

Large magnetocaloric effect in spinel CdCr₂S₄

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Magnetocaloric effect in CdCr₂S₄ was investigated by magnetization and heat capacity measurements. CdCr₂S₄ 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 $\Delta T_{\text{ad}} \sim 2.6$ 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 Gd₅Si_{4–x}Gex,^{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, AB₂X₄-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)Cr₂(S,Se)₄, have ferromagnetic spin configuration and large spontaneous magnetization.¹⁷ CdCr₂S₄ is a member of the chalcogenide ACr₂S₄ spinels with ferromagnetically coupled Cr³⁺ 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 CdCr₂S₄, indicating that the sulfospinel probably is a promising candidate as working material in magnetic refrigeration technology.

Polycrystalline sample of CdCr₂S₄ was prepared by the solid-state reaction method. A stoichiometric powder mixture of FeS(99.9%), CdS(99.9%), and Cr₂S₃(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 CdCr₂S₄ with $2\theta = 10^\circ - 100^\circ$. 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 $Fd\bar{3}m$ with Cr³⁺ octahedrally and Cd²⁺ 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).

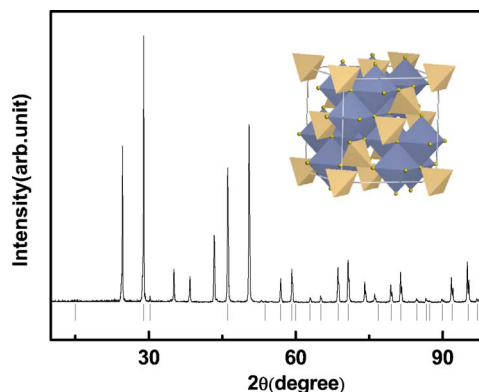


FIG. 1. X-ray diffraction pattern of CdCr₂S₄. Bragg reflections are indicated by vertical bars. The inset shows the crystal structure of CdCr₂S₄ consisting of Cr₆ octahedrons and CdS₄ tetrahedrons.

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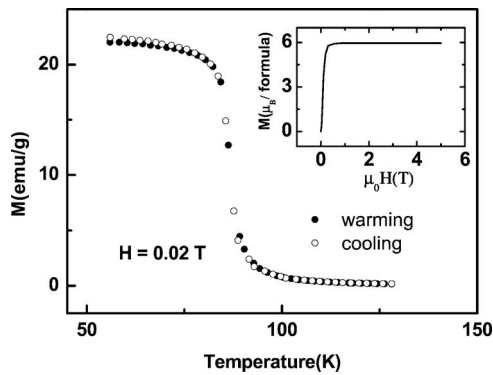


FIG. 2. Temperature dependence of magnetization of CdCr_2S_4 from 56 to 128 K under a magnetic field of 0.02 T. The inset shows the magnetic field dependence of magnetization for CdCr_2S_4 at 2 K.

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 $\sim 5.96\mu_B$ 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_2S_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_2S_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

$$\Delta S_m(T, H) = S_m(T, H) - S_m(T, 0) = \int_0^H \left(\frac{\partial M}{\partial T} \right)_H dH, \quad (1)$$

and can be evaluated by the expression

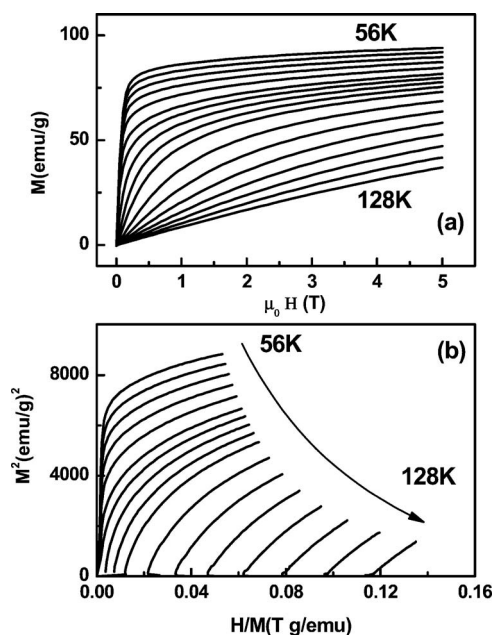


FIG. 3. (a) Magnetization as a function of applied field of CdCr_2S_4 measured near the Curie temperature. (b) The Arrott plots of CdCr_2S_4 .

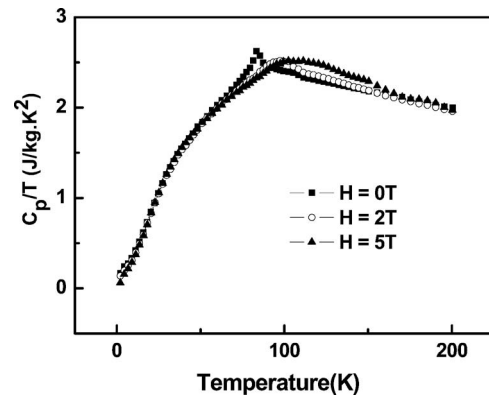


FIG. 4. Heat capacity of CdCr_2S_4 measured under the fields of $H=0, 2,$ and 5 T.

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

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 $|\Delta S_m^{\text{max}}|$ is 3.92 and 7.04 J/kg K for the field changes of 2.0 and 5.0 T. The $|\Delta S_m^{\text{max}}|$ 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 $\text{RCP} = -\Delta S_m^{\text{max}} \times \delta T$,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

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

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 $\Delta S_{\text{heat}}(T) = \int_0^T [C_p(2T) - C_p(0)] dT/T$. 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_2S_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

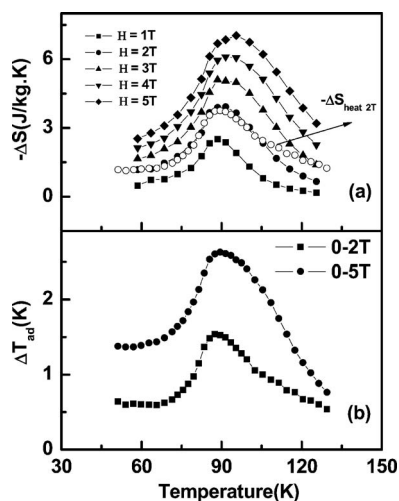


FIG. 5. (a) Entropy changes in CdCr_2S_4 extracted from magnetization measurements (full symbols) with the magnetic field changes from 0 to 1.0, 2.0, 3.0, 4.0, and 5.0 T and from heat capacity measurements with the magnetic field change from 0 to 2.0 T (open symbols). (b) Temperature dependence of adiabatic temperature rise ΔT_{ad} in CdCr_2S_4 induced by a magnetic field change of 2 and 5 T.

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