Magnetic properties and magnetic entropy change in spinels $(Cd,M)Cr_2S_4$ with M=Cu or Fe

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Magnetic properties and magnetic entropy changes in spinels $(Cd,M)Cr_2S_4$ with M=Cu or Fe have been studied. The saturation moments per formula unit are about $4.77\mu_B$ for $Cd_{0.8}Cu_{0.2}Cr_2S_4$ and $4.41\mu_B$ for $Cd_{0.7}Fe_{0.3}Cr_2S_4$. Magnetic transition in Cu- and Fe-doped samples are of second order in nature, and their Curie temperatures are T_C=86 and 119 K, respectively. The maximum values of magnetic entropy change ΔS are found to be 5.1 and 5.4 J/kg K for $Cd_{0.8}Cu_{0.2}Cr_2S_4$ and $Cd_{0.7}Fe_{0.3}Cr_2S_4$ for a field change from 0 to 5 T, respectively. The significant ΔS suggests a potential of the sulfospinel as a magnetic refrigerant in the corresponding temperature range. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2830973]

I. INTRODUCTION

Room-temperature magnetic refrigeration based on the magnetocaloric effect (MCE) has been demonstrated to be a very promising alternative to conventional vapor-cycle refrigeration due to its potential impact on energy savings and environmental concerns.[1–3] Therefore, it has aroused the worldwide interest in the development of new magnetic refrigerants with a large MCE. A variety of prototype materials involving second-order and first-order magnetic transitions had been investigated theoretically and experimentally in an attempt to achieve a large MCE.[4–10] A first-order transition tends to concentrate magnetic entropy change ΔS to a narrow temperature range around the transition temperature compared with second-order one, which implies that a large ΔS is much easier to obtain in the vicinity of transition temperature. Although ΔS of materials with second-order magnetic transition are generally lower than those with first-order one, they exhibit a good reversible behavior in the magnetization as functions of temperature and magnetic field, which is very useful for magnetic refrigeration applications.

Recently, the AB_2X_4-type sulfospinel has attracted much attention because of its colossal magnetocapacitive effects[11] (CMC) and large magnetoresistance effect[12] observed in $CdCr_2S_4$. Most of them are possessed of ferromagnetic spin ordering and large spontaneous magnetization. $CdCr_2S_4$ exhibits a second-order magnetic transition at T_C=87 K with ferromagnetically coupled Cr^{3+} spins (S=3/2).[11] Very recently, our studies revealed that $CdCr_2S_4$ could also be a promising candidate for magnetic refrigerant because of its large MCE.[13] A maximum value of ΔS is found to be 7 J/kg K for a field change of 0–5 T around its Curie temperature. In the present paper, we report on the effects of substitution of Cu and Fe for Cd in $CdCr_2S_4$ on magnetic properties and magnetic entropy changes.

II. EXPERIMENTAL DETAILS

Polycrystalline samples $Cd_{0.8}Cu_{0.2}Cr_2S_4$ and $Cd_{0.7}Fe_{0.3}Cr_2S_4$ were prepared by using the solid-state reaction method. A stoichiometric powder mixture of CdS(99.9), CuS(99.9), FeS(99.9), and Cr_2S_3(99%) available from the Alfa Aesar Company was well ground, then pressed into pellets and sealed in evacuated quartz tubes. Afterward, these tubes were heated up to 780 °C and kept at this temperature for 4 days to obtain a single phase. X-ray diffraction (XRD) measurement was performed by using Cu $K\alpha$ radiation to identify the phase and the crystal structure. Magnetic measurement was carried out by using a superconducting quantum interference device magnetometer.

III. RESULTS AND DISCUSSION

Figure 1 shows the room-temperature powder XRD patterns for $Cd_{0.8}Cu_{0.2}Cr_2S_4$ and $Cd_{0.7}Fe_{0.3}Cr_2S_4$. It can be found that $Cd_{0.7}Fe_{0.3}Cr_2S_4$ crystallized in a very clean single phase of a normal spinel structure with the space group of $Fd3m$. For $Cd_{0.8}Cu_{0.2}Cr_2S_4$, all the diffraction peaks can be indexed by using the JADE 5.0 program[14] to a face-centercubic cell, except some smaller peaks (centered at about 33.6°, 36.3°, and 41.5°), which indicates the existence of a

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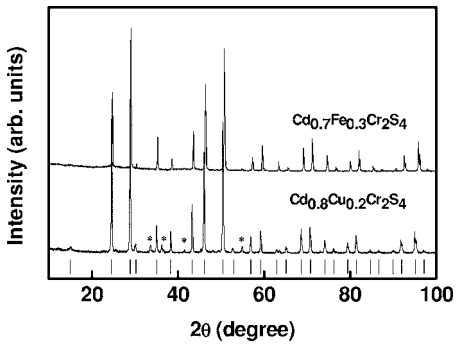

FIG. 1. Room-temperature powder XRD patterns for $Cd_{0.8}Cu_{0.2}Cr_2S_4$ and $Cd_{0.7}Fe_{0.3}Cr_2S_4$. Bragg reflections (small vertical lines) are also shown.

minor Cr_2O_3 as an impurity phase. The lattice parameters are found to be 10.246 Å for $Cd_{0.8}Cu_{0.2}Cr_2S_4$ and 10.174 Å for $Cd_{0.7}Fe_{0.3}Cr_2S_4$.

Figure 2 shows the thermomagnetic *M-T* curves for $Cd_{0.8}Cu_{0.2}Cr_2S_4$ and $Cd_{0.7}Fe_{0.3}Cr_2S_4$ in a magnetic field of 0.01 T on heating and cooling. The Curie temperature T_C is defined as the temperature with a maximum slope in the *M-T* curves. The value of T_C for $CdCr_2S_4$ is 86 K.[13] The partial replacement of Cd by Cu can exert a little influence on the magnetic coupling, and only a small shift of T_C from 86 to 88 K is observed. In contrast, a significant increase of T_C from 86 to 119 K is observed, which stems from the substitution of Fe for Cd. As shown in Fig. 2, the magnetic transition is completely reversible for the temperature increase-decrease cycling, which is indicative of the second-order character of the magnetic transition. However, the magnetizations of $Cd_{0.8}Cu_{0.2}Cr_2S_4$ and $Cd_{0.7}Fe_{0.3}Cr_2S_4$ are strongly dependent on their thermal history at low temperatures. The heating and cooling magnetization curves each

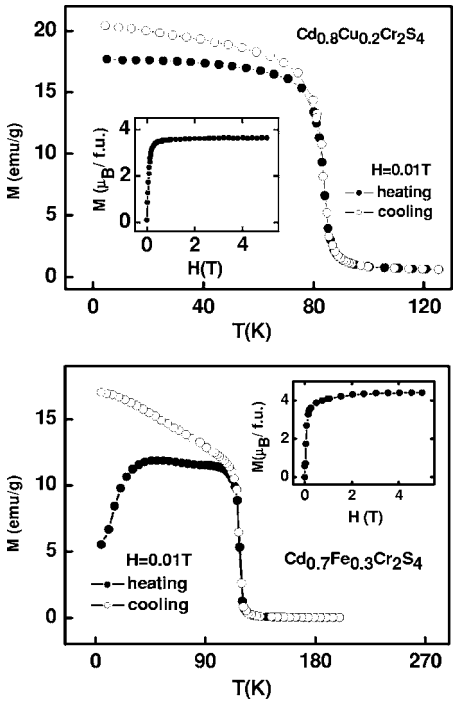

FIG. 2. Temperature dependence of magnetization for $Cd_{0.8}Cu_{0.2}Cr_2S_4$ and $Cd_{0.7}Fe_{0.3}Cr_2S_4$ measured on heating and cooling in a magnetic field of 0.01 T. The insets show the magnetic field dependences of magnetization for $Cd_{0.8}Cu_{0.2}Cr_2S_4$ and $Cd_{0.7}Fe_{0.3}Cr_2S_4$ at 5 K, respectively.

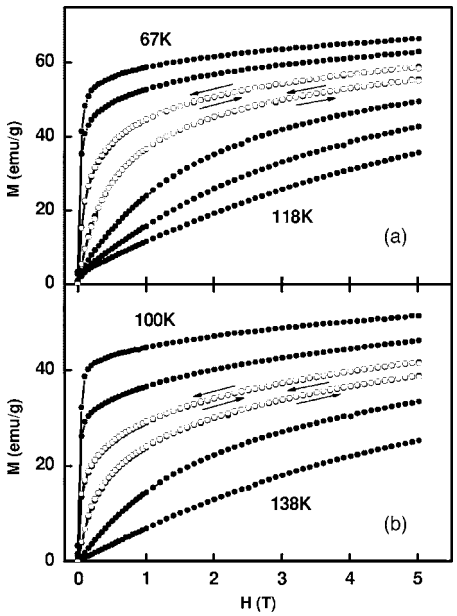

FIG. 3. Isothermal magnetization curves for $Cd_{0.8}Cu_{0.2}Cr_2S_4$ (a) and $Cd_{0.7}Fe_{0.3}Cr_2S_4$ (b) around the Curie temperature in magnetic fields up to 5.0 T.

manifest a strong irreversibility below T_C. The magnetization curves at 5 K of $Cd_{0.8}Cu_{0.2}Cr_2S_4$ and $Cd_{0.7}Fe_{0.3}Cr_2S_4$ are shown in the insets of Fig. 2, respectively. The magnetization curves show that a full saturation state is achieved under a field of ~0.8 T. Saturation moments per formula unit are about 4.77 and $4.41\mu_B$ for $Cd_{0.8}Cu_{0.2}Cr_2S_4$ and $Cd_{0.7}Fe_{0.3}Cr_2S_4$, respectively, indicating the formation of a ferromagnetic spin configuration due to the Cr–S–Cr superexchange interaction.[15] The evaluated values of saturated moments for $Cd_{0.8}Cu_{0.2}Cr_2S_4$ and $Cd_{0.7}Fe_{0.3}Cr_2S_4$ are 5.8 and $4.8\mu_B$/f.u. based on the ideal Cu^{1+}, Cr^{3+}, Cr^{4+}, and Fe^{2+} ions.[16] The measured smaller values must arise from the formation of low spin state Cr^{2+} due to the sulfur loss in the sintering process.[17]

Figure 3 shows the isothermal magnetization curves for $Cd_{0.8}Cu_{0.2}Cr_2S_4$ and $Cd_{0.7}Fe_{0.3}Cr_2S_4$ in a wide temperature range around the Curie temperature with different temperature steps in magnetic fields up to 5.0 T. The temperature steps are chosen to be 2 and 5 K in the vicinity of T_C and in the regions far away from T_C, respectively. The sweep rate of the field is quite slow to ensure that the *M-H* curves are recorded in an isothermal process. Each isotherm shows a reversible behavior for the field ascending and descending and there is no inflection or negative slope that occurs in the Arrott plots as a feature of metamagnetic transition above the T_C, indicating a nature of second-order phase transition.

The magnetic entropy change ΔS is calculated from the Maxwell relation

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

by using the isothermal magnetization data and can be evaluated from the expression

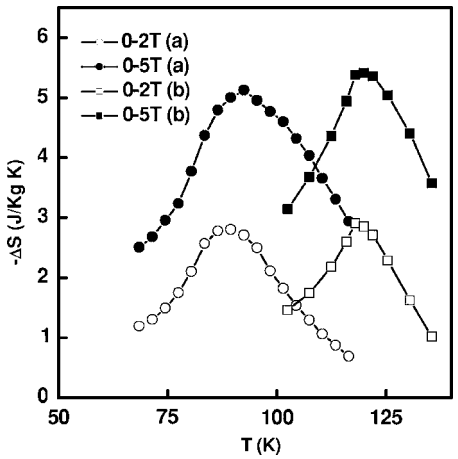

FIG. 4. Temperature dependence of the magnetic entropy change for $Cd_{0.8}Cu_{0.2}Cr_2S_4$ (a) and $Cd_{0.7}Fe_{0.3}Cr_2S_4$ (b) for magnetic field change from 0 to 2 T and from 0 to 5 T.

$$|\Delta S| = \sum_i \frac{M_i - M_{i+1}}{T_{i+1} - T_i} \Delta H_i.$$

Figure 4 shows the values of ΔS for $Cd_{0.8}Cu_{0.2}Cr_2S_4$ and $Cd_{0.7}Fe_{0.3}Cr_2S_4$ as functions of temperature for a field change from 0 to 2 T and from 0 to 5 T, respectively. Around Curie temperatures, a negative peak can be observed from the curves and the maximum values of ΔS for a magnetic field change from 0 to 5 T are found to be 5.1 and 5.4 J/Kg K, respectively. The values of ΔS in the present samples exhibit a small decrease compared with those of $CdCr_2S_4$ (Ref. 13) due to the decrease of magnetization caused by the addition of Cu and Fe. Although the maximum ΔS in $CdCr_2S_4$ based spinels is smaller than that of the most conspicuous magnetocaloric material,[6–10] the ΔS distribution is much more uniform than that of typical first-order phase transition, which is desirable for an Ericsson-cycle magnetic refrigerator.[18] For $Cd_{0.8}Cu_{0.2}Cr_2S_4$ and $Cd_{0.7}Fe_{0.3}Cr_2S_4$, the widths of the ΔS peak, δT_{FWHM}, defined as the temperature interval corresponding to the half maximum of ΔS, approach to ~55 and ~46 K, respectively, in the magnetic field change from 0 to 5 T. According to the mean field theory, the relation between magnetic entropy change and the magnetic field near the Curie temperature is described as[19]

$$\Delta S \approx -1.07qR\left(\frac{g\mu_B JH}{kT_c}\right)^{2/3},$$

where q is the number of magnetic ions, R is the gas constant, and g is the Laude factor. Figure 5 shows the $H^{2/3}$ dependence of the ΔS for $Cd_{0.8}Cu_{0.2}Cr_2S_4$ and $Cd_{0.7}Fe_{0.3}Cr_2S_4$.

It is found that the ΔS well linearly depends on the $H^{2/3}$ near Curie temperature, implying the strong localization of $3d$ electrons and the second-order character of magnetic transition.[20] The value of isothermal magnetic entropy change will rise with the increase of magnetic field. A large ΔS for the present samples results from the sharp drop in magnetization as the temperature passes through T_C.

In summary, we have investigated the effects of the substitution of Cu and Fe for Cd on magnetic properties and magnetic entropy changes, based on the discovery of large magnetocaloric effect in $CdCr_2S_4$.[13] It is found that the substitution of Cu or Fe for Cd in $CdCr_2S_4$ may lead to a decrease in the spontaneous magnetization and an increase in the Curie temperature. The large values of ΔS for $Cd_{0.8}Cu_{0.2}Cr_2S_4$ and $Cd_{0.7}Fe_{0.3}Cr_2S_4$ compounds with a second-order magnetic transition amount to 5.1 and 5.4 J/kg K for a magnetic field change of 0–5 T. A reversible behavior of the magnetization with temperature and magnetic field and a broad distribution of ΔS peak have been achieved.

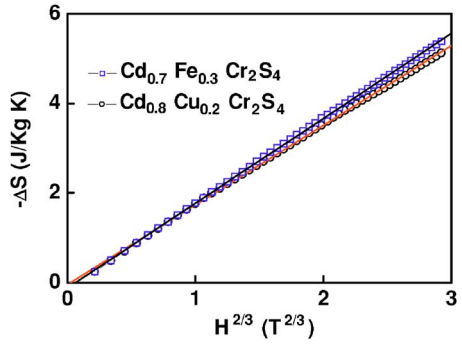

FIG. 5. (Color online) Relation between maximum ΔS and $H^{2/3}$ near Curie temperature for $Cd_{0.8}Cu_{0.2}Cr_2S_4$ and $Cd_{0.7}Fe_{0.3}Cr_2S_4$. The straight line gives the linear fitted to data.

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