Experimental Study of the Magnetocaloric Effect in Ni(en)(H$_2$O)$_4$SO$_4$ · 2H$_2$O — An S = 1 Molecular Magnet with Easy-Plane Anisotropy

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Magnetocaloric properties of Ni(en)(H$_2$O)$_4$SO$_4$ · 2H$_2$O powder were investigated in temperature range from 2 K to 30 K in magnetic fields up to 7 T using isothermal magnetization measurements. The maximum value of the isothermal entropy change in the field 7 T is about 8 J/(kg K), with a refrigerant capacity of 55 J/kg. Temperature dependence of the isothermal entropy change under different magnetic fields is in good agreement with theoretical predictions from crystal electric field parameters.

1. Introduction

Magnetic coolants made of molecule-based paramagnetic complexes have become a focus of interest in recent years owing to their promising application in future cryogenic technique [1–3]. The magnetocaloric effect (MCE) that dictates the capacity of the refrigerants is determined by the isothermal magnetic entropy change (ΔS_M) and the adiabatic temperature change (ΔT_{ad}) induced by the change of the external field [4, 5].

The title compound Ni(en)(H$_2$O)$_4$SO$_4$ · 2H$_2$O (NEHS) (en = ethylendiamine = C$_2$N$_2$H$_8$) has been previously identified as a spin 1 single-molecule magnet with a nonmagnetic ground state introduced by easy-plane single-ion anisotropy $D/k_B = 11.6$ K and neglecting in-plane anisotropy $E/D = 0.1$. The good agreement between the experimental value of magnetic entropy and the theoretical entropy for spin 1 indicates the absence of a phase transition to the ordered state below 1.8 K and the crystal field effects play a dominant role for magnetic properties [6].

In this paper, the magnetocaloric study of powder sample NEHS, investigated above 2 K is presented.

2. Experimental details

The crystal structure of NEHS is monoclinic (space group $C2/c$) with lattice parameters $a = 9.523$ Å, $b = 12.185$ Å, and $c = 11.217$ Å [6]. The crystal structure of the compound is built of [Ni(en)(H$_2$O)$_4$]$^{2+}$ cations, [SO$_4$]$^{2-}$ anions and two water molecules comprising basic structural units (Fig. 1). The units are mutually connected by a large number of hydrogen bonds forming a

three-dimensional crystal structure. NEHS has been prepared in the form of blue prisms from an aqueous solution of nickel sulphate and en in stoichiometric amounts.

Magnetocaloric studies have been performed on powder sample of weight 54.66 mg in the temperature range from 2 K to 30 K in magnetic fields up to 7 T using isothermal magnetization curves measured in a commercial Quantum Design SQUID magnetometer.
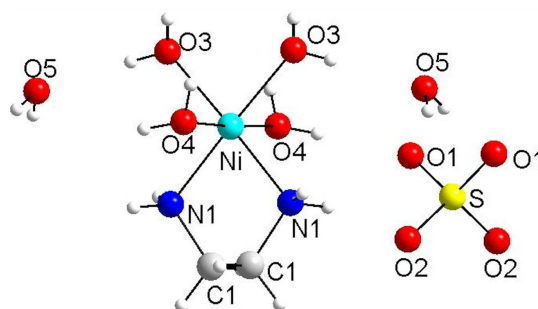

Fig. 1. Structural unit of NEHS.

3. Results and discussion

Isothermal magnetization curves are shown in Fig. 2. We can see that a magnetization does not achieve a saturation in magnetic fields up to 7 T. Since no hysteresis was observed at these temperatures and magnetic fields, a reversible MCE can be expected.

The isothermal magnetic entropy change ΔS_M has been calculated using the Maxwell relation [7]:

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

where B_i and B_f represent initial and final magnetic field.
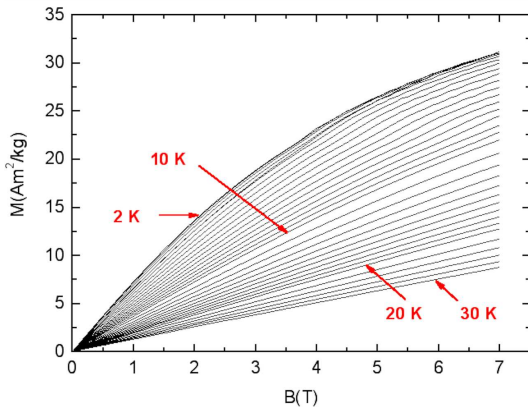
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Fig. 2. Isothermal magnetization curves of NEHS, temperature step $\Delta T = 0.5$, 1, and 2 K for intervals 2–10, 10–20, and 20–30 K, respectively.
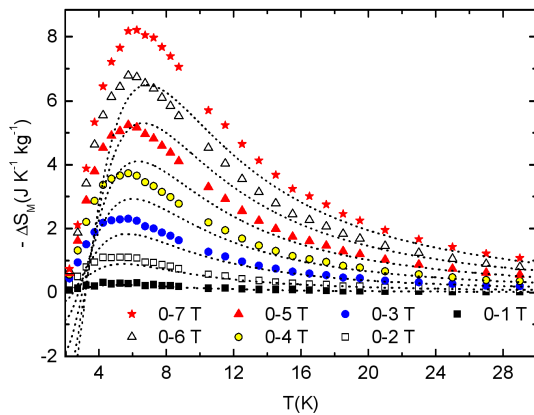

Fig. 3. Temperature dependence of the isothermal entropy change in NEHS under different magnetic field. Symbols represent $-\Delta S_M$ values obtained from experimental magnetization curves; lines represent $-\Delta S_M$ values calculated for the $S = 1$ paramagnet with $E/D = 0.1$ and $D/k_B = 11.6$ K.

Temperature dependence of $-\Delta S_M$ derived from experimental magnetization data for $B_i = 0$ and several values of B_f is shown in Fig. 3. For comparison, we also calculated theoretical magnetizations and corresponding $-\Delta S_M$ values for the $S = 1$ paramagnet with $E/D = 0.1$ and $D/k_B = 11.6$ K. It should be noted that theoretical magnetizations were obtained as average from three principal orientations. We observed increasing isothermal entropy change from lowest temperature up to approximately 6 K for all changes of magnetic field. On the other hand, $-\Delta S_M$ values decrease above 6 K. This experimental behaviour is in good agreement with theoretical predictions from crystal electric field parameters. Large conventional magnetocaloric effect ($-\Delta S_M \approx 8$ J/(kg K)) was observed around 6 K in the magnetic field 7 T. In order to assert NEHS to work in thermodynamic cycles, the refrigerant capacity (RC) was estimated using a relation

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

where T_{cold} and T_{hot} denote a working temperature interval of the refrigerant [7] (Fig. 4). We used $T_{cold} = 2$ K, while T_{hot} is a temperature, at which the quantity $-\Delta S_M$ reaches half of the maximum value, which is a characteristic parameter for magnetocaloric materials. It can be seen that RC of the studied sample is close to 55 J/kg for the maximum external magnetic fields of 7 T.
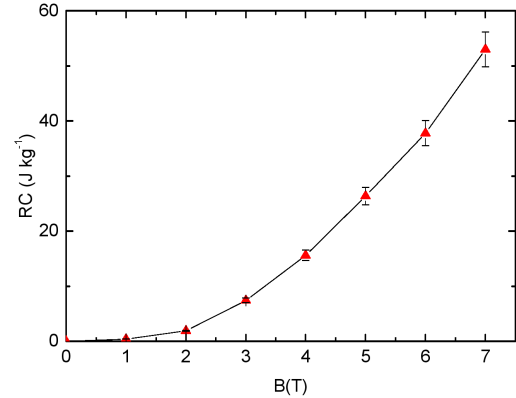

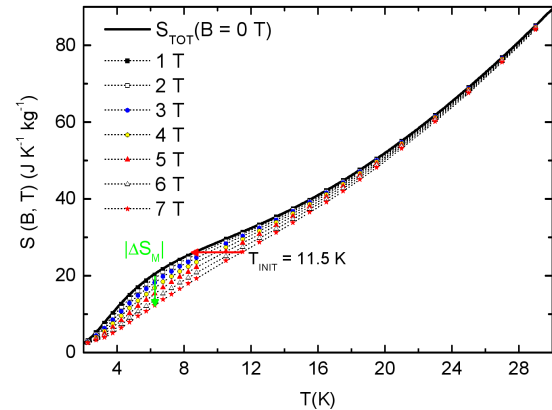Fig. 4. Field dependence of the refrigerant capacity in NEHS.

Fig. 5. Temperature dependence of the entropy in NEHS. A thick line represents total entropy (lattice and magnetic contribution) calculated from the experimental specific heat in $B = 0$ T. Symbols represent the entropies in magnetic field. For illustration, the horizontal arrow shows how much the sample is cooled from temperature T_{INIT} during adiabatic demagnetizing from magnetic field of 7 T, while the vertical arrow shows the isothermal entropy change during magnetizing to magnetic field of 7 T.

Temperature dependence of the entropy $S(B,T)$ shown in Fig. 5, was obtained using a relation $S(B,T) = S_{TOT}(B = 0 \text{ T}) - |\Delta S_M(B,T)|$. The expressions $S_{TOT}(B = 0 \text{ T})$ and $|\Delta S_M(B,T)|$ denote a total (lattice and magnetic) entropy, calculated from the experimental specific heat in $B = 0$ T [6] and absolute values
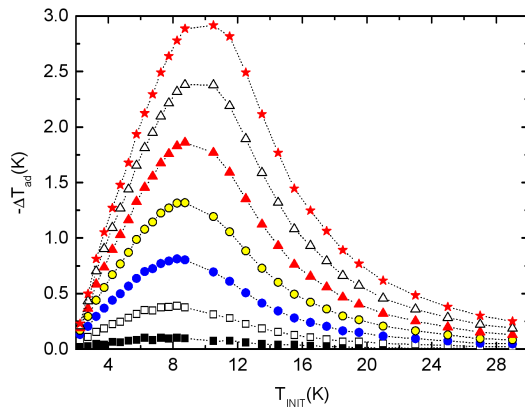
Fig. 6. Temperature change in NEHS as a function of initial temperature during adiabatic demagnetizing from magnetic field of 1 T (solid black square), 2 T (open square), 3 T (solid blue circle), 4 T (solid yellow circle), 5 T (solid red triangle), 6 T (open triangle) and 7 T (red star).

of isothermal entropy changes in applied external magnetic field, respectively. We estimated from temperature dependence of entropy the temperature change as a function of initial temperature during adiabatic demagnetizing from magnetic field (Fig. 6). The resulting dependences, $-\Delta T_{ad}$ vs. initial temeperature, are characterized by a maximum, standardly shifting to lower temperatures in lower magnetic fields. It can be seen that adiabatic demagnetization from field 7 T at an initial temperature 10 K leads to $-\Delta T_{ad} \approx 3$ K.

4. Conclusions

We studied magnetocaloric properties of the powder $Ni(en)(H_2O)_4SO_4 \cdot 2H_2O$. The maximum value of the isothermal entropy change in the field 7 T is about 8 J/(kg K), with a refrigerant capacity of 55 J/kg. Temperature dependence of the isothermal entropy change under different magnetic fields is in good agreement with theoretical predictions from crystal electric field parameters.

Acknowledgments

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