Long-range ferromagnetism and giant magnetocaloric effect in type VIII $Eu_8Ga_{16}Ge_{30}$ clathrates

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Long-range ferromagnetism and low-field giant magnetocaloric effect are observed in $Eu_8Ga_{16}Ge_{30}$ with the type VIII clathrate crystal structure, a material that is better known for its thermoelectric properties. Magnetization and modified Arrott plots indicate that the system undergoes a second-order ferromagnetic-paramagnetic phase transition at ~13 K. The low-field giant magnetic entropy change ($-\Delta S_M \sim 11.4$ J/kg K for $\Delta\mu_0 H = 3$ T) coupled with the absence of thermal hysteresis and field hysteresis makes the system very attractive for low temperature magnetic refrigeration. The giant magnetic entropy change originates from the large magnetization ($7.97\mu_B$ per Eu ion) and the sharp change with temperature at the paramagnetic-ferromagnetic transition. [DOI: 10.1063/1.3055833]

Magnetic refrigeration based on the magnetocaloric effect (MCE) is a topic of great interest.[1] While the concept itself is very old and magnetic cooling for producing ultralow temperatures dates back to the 1920s, the discovery of alloys exhibiting the so-called giant MCE has renewed interest for solid-state cooling applications in the intermediate to room temperature (77–300 K) range.[1–3] Therefore, magnetic refrigeration technology is a promising alternative to conventional gas compression techniques.[1,2] A number of materials that undergo first-order magnetic phase transitions have been found to possess giant MCE, such as Gd–Si–Ge,[1] Mn–Fe–P–As,[4] Mn–As–Sb,[5] and Ni–Mn–Ga (Ref. 6) alloys. However, due to structural transitions that often accompany first-order magnetic transitions, these materials show relatively large thermal hysteresis and field hysteresis, which are, in practical applications, undesirable for active magnetic refrigeration. In addition, large MCE can only be achieved upon application of high magnetic fields (>2 T) that cannot be readily supplied using permanent magnets.[1–6] These factors, to some extent, limit these materials from practical use. Therefore a search for materials that exhibit not only the giant MCE but also have zero or negligible thermal hysteresis and field hysteresis is of current interest.[7,8]

Materials with the clathrate hydrate crystal structure have demonstrated interesting physical properties that are directly related to the fact that "guest" atoms reside inside "host" polyhedra that are formed by other species.[9–11] One of the interesting guests that form clathrates is europium. The composition $Eu_8Ga_{16}Ge_{30}$ can form in two completely different clathrate structure types. In type I (Pm-$3n$) clathrate structure Eu resides inside two different polyhedra, two dodecahedra, and six tetrakaidecahedra per unit cell, formed by the (Ga,Ge) framework while in the type VIII (I-$43m$) clathrate structure eight distorted pentagonal dodecahedra containing 23 vertices surround the Eu ions.[9,10] The resulting guest-host interaction is one of the most conspicuous aspects of these materials. Herein we report on the observed long-range ferromagnetism and low-field giant MCE in type VIII clathrate $Eu_8Ga_{16}Ge_{30}$. Our results indicate that this material undergoes a second-order, ferromagnetic-paramagnetic transition at ~13 K, with long-range ferromagnetic ordering. The low-field giant MCE, together with the absence of thermal hysteresis and field hysteresis, makes it a very promising candidate material for active magnetic refrigeration in the low temperature regime below 20 K.

High-quality polycrystalline $Eu_8Ga_{16}Ge_{30}$ clathrate with type VIII crystal structure was synthesized as follows. After melting a stoichiometric mixture of the high purity elements employing a BN crucible with a nitrogen atmosphere in an induction furnace at 1000 °C for 10 min, the specimen was water quenched. It was then annealed at 635 °C for 2 weeks. The crystal structure and phase purity was confirmed by x-ray diffraction analyses. Magnetic measurements were performed using a commercial physical property measurement system from Quantum Design in the temperature range of 5–300 K at applied fields up to 7 T. The magnetic isotherms were measured with a field step of 0.05 mT in the range of 0–3 T and with a temperature interval of 3 K (1 K in the proximity of the Curie temperature, T_C) over a temperature range of 5–62 K.

Figure 1 shows the temperature dependence of magnetization taken at a low applied field of 0.01 mT. The inset in

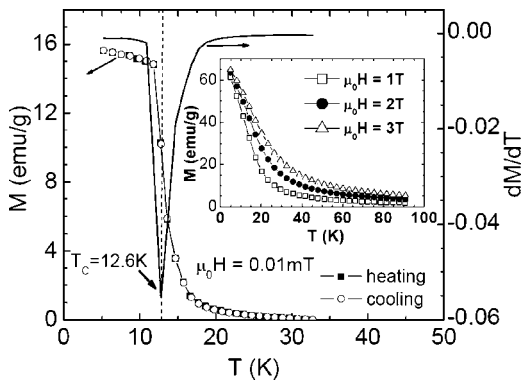

FIG. 1. Magnetization curves taken at 0.01 mT with increasing (heating) and decreasing (cooling) temperature. The corresponding dM/dT curve for the heating branch is also overlaid to mark the transition temperature. The inset shows the magnetization curves taken at applied fields of 1, 2, and 3 T.

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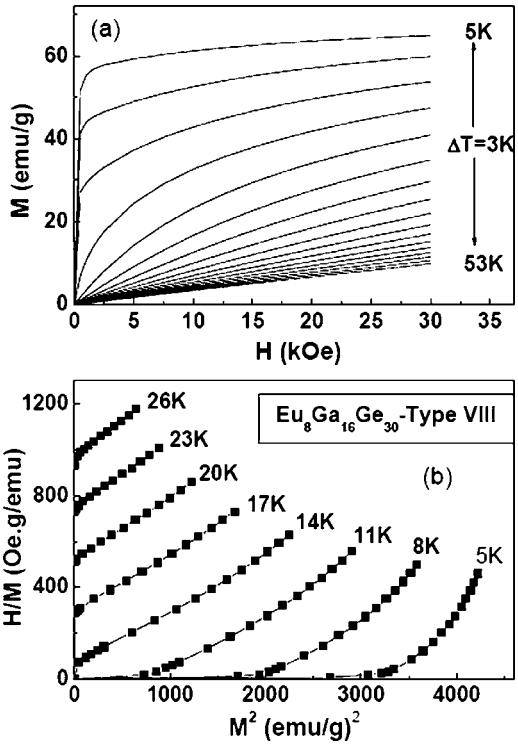

FIG. 2. (a) Magnetization isotherms measured at different temperatures between 5 and 53 K with 3 K interval. (b) The H/M vs M^2 plots for representative temperatures around the T_C.

Fig. 1 shows data at higher fields of 1, 2, and 3 T. The Curie temperature (T_C) of 12.6 K is defined by the minimum in dM/dT (also shown overlaid on the M-T curve in Fig. 1). To check for the presence of any thermal hysteresis in the transition region, we measured the magnetization both while heating and cooling the specimen. As shown in Fig. 1, no thermal hysteresis is detected. This is beneficial for active magnetic refrigeration.[3] An expected broadening of the transition takes place at larger applied fields but remains reasonably sharp even at a field of up to 3 T (inset of Fig. 1). In a study reported by Hu *et al.*[6] the compound $MnAs_{0.9}Sb_{0.1}$ displayed a smooth temperature variation of the magnetization under high fields, whereas the shape of the M-T curve for MnAs was almost unchanged. As a result, MnAs exhibited a larger MCE compared to $MnAs_{0.9}Sb_{0.1}$.[6] Our experimental observation reported here leads to a similar expectation that type VIII $Eu_8Ga_{16}Ge_{30}$ clathrate compound would show a large magnetic entropy change in the vicinity of its T_C. In Fig. 2(a) we show a series of M-H isotherms taken at temperature intervals of ΔT=3 K from 5 to 53 K spanning the ferromagnetic transition region. A sharp change in magnetization is clearly observed in Fig. 2(a) as the temperature nears and eventually crosses over T_C from ferromagnetic to paramagnetic states. A noticeable feature in Fig. 2(a) is that a large proportion of the change in magnetization occurs below 2 T. This is beneficial for practical application of MCE materials at modest fields.[1–3]

Since the magnitude of MCE and its dependence on temperature and magnetic field are strongly dependent on the nature of the corresponding magnetic phase transition,[4] it is essential to analyze the magnetic transition further in this material. To do this, the measured data of the M-H isotherms were converted into H/M versus M^2 plots (the so-called Arrott plots). These are shown in Fig. 2(b) for representative

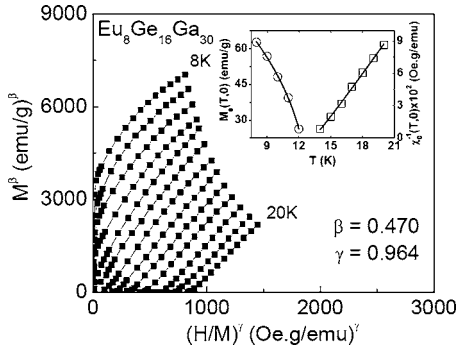

FIG. 3. Modified Arrott plot isotherms with 1 K temperature interval for type VIII $Eu_8Ga_{16}Ge_{30}$. The inset shows spontaneous M_s (circles) and inverse initial susceptibility χ_o^{-1} (square) vs temperature; solid lines are fitting curves to Eq. (1) and (2), respectively.

temperatures near T_C. According to the Banerjee criterion,[12] the magnetic transition is of second order if all the H/M versus M^2 curves have a positive slope. On the other hand, if some of the H/M versus M^2 curves show a negative slope at some point, the transition is of first order.[12,13] For the case of $Eu_8Ga_{16}Ge_{30}$, the presence of the positive slope of the H/M versus M^2 curves indicates that the magnetic transition is of second order. This result is consistent with the absence of thermal hysteresis (see Fig. 1) and the specific heat data,[10] all of which points toward a second-order magnetic transition.

To shed light on the nature of the magnetic critical phenomena in the phase-transition region, we have made quantitative fits to the Arrott plots using the following equations:[14]

$$M_s(T) = \lim_{H\to 0}(M) = M_0(-\varepsilon)^{\beta}, \quad \varepsilon < 0, \tag{1}$$

$$x_0^{-1}(T) = \lim_{H\to 0}(H/M) = (h_0/M_0)\varepsilon^{\gamma}, \quad \varepsilon > 0, \tag{2}$$

where M_0 and h_0 are the constants, and $\varepsilon=(T-T_C)/T_C$ is the reduced temperature. The fitting procedure can briefly be described as follows. By selecting initial values for β and γ, we first plot $M^{1/\beta}$ versus $(H/M)^{1/\gamma}$. Then we determine M_s from the intersection of the linearly extrapolated curve with the $M^{1/\beta}$ axis and plot M_s as a function of temperature, $M_s(T)$. A similar procedure is also used for $\chi_0^{-1}(T)$ with the $(H/M)^{1/\gamma}$ axis. Values for the critical exponents are obtained that are then reintroduced into the scaling of the modified Arrott plot. These procedures are repeated until the iterations converge and lead to the optimum fitting values. Figure 3 displays the plot of $M^{1/\beta}$ versus $(H/M)^{1/\gamma}$ with optimized $\beta=0.470\pm0.3$ and $\gamma=0.964\pm0.4$ values, deduced from fitting $M_s(T)$ and $\chi_0^{-1}(T)$ data using Eqs. (1) and (2), as shown in the inset of Fig. 3. Using the Widom scaling relationship,[15] $\delta=1+\gamma/\beta$, δ is determined to be 3.051 ± 0.4. This value is in good agreement with that (3.014 ± 0.3) determined from the $M \alpha H^{1/\delta}$ relationship at $T=T_C$ (not shown). The critical values for type VIII $Eu_8Ga_{16}Ge_{30}$ match very well with those predicted from the mean field model[16] ($\gamma=1$, $\beta=0.5$, and $\delta=3$), indicating the existence of a long-range ferromagnetic order in this material. While magnetism in this class of material has been investigated in the past by other groups,[10] our work here presents critical exponent analysis and confirmation regarding the long-range nature of ferromagnetism in this system. Thus this finding provides further insights into the nature of the Ruderman–Kittel–

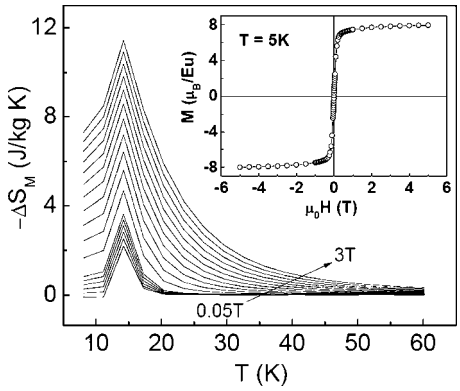

FIG. 4. Magnetic entropy change (ΔS_M) as a function of temperature (T) extracted from M-H-T curves via the Maxwell relation. The inset shows the hysteresis loop measured at 5 K.

Kasuya–Yosida interaction that is believed to be responsible for the ferromagnetism of type VIII clathrate $Eu_8Ga_{16}Ge_{30}$ with large separation distance of Eu–Eu (5.562 å).[10]

Finally, to elucidate the influences of the magnetic transition and long-range ferromagnetism on the MCE in $Eu_8Ga_{16}Ge_{30}$, the magnetic entropy change $\Delta S_M(T)$ is calculated from a family of isothermal M-H curves (Fig. 2) using the Maxwell relation,[1]

$$\Delta S_M = \mu_0 \int_0^{H_{\max}} \left(\frac{\partial M}{\partial T}\right)_H dH, \tag{3}$$

where M is the magnetization, H is the magnetic field, and T is the temperature. Figure 4 shows the magnetic entropy change (ΔS_M) as a function of temperature for different magnetic field changes up to 3 T. From Fig. 4 $-\Delta S_M$ reaches a very high value of 11.4 J/kg K at ~13 K for $\Delta\mu_0 H=3$ T, indicating that this clathrate belongs to a class of giant MCE materials. This value is about twice as large as that reported for DySb (Ref. 8) (~6.5 J/kg K at 11 K for $\Delta\mu_0 H=3$ T) and is almost equal to that reported for $ErRu_2Si_2$ (Ref. 7) (~12 J/kg K at 5.5 K for $\Delta\mu_0 H=3$ T) within a similar temperature range. It is also much larger than that of Gd (Ref. 3) (~10.2 J/kg K for $\Delta\mu_0 H=5$ T) and comparable with those of $Gd_5Si_2Ge_2$ (Ref. 1) (~18 J/kg K for $\Delta\mu_0 H=5$ T) and $MnFeP_{0.45}As_{0.55}$ (Ref. 4) (~18 J/kg K for $\Delta\mu_0 H=5$ T) near the transition region, although the transition temperatures vary in these latter materials. The relative cooling capacity, estimated using standard methods,[3] is significantly larger for type VIII clathrate $Eu_8Ga_{16}Ge_{30}$ (~87 J/kg) than for DySb (Ref. 8) (~34 J/kg) and $ErRu_2Si_2$ (Ref. 7) (~55 J/K g) for the same field change of 2 T. Compared to other magnetocaloric materials,[1,5,6] $Eu_8Ga_{16}Ge_{30}$ has additional distinct technological advantages, such as no thermal hysteresis (Fig. 1) and field hysteresis (inset of Fig. 4), which are desirable for active magnetic refrigeration cycles.[1–3] These results indicate that this composition is a promising candidate for magnetic refrigeration in the low temperature region useful for helium and hydrogen liquefaction. The origin of the giant magnetic entropy change in $Eu_8Ga_{16}Ge_{30}$ lies in the abrupt reduction in magnetization at the transition temperature. Moreover, the magnetic moment of $7.97\mu_B$ for this material, as determined from the magnetization curve at 5 K (see inset of Fig. 4), is nearly equal to the free-ion moment of $7.94\mu_B$. This, together with the existence of the long-range ferromagnetic order, clearly indicates a parallel alignment of all the Eu^{2+} magnetic moments and a strong coupling between these moments via the conduction-electron spins.[10] This coupling remains strong at the transition temperature (T_C), as evidenced by the fact that the M-T curves remain sharp under high applied fields (see inset of Fig. 1). Therefore the additional entropy change is attributed to the fact that the magnetic transition greatly enhances the effect of the applied magnetic field as the system enters a long-range three-dimensional ferromagnetic order completely from the paramagnetic phase within a narrow temperature range around the T_C. A recent study has shown that the existence of a short-range ferromagnetic order (i.e., the presence of magnetic clusters) is a major obstacle for obtaining a large MCE response in magnetic materials due to the high energy required to realign the individual spins by the applied magnetic field.[17]

In summary, we report evidence for long-range ferromagnetism and low-field giant MCE in type VIII clathrate $Eu_8Ga_{16}Ge_{30}$ making this material an attractive candidate for active magnetic refrigeration in the sub-20-K region.

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