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Large reversible magnetocaloric effect in ferromagnetic semiconductor EuS

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ABSTRACT

We present the large reversible magnetocaloric effect (MCE) of the ferromagnetic semiconductor EuS, which shows a maximum magnetic entropy change of $-\Delta S_m^{max} \sim 37\ \mathrm{J\,kg^{-1}\,K^{-1}}$, an adiabatic temperature change of $\Delta T_{ad} \sim 10.4$ K and a relative cooling power of $RCP \sim 782\ \mathrm{J\,kg^{-1}}$ at 18.5 K for a magnetic field change $\Delta H = 5$ T. Particularly, the large MCE is isotropic and without hysteresis loss, even for a magnetic field change of 2 T the values of $-\Delta S_m^{max}$, ΔT_{ad} and RCP reach as high as $22\ \mathrm{J\,kg^{-1}\,K^{-1}}$, 7.5 K and $284\ \mathrm{J\,kg^{-1}}$, respectively. These results indicate that EuS has excellent refrigeration performance at the temperatures near 20 K, and thus can be considered as the potential magnetic refrigerant material for liquefaction of hydrogen.

1. Introduction

In recent years, there is an increased interest in investigation of magnetic refrigeration technology due to the severe situations of the energy and the environment. As a key issue of the magnetic refrigeration technology, exploration of large magnetocaloric effect (MCE) materials with large relative cooling power (RCP) and different working temperatures has been the main objective of the studies in this research field [1]. In general, a good magnetic refrigerant material requires both large values of MCE and RCP. The former means that the magnetic material exhibits large magnetic entropy change (ΔS_m) and large adiabatic temperature change (ΔT_{ad}), which reach their maximum in the vicinity of the ferromagnetic (FM) or antiferromagnetic (AFM) ordering temperature (T_C or T_N, respectively) for a certain magnetic field change (ΔH). The latter is usually associated with a large ΔS_m and a wide temperature range where magnetic phase transition occurs. Since the discovery of the giant MCE system Gd5Si2Ge2 in 1997, many magnetic materials with large ΔS_m have been found. These materials can be divided into two main classes according to their working temperature regions [2,3]: class one includes the room temperature materials such as $Gd_5(SiGe)_4$ [4,5], $La(Fe_{1-x}Si_x)_{13}$ [6,7], $MnAs_{1-x}Sb_x$ [8,9] and $MnFeP_{1-x}As_x$, [10] and class two includes the low temperature (mainly below the liquid N_2 temperature) materials such as $ErRu_2Si_2$ ($T_N \sim 5.5$ K) [11], Ho_5Pd_2 ($T_N \sim 28$ K) [2], ErFeSi ($T_C \sim 22$ K) [12], R_3Ni_2 (R=Ho and Er) ($T_N \sim 15.5$ and 7 K) [13], and $(Dy_{1-x}Er_x)Al2$ ($T_C \sim 13$–65 K) [14].

As a part of our continuing exploration of the better active magnetic refrigerant material, we are recently interested in the magnetic materials that exhibit large MCE and high RCP, and can be used for liquefaction of hydrogen. As described by Zhang et al. in the Ref. [12] hydrogen can be considered as one of the most possible candidates for clean energy sources, because it is environmentally friendly and its reserve is very rich. From the point of view of storage and transportation, exploration of large MCE (RCP) material used for liquefaction of hydrogen has very important significance.

Binary compound EuS is a well-known ferromagnetic semiconductor, which crystallizes in the cubic NaCl-type structure and undergoes a magnetic second order phase transition from paramagnetic (PM) to FM state at Curie temperature $T_C \sim 18$ K [15]. Divalent Eu in EuS has a $4f^7$ configuration and is an S state ion with spin 7/2. The crystalline electric field effect and magnetic anisotropy in this system are expected to be quite weak. Thus, EuS has been investigated as a standard model of Heisenberg ferromagnet in wide research areas including electrical, magnetic, magnetooptical, mechanical and optical properties. On the other hand, considering that many Gd-based compounds with the similar electronic configuration and the same ion moments have been confirmed to be good magnetic refrigerant materials, large and

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isotropic MCE is naturally expected also for EuS and other europium monochalcogenides. This expectation has been confirmed for EuSe [16] and EuO [17]. The former exhibits very large MCE around the temperature T_N~4.6 K, where a first-order magnetic transition (FOMT) from PM to AMF state occurs, and the latter undergoes a second-order magnetic transition (SOMT) from PM to FM state at the temperature T_C~69 K, where large MCE was observed. As for EuS, the only experimental study on MCE was reported by Bredy and Seyfert in 1988 [18]. They used a flat sintered polycrystalline EuS sample and determined its ΔS_m for a field change up to 3 T by measuring the heat flux. Although a larger $-\Delta S_m$ (~22.7 J kg^{-1} K^{-1} at ~17 K) was estimated for ΔH=3 T, this value is much smaller than that expected and no other parameter related to the refrigeration performance was provided. We have systematically measured the MCE on a high quality single crystalline EuS including magnetic susceptibility, magnetization and specific heat in the temperature range between 2 and 80 K under magnetic fields up to 5 T applied along the [100] and [110] directions. In this paper, we present the temperature and field dependences of magnetic entropy change, adiabatic temperature change and relative cooling power calculated from the magnetization and specific heat measurements.

2. Experimental

The EuS single crystal was prepared in a closed tungsten crucible by the Bridgman method that has been used in EuSe single crystal growth and described in Ref. [16]. X-ray diffraction patterns reveal that the obtained single crystalline EuS is single phase with the NaCl-type structure and no impurity phase can be detected. Magnetization was measured as functions of both temperature (between 2 and 300 K) and magnetic field (between 0 and 5 T) by using a superconducting quantum interference device (SQUID, Quantum Design) magnetometer. The thermal-relaxation technique was employed for specific heat measurement in the temperature range between 2 and 70 K by using a physical properties measurement system (PPMS, Quantum Design).

3. Experimental results

Fig. 1(a) and (b) show the temperature dependence of field-cooling (FC) and zero-field-cooling (ZFC) magnetization [$M(T)$] for EuS in a field of 100 Oe applied along the [100] and [110] direction, respectively, plotted as M/H~T. It is clear from these figures that no difference can be detected from the FC and ZFC curves over the temperature range measured for both the [100] and [110] directions. This phenomenon indicates that there are no or very weak thermomagnetic irreversibility and magnetic anisotropy in this system. Both M[100](T) and M[110](T) show a PM to FM transition around the defined Curie temperature T_C=18.2 K, where $|dM/dT|$ reaches the maximum value. Above T_C, the $M(T)$ behavior (see the insets of Fig. 1) can be well described by Curie-Weiss expression with the values of PM Curie temperature θ_P=17.2 and 16.9 K and the effective magnetic moment μ_{eff}=7.79 and 7.91 μ_B for $H\parallel$[100] and $H\parallel$[110], respectively.

Isothermal magnetization, $M(H,T)$, of the EuS sample is measured as a function of magnetic field applied along the [100] and [110] directions around T_C. As seen in Fig. 2(a) and (b), M[100](H,T) and M[110](H,T) show the same FM behavior at low temperatures with almost the same value for a given field and temperature. Below T_C, both M[100] and M[110] demonstrate the saturation trend when H is increased greater than ~1 T, and their values decrease with increasing T. Fig. 3(a) and (b) presents the Arrott plots of the M[100](H,T) and M[110](H,T) data. The positive slop of

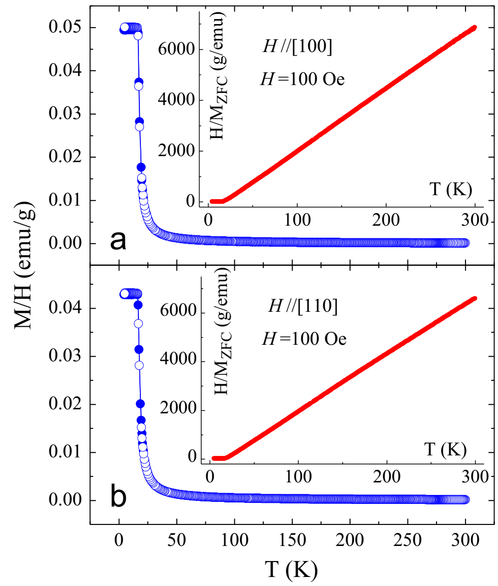

Fig. 1. (Color online) Temperature dependences of ZFC (closed symbols) and FC (open symbols) magnetization of EuS plotted as M/H~T for $H\parallel$[100] (a) and $H\parallel$[110] (b). The insets show the H/M~T plots.

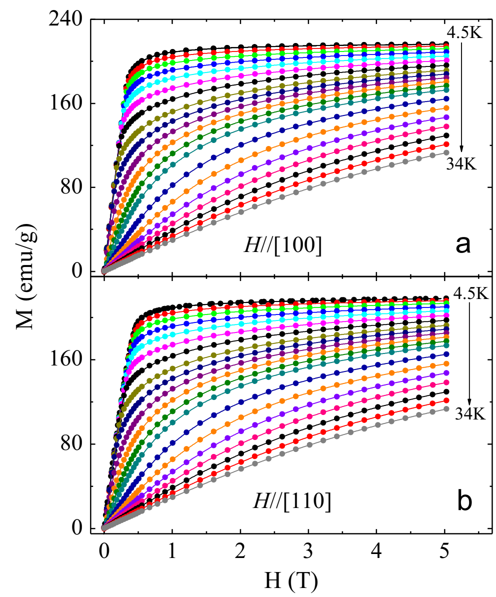

Fig. 2. (Color online) Magnetization of EuS as a function of magnetic field measured at different constant temperatures with $H\parallel$[100] (a) and $H\parallel$[110] (b).

the Arrott plots (M^2 versus H/M) around T_C indicates the characteristic feature of second-order PM-FM transition.

In this work, we focus our attention on MCE of the EuS single crystal. Based on the magnetization data illustrated in Fig. 2(a) and (b), magnetic entropy change ΔS_m of the EuS sample was calculated by using the Maxwell relation $\Delta S_m(T,H) = \int_0^H [\partial M(T,H)/\partial T]_H dH$, and the results are displayed in Fig. 4. Magnetic hysteresis effect was ignored in this calculation, since no magnetic hysteresis can be observed in the $M(H)$ curves for both the [100] and [110] directions at the temperature

range considered. It is found that the -ΔS_m[100](ΔH, T) and $-\Delta S_m$[110](ΔH, T) curves are well coincide with each other as expected, while both $-\Delta S_m$[100] and $-\Delta S_m$[110] show the positive values at the temperature range measured as observed