Large magnetocaloric effect in spinel CdCr₂S₄

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Magnetocaloric effect in $CdCr_2S_4$ was investigated by magnetization and heat capacity measurements. $CdCr_2S_4$ is of a cubic spinel structure with soft ferromagnetism and performs reversible magnetic entropy in the whole experimental temperature range from 56 to 128 K. A large magnetic entropy change ~ 7.04 J/kg K and adiabatic temperature change $\Delta T_{ad} \sim 2.6$ K are revealed for a field change of 0–5 T near the Curie temperature of 87 K. These results suggest that sulfospinel probably is a promising candidate as working material in magnetic refrigeration technology. © *2007 American Institute of Physics.* [DOI: 10.1063/1.2751576]

Magnetic materials with large magnetocaloric effects (MCEs) have been investigated theoretically and experimentally as a promising magnetic refrigerant material.[1–13] The key problem in application of magnetic refrigeration is to seek proper materials to produce a large entropy change and a good magnetic reversibility. Although giant magnetic entropy changes have been observed with the first-order phase transition in $Gd_5Si_{4-x}Ge_x$,[2,3] $La(Fe,M)_{13}$ (M=Si, Al, Co),[4] $MnFeP_xAs_{1-x}$,[5] polycrystalline perovskite manganese oxides[6–8] and shape memory alloys,[9,10] the irreversibility limits their practical application. It should be realistic to search for materials with second-order phase transition since they generally exhibit a good reversible behavior in the magnetization as a function of temperature and magnetic field.

Recently, AB_2X_4-type sulfospinels have attracted much attention due to their colossal magnetocapacity effects[14,15] and large magnetoresistance effects.[16] Many of sulfospinels, e.g., $(Cd,Hg)Cr_2(S,Se)_4$, have ferromagnetic spin configuration and large spontaneous magnetization.[17] $CdCr_2S_4$ is a member of the chalcogenide ACr_2S_4 spinels with ferromagnetically coupled Cr^{3+} spins ($S=3/2$). Based on the local magnetic moment model, the maximal magnetic entropy change would be $\Delta S = Nk_B \ln(2J+1) \sim 67$ J/kg K, where N is the number of spins, J the quantum number of the spin, and k_B the Boltzmann constant.[18] In this letter, the MCE with magnetic reversibility was investigated by magnetic and calorimetric measurements in $CdCr_2S_4$, indicating that the sulfospinel probably is a promising candidate as working material in magnetic refrigeration technology.

Polycrystalline sample of $CdCr_2S_4$ was prepared by the solid-state reaction method. A stoichiometric powder mixture of FeS(99.9%), CdS(99.9%), and Cr_2S_3(99%) from Alfa Aesar Co. was well ground, then pressed into pellets and sealed into evacuated quartz tubes. The tubes were heated to 780 °C and kept for four days to obtain a single phase. The phase composition and structure was characterized by x-ray diffraction (XRD) using Rigaku RINT2400 diffractometer. The magnetization and heat capacity were measured under applied magnetic field of 0–5.0 T, using a physical property measurement system (Quantum Design).

Figure 1 displays the XRD pattern of $CdCr_2S_4$ with $2\theta = 10° - 100°$. All diffraction peaks can be indexed into a face-centered-cubic cell with the lattice parameter $a = 10.2433(8)$ Å via the JADE 5.0 program.[19] It is consistent with a normal spinel structure of space group $Fd3m$ with Cr^{3+} octahedrally and Cd^{2+} tetrahedrally surrounded by sulfur ions (see the inset of Fig. 1).

The temperature dependence of magnetization in an external magnetic field H=0.02 T is plotted in Fig. 2. The Curie temperature T_C=87 K, defined as the temperature of the maximum slope in the M-T curves. The warming and cooling curves show a quite small thermal hysteresis (<1 K).
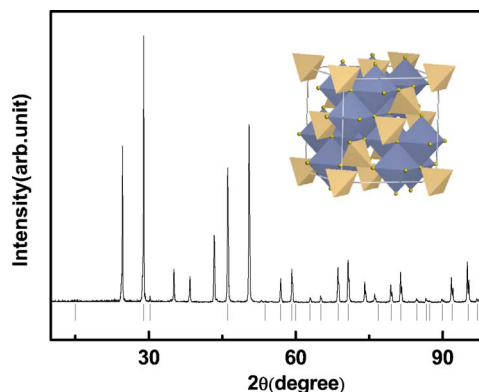

FIG. 1. X-ray diffraction pattern of $CdCr_2S_4$. Bragg reflections are indicated by vertical bars. The inset shows the crystal structure of $CdCr_2S_4$ consisting of CrS_6 octahedrons and CdS_4 tetrahedrons.

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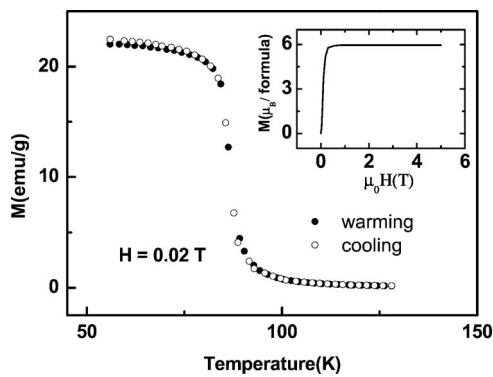
FIG. 2. Temperature dependence of magnetization of CdCr$_2$S$_4$ from 56 to 128 K under a magnetic field of 0.02 T. The inset shows the magnetic field dependence of magnetization for CdCr$_2$S$_4$ at 2 K.

From the magnetization curve at 2 K (the inset of Fig. 2), one can find that a full saturation state is achieved under a field of ~0.5 T with a moment of ~5.96μ_B per formula in agreement with ferromagnetically ordered Cr^{3+} spins due to the superexchange interaction between Cr–S–Cr atoms.[20] We note that CdCr$_2$S$_4$ is a typical soft ferromagnet with coercivity less than ~20 Oe from its magnetic hysteresis loops measured at various temperatures.

Isothermal magnetization curves were recorded in the temperature range of 56–128 K in the magnetic field up to 5.0 T [see Fig. 3(a)]. The temperature step of 3 K is chosen for 81–93 K and of 5 K for the other regions. The sweep rate of field is 40 Oe/s to ensure that *M-H* curves are recorded in an isothermal process. Figure 3(b) shows Arrott plots of CdCr$_2$S$_4$ in which neither the inflection point nor the negative slope is observed above T_C, suggesting the occurrence of second-order magnetic transition.

The magnetic entropy change is given by

$$\Delta S_m(T,H) = S_m(T,H) - S_m(T,0) = \int_0^H \left(\frac{\partial M}{\partial T}\right)_H dH, \qquad (1)$$
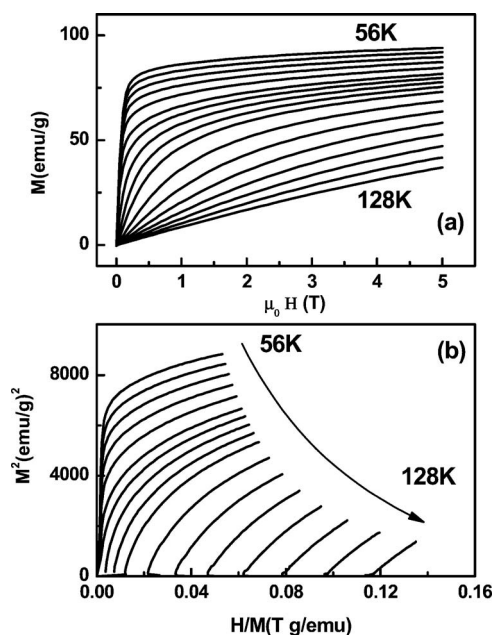
and can be evaluated by the expression

FIG. 3. (a) Magnetization as a function of applied field of CdCr$_2$S$_4$ measured near the Curie temperature. (b) The Arrott plots of CdCr$_2$S$_4$.
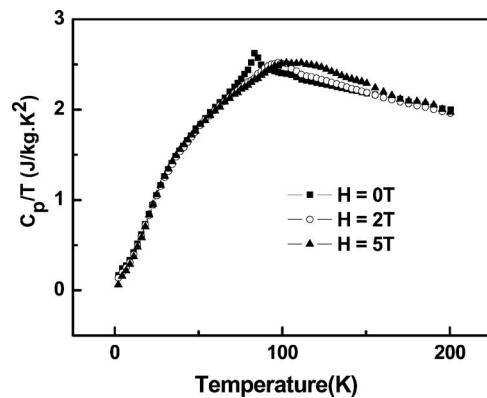

FIG. 4. Heat capacity of CdCr$_2$S$_4$ measured under the fields of *H*=0, 2, and 5 T.

$$|\Delta S_m| = \sum_i \frac{M_i - M_{i+1}}{T_{i+1} - T_i}\Delta H_i, \qquad (2)$$

where M_i is the magnetization at temperature T_i.

Magnetic entropy change versus temperature derived from Eq. (2) is shown in Fig. 5(a). Near the Curie temperature, the maximum entropy change $|\Delta S_m^{max}|$ is 3.92 and 7.04 J/kg K for the field changes of 2.0 and 5.0 T. The $|\Delta S_m^{max}|$ temperature under *H*=1 T (~87 K) is the same as T_C extracted from low field magnetization data, but shifts to ~95 K under *H*=5 T. Moreover, the ΔS_m spans in a wide temperature range, the full width of half maximum (δT) approaches to ~33 and ~51 K in the magnetic field changes from 0 to 2 T and to 5 T, respectively. Consequently, relative cooling power (RCP), evaluated by RCP=$-\Delta S_m^{max} \times \delta T$,[21] reaches, respectively, to ~130 and ~360 J/kg. According to thermodynamics, the adiabatic temperature change at an arbitrary temperature T_0 can be expressed as

$$\Delta T \cong -\Delta S_m(T_0,H)\frac{T_0}{C_p(T_0,H)}, \qquad (3)$$

where C_p is the specific heat. We further performed the measurements of the heat capacity in the fields of *H*=0, 2, and 5 T (Fig. 4). An obvious thermal anomaly near ~87 K in zero field corresponds to the magnetic transition. An applied field broadens this peak and rounds it off in high field, which further indicates a second-order phase transition.[2,22] The isothermal magnetic entropy change ΔS_{heat} can be also calculated from the heat capacity data by $\Delta S_{heat}(T)=\int_0^T [C_p(2T) - C_p(0)]dT/T$. As shown in Fig. 5(a) by open circles, the entropy change ΔS_{heat} exhibits a similar behavior to ΔS_M, implying that the two techniques yield consistent results. Based on the formula (3), the adiabatic temperature rise (ΔT_{ad}) is presented in Fig. 5(b). The maximum ΔT_{ad} are about 1.5 and 2.6 K for magnetic field changes of 2 and 5 T, respectively.

In conclusion, CdCr$_2$S$_4$ shows a large reversible magnetic entropy change with its second-order magnetic transition. It seems to imply that the sulfospinel is probably a promising candidate as working material in magnetic refrigeration technology because of (1) large magnetic entropy change, (2) soft magnetism and reversible MCE, (3) wide temperature span of ΔS_m and large RCP, and (4) relatively low cost of components and fabrication using the powder of Cd, Cr, and S elements.[23]
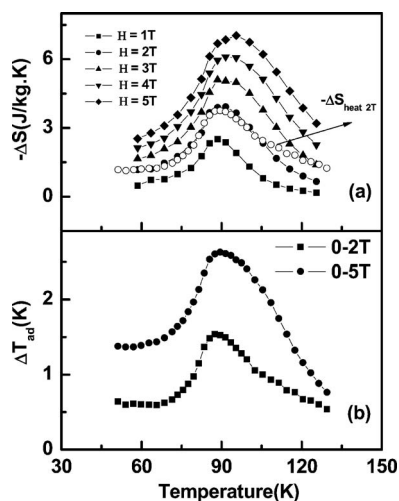
FIG. 5. (a) Entropy changes in CdCr$_2$S$_4$ extracted from magnetization measurements (full symbols) with the magnetic field changes from 0 to 1.0, 2.0, 3.0, 4.0, and 5.0 T and from heat capacity measurements with the magnetic field change from 0 to 2.0 T (open symbols). (b) Temperature dependence of adiabatic temperature rise ΔT_{ad} in CdCr$_2$S$_4$ induced by a magnetic field change of 2 and 5 T.

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