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Magnetocaloric Study of $S = 1/2$ Low-Dimensional Heisenberg Antiferromagnet $[\mathrm{Cu(phen)(H_2O)_2]SO_4}$

L. Sedláková, M. Orendáč, M. Kajňaková,
A. Orendáčová and A. Feher

Centre of Low Temperature Physics, Faculty of Science, P.J. Šafárik University
and Institute of Physics, SAS, Park Angelinum 9, 041 54 Košice, Slovakia

We present the experimental study of magnetocaloric effect on powder sample $[\mathrm{Cu(phen)(H_2O)_2]SO_4}$ (phen = phenantroline = $C_{12}H_8N_2$) in the temperature range from nominally 0.2 K to 4 K and in magnetic fields up to 2 T. The values of total entropy were extracted from the experimental data obtained by adiabatic demagnetization. The comparison was performed with the temperature dependence of the entropy for $S = 1/2$ paramagnet calculated at selected magnetic fields. The deviations observed below 0.6 T were attributed to internal field mediated by exchange coupling. In addition, the temperature response observed in $[\mathrm{Cu(phen)(H_2O)_2]SO_4}$ revealed very short relaxation time below 1 K. The comparison of the behavior observed at the end of the demagnetization in $[\mathrm{Cu(phen)(H_2O)_2]SO_4}$ and other systems suggests that the magnetocaloric effect can serve as an alternative tool for studying slow magnetic relaxation.

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1. Introduction

The magnetocaloric effect (MCE) is a magnetothermodynamic phenomenon based on the change in temperature caused by a material's exposure to a magnetic field. In the recent years, low-dimensional systems and frustrated magnets are considered good candidates for enhanced MCE at low temperatures. This is because of macroscopic degeneracy of the ground state and resulting residual entropy present in this class of materials [1]. In this paper we present results obtained in $[\mathrm{Cu(phen)(H_2O)_2]SO_4}$ (CPHS). The previous experimental studies including specific heat, magnetization, and magnetic susceptibility [2] enabled to characterize the compound as a representative of a frustrated quantum spin $S = 1/2$ Heisenberg antiferromagnetic zigzag ladder [3]. In the present work adiabatic temperature changes in the range of temperatures from 0.2 K to 4 K in magnetic fields to 2 T were studied.

2. Experimental

MCE was investigated using commercial dilution refrigerator TLE 200 down to nominally 0.2 K. [Cu(phen)$(H_2O)_2$]SO_4 was in the form of a coin shaped pellet of weight 1.061 g. The sample was connected to a metal frame using nylon threads of diameter 0.08 mm and length 2.5 cm. The temperature of the sample was monitored using RuO_2 thermometer mounted on the sample. The magnetic field was produced by a superconducting magnet. In order to minimize demagnetizing effect, the magnetic field was oriented along the flat side of the pellet. During the demagnetization the temperature of the frame followed the actual temperature of the sample to suppress the heat transport via threads. The specific heat measurements of CPHS in magnetic field were performed in commercial PPMS.

3. Results and discussion

The adiabatic demagnetization was performed from various initial temperatures. The temperature was measured under applied magnetic field decreasing from 2 to 0 T linearly in time. The adiabatic change of temperature with changing magnetic field is governed by the thermodynamic relation

$$\left(\frac{\partial T}{\partial B}\right)_S = -\frac{T}{C}\left(\frac{\partial S}{\partial B}\right)_T,$$

where C represents specific heat in field B and the quantity $(\partial T/\partial B)_S$ can be obtained from the demagnetization. The demagnetization curves of CPHS for three various values of initial temperatures are shown in Fig. 1. The observed nonlinearity above 2.5 K remains the subject of future investigation. The experimental data were compared with the theoretical prediction for the entropy behavior of $S = 1/2$ paramagnet. The direct measurement of entropy is not possible, but we are able to make the indirect comparison using the experimental data obtained by the adiabatic demagnetization. Specifically, for each run, the value of the entropy was determined from the initial temperature and the curve of the entropy calculated at 2.1 T, where the behavior of CPHS should be well approximated by $S = 1/2$ paramagnet. Using the fact that during the demagnetization the entropy remains constant, subsequent points were obtained by detecting the temperatures at those values of magnetic fields for which the temperature dependences of entropy were calculated. Three series of experimental points were obtained for three various demagnetizations and are displayed in Fig. 2a. The deviations between the theoretical predictions and the experimental data observed below 0.6 T were attributed to internal magnetic field B_{int} mediated by exchange coupling. Using molecular field approach an estimate of the internal field B_{int} may be obtained by equating two energies at a critical temperature T_{C}, namely $gS\mu_{\mathrm{B}}B_{\mathrm{int}} = k_{\mathrm{B}}T_{\mathrm{C}}$. The molecular field theory provides $\Theta/T_{\mathrm{C}} = 1$. The study of inverse susceptibility in the temperature range (2–70 K) provided a value of $\Theta = -0.44$ K [2]. The estimation of the internal field based on the analysis of high-temperature susceptibility data for $z = 4$ yielded $B_{\mathrm{int}} = 0.59$ T. Different approach for the determination of

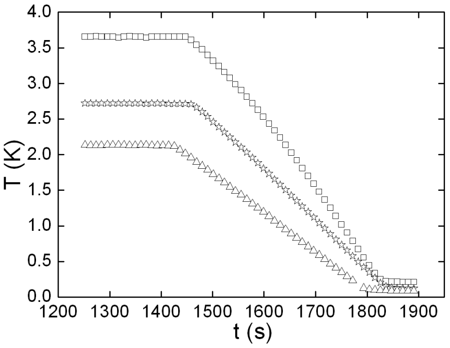

Fig. 1. The time dependence of the temperature during demagnetization for selected initial temperatures.

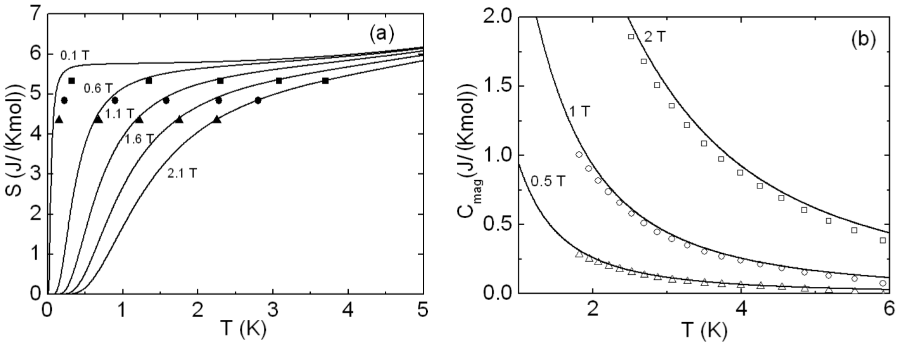

Fig. 2. The temperature dependence of the entropy in magnetic fields (a). The temperature dependence of the specific heat in magnetic fields (b). The opened symbols and solid lines denote the experimental points and theoretical predictions for $S = 1/2$ paramagnet, respectively.

the internal field was adopted using high-temperature specific heat. The constant of exchange coupling was estimated from the expression $a = (3/32)(J/k_\mathrm{B})^2zR$ [4], a represents a fit parameter of magnetic contribution for the specific heat in the high-temperature limit. Comparison of the Zeeman energy and energy of exchange coupling leads to $S\mu_\mathrm{B}gB_\mathrm{int} = \mathrm{zJS}^2$ and straightforward calculation yields $B_\mathrm{int} = 0.38$ T. Alternatively, B_int may also be estimated from the demagnetization data using the relation $T(t)/[B(t) + B_\mathrm{int}] = \mathrm{const}$. However, the single value of the internal field, for which satisfactory agreement between the sets of demagnetization data and the considered model for $S = 1/2$ paramagnet would be obtained, was not found. The comparison of the specific heat data with the prediction for $S = 1/2$ paramagnet in magnetic field indicates that CPHS obeys paramagnetic behavior above 2 K, Fig. 2b. The thermal response after the demagnetization of CPHS is presented in Fig. 3. The response revealed rather short relaxation time below 1 K.

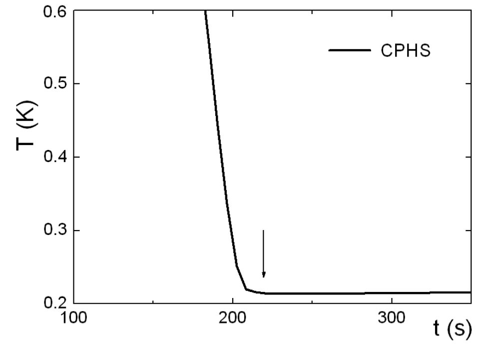

Fig. 3. The time dependence of the temperature at the end of the demagnetization of CPHS using sweeping rate 10 mT/s. The moment when magnetic field reaches zero value is denoted by the arrow.

The comparison of the behavior observed at the end of demagnetization in [Cu(phen)$(H_2O)_2$]SO_4 and other materials [5] suggests that the technique of magnetocaloric effect can be used to study slow relaxation processes.

4. Conclusion

The study of magnetocaloric effect on powder sample [Cu(phen)$(H_2O)_2$]SO_4 was performed. Internal magnetic field $B_{\rm int}$ estimated from the experimental data indicates weak magnetic correlations.

Acknowledgments

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