ in a wider temperature region, the effect of crystal field was considered as a major mechanism responsible for the magnetocaloric response in the studied material.

Assuming the uniaxial symmetry of the CEF with $B_2^0 = -0.0557$ K [16], $-\Delta S_M$ values for a powder sample were calculated in the extended range of temperatures and magnetic fields. The values were obtained by averaging of the theoretical $-\Delta S_M$ curves calculated for the magnetic fields applied parallel to *a*, *b*, and *c* crystallographic axes. The individual $-\Delta S_M$ curves were obtained as following; in the first step, temperature dependence of the magnetic entropy $S_{CEF}(B = 0, T)$ and $S_{CEF}(B, T)$ has been derived from the energy levels scheme of the CEF model in $B = 0$ and $B \neq 0$, respectively (Fig. 1b). Then, $-\Delta S_M$ values for a given temperature were calculated, $-\Delta S_M(T) = -[S_{CEF}(B, T) - S_{CEF}(B = 0, T)]$. As can be seen, excellent agreement with experimental data was obtained (Fig. 1b). The magnetic entropy, $S_{CEF}(B = 0, T)$ creates a low-temperature envelope of the $-\Delta S_M$ for individual B_f values. At high temperatures, $S_{CEF}(B = 0, T)$ approaches a maximum value $S_{max} = ln(2S + 1)R/M$ (R and M represent a gas constant and a molar mass, respectively). For $CsGd(MoO_4)_2$, S_{max} achieves 28.34 J/kg K. At low temperatures, a two-fold degeneracy of the CEF ground state leads to $S_{CEF}(B = 0, T) = \ln(2)R/M = 9.45$ J/kg K. Our simulations suggest that to achieve the maximal $-\Delta S_M = S_{max}$, a magnetic field above 7 T is required.

Since an excellent agreement between experimental and theoretical $-\Delta S_M$ values was obtained, for the estimation of the refrigerant capacity, *RC*, theoretical curves were used in the relation $RC = \int_{T_{cold}}^{T_{hot}} |\Delta S_M(T)| dT$. Since $CsGd(MoO_4)_2$ orders at 0.45 K, we used for the calculation $T_{cold} = 0.5$ K, while T_{hot} is a temperature, at which the quantity $-\Delta S_M$ reaches half of the maximum value. In the magnetic field $B_f = 7$ T, *RC* achieves 235 J/kg (Fig. 2a inset).

As illustrated in the Fig. 2a, the adiabatic temperature change, $-\Delta T_{ad}$ is connected with the isentropic change from initial magnetic field, B_i, to the final $B_f = 0$ T. The entropy curves in the magnetic field were constructed using the relation [19] $S(B, T) = S_{C,TOT}(B = 0, T) - |\Delta S_M(B, T)|$ at temperatures down to the lowest experimental temperature 2 K. For temperatures exceeding experimental window, the approximation with S_{CEF} was used. Maximum $-\Delta T_{ad}$ is around 10 K and it shifts to higher temperatures for higher initial magnetic field (Fig. 2b). It should be noted that starting at the initial temperature $T_{INIT} = 4$ K (liquid helium temperature) and rather low field 1 T, we are able to cool down to 1 K. Thus, such magnetic cooling can potentially serve as an alternative to 1 K pot. It is evident, that required *RC* can be enhanced by larger amount of the refrigerant or simply by increasing magnetic field (Fig. 2a, inset).

3.2. Magnetic relaxation

Frequency dependence of ac susceptibility was measured in the field 1 T and constant temperatures ranging from 2 to 8 K. Real part of the ac susceptibility, χ' and imaginary part of ac susceptibility, χ'' were used for the construction of Cole-Cole diagrams (Fig. 3a). The frequency increases from right to the left side of the diagram. At least three separate relaxation processes at a different time scale can be distinguished at 2.5 K. To obtain quantitative information about the relaxation, a modified Cole-Cole equation [20] was used for the fitting of the diagrams

$$\chi(\omega) = \chi_{S_N} + \sum_{n=1}^{N} \frac{\chi_{T_n} - \chi_{S_n}}{1 + (i\omega\tau_n)^{1-\alpha_n}}, \; n = 1, 2, \ldots, N. \quad (2)$$

The parameter α describes the distribution of relaxation times around the median relaxation time, τ_n. The value $\alpha = 1$ corresponds to the infinitely wide distribution, while $\alpha = 0$ describes a relaxation effect with a single relaxation time. χ_S and χ_T denote the adiabatic ($\chi'(\omega \to \infty)$) and isothermal ($\chi'(\omega \to 0)$) susceptibility, respectively. Finally, parameter n denotes a number of relaxation processes. In the analysis, three relaxation processes ($n = 3$) were considered, namely two slow relaxation processes (SRP1 and SRP2) and one fast relaxation process (FRP). While the relaxation process SRP2 is characterized by the parameter $\alpha \approx 0$ in the whole temperature region, for SRP1 the parameter grows from $\alpha \approx 0$ at 2 K to $\alpha \approx 0.25$ at 8.5 K. Concerning the FRP process, only mild decrease of α was detected with