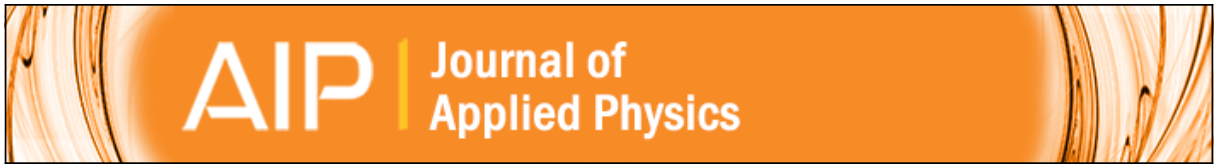

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Magnetocaloric effect and refrigerant capacity in Sr-doped $Eu_8Ga_{16}Ge_{30}$ type-I clathrates

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Magnetic properties, the magnetocaloric effect (MCE) and refrigerant capacity (RC) were investigated in $Eu_8Sr_{8-x}Ga_{16}Ge_{30}$ (x=0,4) type-I clathrates. The substitution of Sr for Eu decreases the Curie temperature (T_C) and saturation magnetization (M_S) from 35 K and 65 emu/g for the x=0 composition to 15 K and 35 emu/g for the x=4 composition. This is attributed to the increase in the Eu–Eu distance with Sr substitution. The large MCE and RC are achieved in both specimens. For a field change of 3 T, the MCE and RC reach the largest values of 5.8 J/kg K and 127.6 J/kg for x=0 composition and 4.3 J/kg K and 72.1 J/kg for x=4 composition. The broadening of the MCE curves is likely associated with the ordering of the magnetic moments of Eu that occurs below 10 K. The large values of MCE and RC, in addition to the absence of thermal and field hysteresis indicate that these clathrate materials are very interesting for cryogenic magnetic refrigeration applications. © *2010 American Institute of Physics*. [doi:10.1063/1.3349409]

I. INTRODUCTION

Semiconductors with the clathrate-hydrate crystal structure have demonstrated interesting physical properties that are directly related to their crystal structure. In these materials, "guest" atoms reside inside "host" framework polyhedra that are formed by other species. These materials are well known for their excellent thermoelectric properties.[1] One of the guest atoms that has been incorporated in clathrates is europium. Since the magnetic moment of Eu is large ($7.94\mu_B$) and the Eu moments order at low temperatures in $Eu_8Ga_{16}Ge_{30}$ clathrates, these materials are found to exhibit interesting magnetic properties[2,3] and large magnetocaloric effect.[4] It has been shown that the $Eu_8Ga_{16}Ge_{30}$ composition exists in both the type-I and type-VIII clathrate crystal structure.[3] Since the separation distance between neighboring Eu^{2+} ions is relatively large, the Rudermann–Kittel–Kasuya–Yoshida interaction mechanism is believed to be responsible for the ferromagnetism in $Eu_8Ga_{16}Ge_{30}$.[2,3] The average distance between Eu^{2+} ions in the type-I clathrate is ~5.23 Å, which is smaller than that of the type-VIII clathrate (~10 Å). As a result, the type-I clathrate possesses a higher Curie temperature (T_C~35 K) compared to that of the type-VIII clathrate (T_C~13 K). Our recent efforts have been devoted to studying the effect of varying the Eu–Eu distance on the magnetic properties of $Eu_8Ga_{16}Ge_{30}$ (type-I) by substituting Sr for Eu.[5] We found that the substitution of Sr for Eu increased the Eu–Eu distance which consequently decreased the T_C of the material. Therefore, it would be of potential interest to study the influence of Sr substitution for Eu on the magnetocaloric effect (MCE) and refrigerant capacity (RC) in $Eu_8Ga_{16}Ge_{30}$.

Herein we report the first investigation, to the best of our knowledge, of the MCE and RC in $Eu_8Sr_{8-x}Ga_{16}Ge_{30}$ (x=0,4) type-I clathrates. The results obtained reveal that Sr substitution leads to a reduction in both the MCE and RC in $Eu_8Ga_{16}Ge_{30}$. However, large values of MCE and RC are achieved in these clathrates, larger than several other candidate magnetic refrigerant materials reported in the literature in the same operating temperature range.

II. EXPERIMENT

Polycrystalline $Eu_8Ga_{16}Ge_{30}$ with the type-I crystal structure was synthesized as follows. High purity Eu, Ga, and Ge were combined in stoichiometric ratios inside a boron nitride (BN) crucible which was enclosed, in a nitrogen atmosphere, inside a quartz ampoule. The specimen was placed in an induction furnace at 1000 °C for 10 min followed by a rapid water quench. The $Sr_4Eu_4Ga_{16}Ge_{30}$ specimens were prepared in a similar manner. The specimens was reacted in a tube furnace at 950 °C for 3 days, and slowly cooled to 700 °C for another 3 days prior to air quenching.[5–7] X-ray diffraction (XRD) and electron-beam microprobe analyses revealed the presence of the type-I clathrate phase only, with homogenous compositions within the polycrystalline grains of ~10 μm.[8] Magnetic and magnetocaloric measurements were conducted using a commercial Physical Property Measurement System from Quantum Design over a temperature range of 2–60 K at applied fields up to 3 T. The isothermal magnetization curves were collected at different fixed temperatures ranging from 2 to 60 K and were used to calculate the magnetic entropy change (ΔS_M) using the Maxwell relation,

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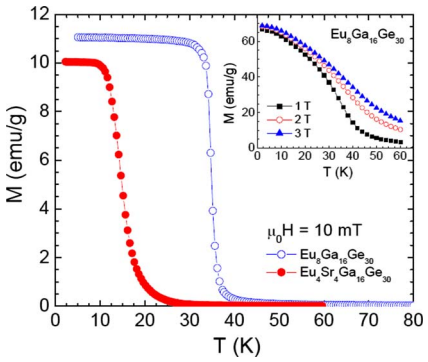

FIG. 1. (Color online) Temperature dependence of magnetization taken at a field of 10 mT for $Eu_8Ga_{16}Ge_{30}$ and $Eu_4Sr_4Ga_{16}Ge_{30}$, and inset shows data taken at higher fields for $Eu_8Ga_{16}Ge_{30}$.

$$\Delta S_M = \mu_0 \int_0^{H_{max}} \left(\frac{\partial M}{\partial T}\right)_H dH, \quad (1)$$

where M is the magnetization, H is the magnetic field, and T is the temperature.

III. RESULTS AND DISCUSSION

Figure 1 shows the temperature dependence of magnetization taken at a low applied field of 10 mT for the $Eu_8Ga_{16}Ge_{30}$ and $Eu_4Sr_4Ga_{16}Ge_{30}$ samples. The inset in Fig. 1 shows data at varying fields of 1, 2, and 3 T for $Eu_8Ga_{16}Ge_{30}$. The paramagnetic to ferromagnetic (PM-FM) transitions in all the specimens are noted. The Curie temperatures (T_C), which are determined from the minimum in dM/dT across the transitions, are 35 and 15 K for $Eu_8Ga_{16}Ge_{30}$ and $Eu_4Sr_4Ga_{16}Ge_{30}$, respectively. As expected,

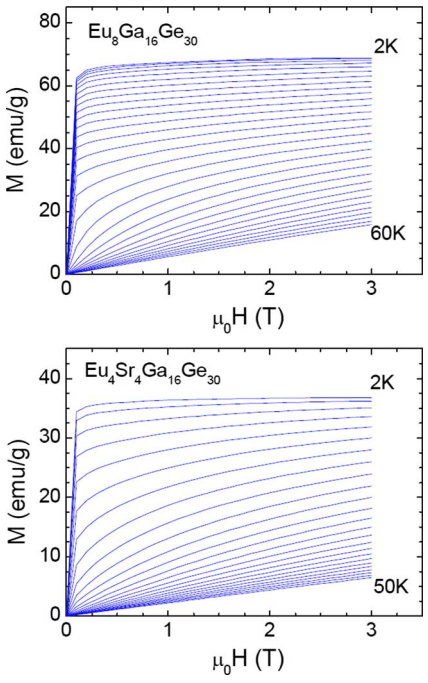

FIG. 2. (Color online) Isothermal magnetization curves taken at different fixed temperatures between 2 and 60 K for $Eu_8Ga_{16}Ge_{30}$ (upper panel) and between 2 and 50 K for $Eu_4Sr_4Ga_{16}Ge_{30}$ (lower panel), with temperature intervals of $\Delta T = 2$ K.

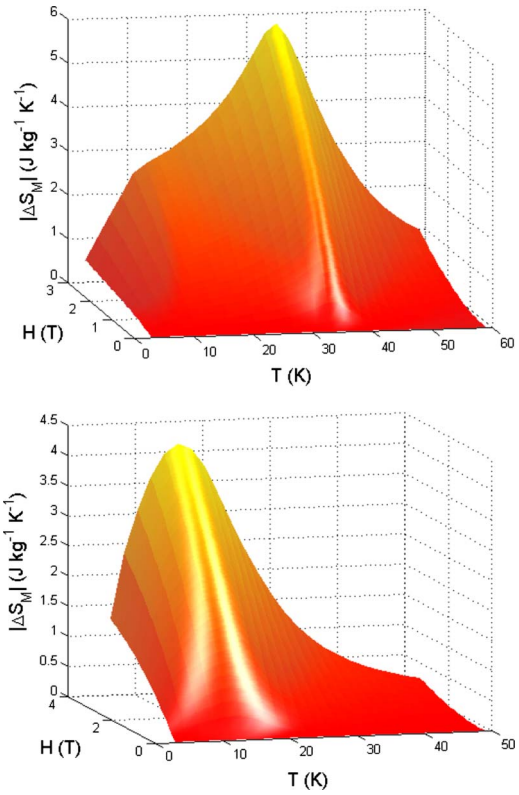

FIG. 3. (Color online) Temperature and magnetic field dependencies of magnetic entropy change ($-\Delta S_M$) for $Eu_8Ga_{16}Ge_{30}$ (upper panel) and $Eu_4Sr_4Ga_{16}Ge_{30}$ (lower panel).

the substitution of Sr for Eu decreases the T_C and saturation magnetization (M_S) as the average Eu–Eu distance increases from 5.23 Å for $Eu_8Ga_{16}Ge_{30}$ to ~10 Å for $Eu_4Sr_4Ga_{16}Ge_{30}$.[5] It is worth noting from the inset of Fig. 1 that the PM-FM transition of $Eu_8Ga_{16}Ge_{30}$ becomes broader at higher applied fields, implying a broadening of magnetic entropy change in the temperature range near T_C, as discussed in detail below.

Figure 2 shows the M-H isotherms taken at 2 K intervals from 2 to 60 K for $Eu_8Ga_{16}Ge_{30}$ and from 2 to 50 K for $Eu_4Sr_4Ga_{16}Ge_{30}$, temperature ranges which span the PM-FM transition regions in these compositions. Consistent with the M-T data shown in Fig. 1, the large changes in magnetization are clearly observed in Fig. 2 as the temperature nears and eventually crosses over T_C from FM to PM states. Using Eq. (1) the magnetic entropy change (ΔS_M) is calculated from the isothermal M-H curves (Fig. 2). The results of the calculated ΔS_M are shown in Fig. 3 for $Eu_8Ga_{16}Ge_{30}$ (upper panel) and $Eu_4Sr_4Ga_{16}Ge_{30}$ (lower panel). As clearly indicated in Fig. 3 for $Eu_8Ga_{16}Ge_{30}$, an additional peak or a shoulder appears to occur at $T_L \sim 10$ K, apart from a main expected peak at $T_C \sim 35$ K for $\Delta S_M(T)$. In the case of $Eu_4Sr_4Ga_{16}Ge_{30}$, however, the broader peak located at 12 K is a combination of the features at T_C (15 K) and T_L (10 K).

To check if the presence of T_L is an intrinsic property or simply arises from contribution of another phase, such as Eu_3O_4 (Ref. 9) that may form during synthesis, we conducted systematic structural and MCE analyses on three different $Eu_8Ga_{16}Ge_{30}$ specimens. While the XRD patters reveal the absence of Eu_3O_4, the MCE data show the presence of T_L

TABLE I. Maximum magnetic entropy change $|\Delta S_M^{max}|$ occurring at the peak temperature T_P for $\Delta(\mu_0 H)=2$ T for several magnetic refrigerant candidate materials.

Material	T_p (K)	$\lvert\Delta S_M^{max}\rvert$ (J/kg K)	RC (J/kg)	Reference
$Eu_8Ga_{16}Ge_{30}$	35	4.64	116	Present
$Eu_4Sr_4Ga_{16}Ge_{30}$	12	3.4	63	Present
$ErRu_2Si_2$	7	4.8	24	14
$Gd_3Fe_5O_{12}$	35	1.75	121	13
[a]Co	13	1.7	31	15
[b]$Co_{core}Ag_{shell}$	13	1.66	33	15

[a]Nanoparticles.
[b]Core/shell nanoparticles.

in all the samples. This suggests that the presence of T_L may be an intrinsic property of type-I $Eu_8Ga_{16}Ge_{30}$. From a crystal structure point of view, the type-I clathrates have two different polyhedral cages: E_{20} pentagonal dodecahedra centered by Eu1 and E_{24} tetrakaidecahedra centered by Eu2.[1] There are two Eu1 (2a sites) and six Eu2 (6d sites) atoms per $Eu_8Ga_{16}Ge_{30}$ formula unit. Since the average distance between Eu2 and Eu2 is smallest (~5.23 Å), the ferromagnetism of the clathrate is mainly dominated by the magnetic interactions between these Eu2 ions. Recent studies have revealed a strong positional disorder associated with the Eu2 sites in the temperature range of 10–300 K, however this effect is largely suppressed below 10 K.[10,11] This thus leads to a general expectation that the magnetic moments of Eu2 would become ordered when the system is cooled below 10 K. It is the ordering of the magnetic moments below 10K that results in the anomalous MCE at this temperature. In the case of $Eu_4Sr_4Ga_{16}Ge_{30}$, Sr mainly replaces Eu2,[7] resulting in a strong decrease in T_C (Fig. 1), M_S (Fig. 2), and as well as MCE (Fig. 3) in the Sr containing specimen. A detailed study of the structure is needed to further elucidate the origin of the low-temperature magnetic anomalies and is beyond the scope of this paper.

From a magnetic refrigeration perspective, the refrigerant capacity, which is a measure of the amount of heat transfer between the cold and hot sinks in an ideal refrigeration cycle, is considered to be the most important factor. The RC is defined as the product of $-\Delta S_M^{max}$ and the full width at half maximum of the $\Delta S_M(T)$ curve.[12] Therefore, a good magnetic refrigerant material with large RC requires both large $-\Delta S_M^{max}$ as well as the broad width of the $\Delta S_M(T)$ curve. In the present study, the clathrate specimens exhibit the large magnetic entropy changes at modest fields (see Fig. 3). Interestingly, the broadening of the $\Delta S_M(T)$ curves around the T_C is observed which contributes to enhanced RC. For a field change of 3 T, the $-\Delta S_M^{max}$ and RC reach the largest values of 5.8 J/kg K and 127.6 J/kg for $Eu_8Ga_{16}Ge_{30}$ and (4.3 J/kg K) and 72.1 J/kg for $Eu_4Sr_4Ga_{16}Ge_{30}$, respectively.

To put our results in perspective, we summarize in Table I the values of $-\Delta S_M^{max}$ and RC of the clathrates and some other cryogenic magnetic refrigerant materials from the literature including previous work from our own group. As one can see clearly from Table I for the same field change (2T) the RC of $Eu_8Ga_{16}Ge_{30}$ (~116 J/kg) is as large as that of the well-known cryogenic magnetic refrigerant $Gd_3Fe_5O_{12}$ (~121 J/kg) (Ref. 13) and is about five times larger than that of $ErRu_2Si_2$ (~24 J/kg K),[14] which was reported to show a high value of $-\Delta S_M^{max}$ (4.8 J/kg K). As an MCE material, $Eu_8Ga_{16}Ge_{30}$ has additional advantages, such as negligible thermal and field hysteresis ($H_C \sim 0.001$ mT), compared with other compositions which is desirable for an ideal magnetic refrigertor.[4] These superior magnetocaloric properties make these clathrates interesting materials, worthy of further investigation, with properties that may be useful in the search for potential candidates for cryogenic magnetic refrigeration.

IV. CONCLUSIONS

We have systematically investigated the MCE and RC in $Eu_8Ga_{16}Ge_{30}$ and $Eu_4Sr_4Ga_{16}Ge_{30}$ type-I clathrates. Both compounds possess large MCE and RC. The large value of MCE originates from the large magnetic moment of Eu, while the broadening of the MCE curve is likely associated with ordering of the magnetic moments of Eu2 that occurs below 10 K. The substitution of Sr for Eu decreases the T_C, M_S, MCE, and RC in $Eu_8Ga_{16}Ge_{30}$. The large values of MCE and RC, in addition to the absence of thermal and field hysteresis, make these clathrates very attractive for cryogenic magnetic refrigeration applications.

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