

# Large reversible magnetocaloric effect caused by two successive magnetic transitions in ErGa compound

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Intermetallic compound ErGa exhibits two successive magnetic transitions: spin-reorientation transition at  $T_{SR}=15$  K and ferromagnetic-paramagnetic transition at  $T_C=30$  K. Both transitions contribute greatly to the magnetic entropy change ( $\Delta S_M$ ), each yielding a significant peak on their  $\Delta S_M$ - $T$  curve and thus a considerable value of refrigerant capacity (RC) without hysteresis loss. For a magnetic field change of 5 T, the maximal values of  $-\Delta S_M$  are 21.3 J/kg K at  $T_C$  and 16.5 J/kg K at  $T_{SR}$ , with an RC value of 494 J/kg. Large reversible magnetocaloric effect and RC indicate the potentiality of ErGa as a candidate magnetic refrigerant at low temperatures. © 2009 American Institute of Physics. [doi:10.1063/1.3233925]

Magnetic refrigeration based on the magnetocaloric effect (MCE) is expected to be a promising alternative technology to the conventional gas compression refrigeration due to its higher energy efficiency and friendly environment.<sup>1-4</sup> To improve the application of this cooling technology, many efforts have been made to explore advanced magnetic refrigerant materials. In the past, much attention has been paid mainly to the materials that possess large isothermal magnetic entropy change  $\Delta S_M$  and/or adiabatic temperature change. However, it is insufficient to evaluate the potentiality in application of a magnetic refrigerant material solely by the large magnetic entropy change ( $\Delta S_M$ ). Besides, one of the most important parameters is the refrigerant capacity (RC), the parameter that is a measure of how much heat can be transferred between the cold and the hot sinks in one ideal refrigeration cycle, which depends on not only the  $\Delta S_M$  value but also the width of  $\Delta S_M$ - $T$  curve. A large number of materials with first-order magnetic transition have been found to exhibit giant MCEs around their transition temperatures,<sup>5-14</sup> yet the majority of them are less efficient in fast-cycling refrigerator because there are considerable thermal and magnetic hysteresis accompanied by the first-order magnetic transition that can greatly reduce the actual RC of the materials. In addition, the first-order magnetic transition is usually accompanied by structure change or remarkable volume variation, which may speed up the fatigue of materials and thus greatly weaken the MCE and the RC after several refrigerant cycles. Therefore, it is necessary to explore magnetic materials with a large reversible MCE and good RC based on the second-order phase transition.

ErGa is a ferromagnet that undergoes two successive magnetic transitions: spin-reorientation (SR) transition at  $T_{SR} \sim 15$  K (Ref. 15) and transition from ferromagnetic (FM) to paramagnetic (PM) states at  $T_C \sim 31$  K.<sup>15,16</sup> In the present paper, we report on the large reversible MCE and high RC in ErGa, which are due to the combined contribution from the SR and FM-PM transitions.

The polycrystalline ErGa compound was prepared by arc melting the constituent elements of purity better than 99.9%

in argon atmosphere. For homogeneity, the ingot was annealed in an evacuated sealed quartz tube at 800 °C for 1 week. The x-ray powder diffraction pattern confirmed the single-phase nature of the compound, crystallizing in the orthorhombic CrB-type structure (space group  $Cmcm$ ). The lattice parameters  $a$ ,  $b$ , and  $c$ , were determined to be 4.263(0), 10.728(8), and 4.030(6) Å, respectively, by using the Rietveld refinement method. The residual factor  $R_{wp}$  was equal to 12.7%. The magnetization and the heat capacity were measured by employing a physical property measurement system from Quantum Design.

Figure 1(a) shows the temperature dependences of zero-field-cooling (ZFC) and field-cooling (FC) magnetizations under a magnetic field of 0.01 T. The anomaly around  $T_{SR} = 15$  K on the  $M$ - $T$  curve indicates the occurrence of SR transition. The SR transition in ErGa had been observed by Nesterov *et al.*<sup>15</sup> and confirmed by Delyagin *et al.*<sup>17</sup> based on

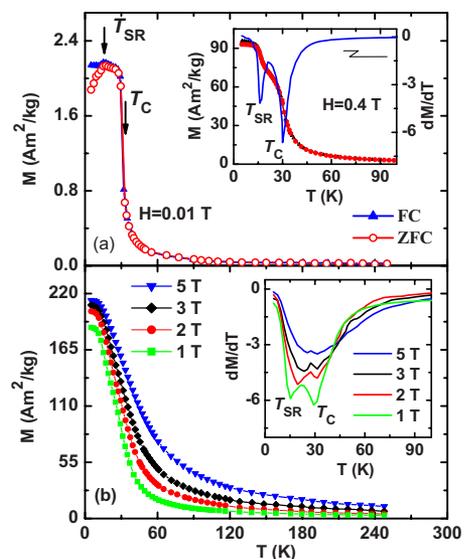


FIG. 1. (Color online) Temperature dependences of the ZFC and the FC magnetization for ErGa under a magnetic field of 0.01 T, where the inset shows the thermomagnetic  $M$ - $T$  curve and its  $dM/dT$  curve under a field of 0.4 T (a). Temperature dependences of the magnetization of ErGa under magnetic fields of 1, 2, 3, and 5 T, where the inset shows the corresponding  $dM/dT$  curves (b).

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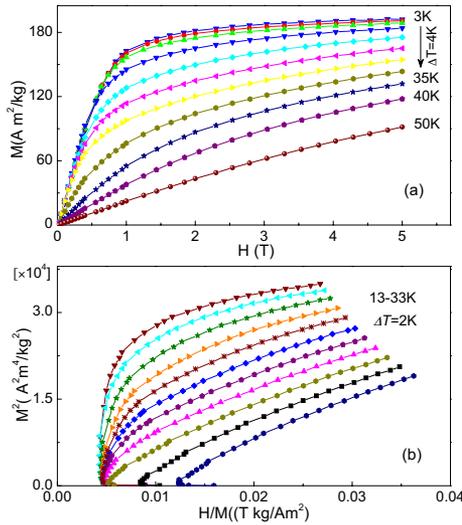


FIG. 2. (Color online) Magnetization isotherms of ErGa in a temperature range of 3–50 K in different temperature steps (a) and Arrott plots of ErGa from 13–33K with a temperature step of 2K (b).

Mössbauer spectroscopy measurements. This transition is easily observable under a magnetic field of 0.4 T and indicated by the fact that the magnetization undergoes a significant decrease around 15 K with the increase of temperature [inset of Fig. 1(a)], and remains sharp even under a field of up to 5 T [Fig. 1(b)]. The value of  $T_{SR}$ , determined by the position of the low-temperature peak on the  $dM/dT$  curve, increases monotonically from 15.3 to 25.5 K with magnetic field increasing from 1 to 5 T [see the inset of Fig. 1(b)], revealing an important effect of magnetic field on magnetic transition. The abrupt change in magnetization data around  $T_C$  corresponds to the magnetic transition from FM to PM states. The Curie temperature  $T_C$  was determined to be 30 K by evaluating the minimum value of the  $dM/dT$  on the ZFC  $M$ - $T$  curve under a field of 0.01 T, which is in good agreement with the previous results.<sup>15,16</sup> In addition, it can be found from Fig. 1(a) that there is an obvious bifurcation between the ZFC and the FC  $M$ - $T$  curves at temperatures lower than 15 K, which may be related to the domain-wall pinning effect. However, it becomes smaller with field increasing and nearly unobservable under a field of 0.4 T [inset of Fig. 1(a)]. Above 15 K, the FC  $M$ - $T$  curve completely overlaps the ZFC one, indicating the good thermal reversibility around  $T_C$  of ErGa.

The isothermal magnetization curves as a function of magnetic field were measured in applied fields of up to 5 T in a wide temperature range as shown in Fig. 2(a). One can find that the curves exhibit typical FM nature at temperatures lower than  $T_C$ . The isothermal magnetization curves obtained well above  $T_C$  show strong curvatures at low fields, indicating the existence of short-range FM correlations in the PM state. Similar results have been observed in many other intermetallic compounds.<sup>18–20</sup> To investigate the reversibility of the magnetic transitions for ErGa, the  $M$ - $H$  curves were measured, respectively, in field increasing and decreasing modes around transition temperatures. There is almost no magnetic hysteresis in each curve, indicating the perfect magnetic reversibility of the magnetic transitions in ErGa. Figure 2(b) shows the  $H/M$  versus  $M^2$  curves, i.e., Arrott plots, at temperatures ranging from 13 to 33 K in temperature steps of 2 K. The positive slopes of plot around

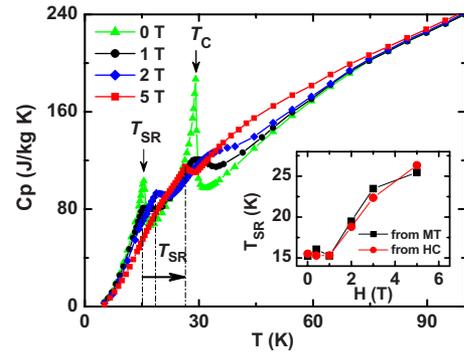


FIG. 3. (Color online) Temperature dependences of the heat capacity for ErGa under magnetic fields of 0, 1, 2, and 5 T, where the inset shows the field dependence of SR temperature  $T_{SR}$  obtained from the heat capacity and the magnetic measurements, respectively.

$T_C$  confirm that the FM-PM transition is of second order,<sup>21</sup> which accords well with the case where both thermal and magnetic hysteresis mentioned above are absent.

The thermal variations of the heat capacity ( $C_p$ ) for some selected magnetic fields are shown in Fig. 3. Two sharp peaks are observed at 15 and 30 K under zero field, corresponding to the SR and FM-PM transitions, respectively. The transition temperatures, determined from the position of thermal anomaly, are fully consistent with the magnetic measurements. With the application of magnetic field, the intensity of the peak at  $T_{SR}$  is reduced greatly, and the peak shifts toward higher temperatures with field increasing, as indicated by arrow. From the inset of Fig. 3, it can be found that the change in  $T_{SR}$  caused by applied fields obtained from heat capacity is quite similar to that derived from magnetization, namely, the value of  $T_{SR}$  is almost unchanged at fields below 1 T while increases monotonically when the field is larger than 1 T. On the other hand, the peak at  $T_C$  spreads to a broad anomaly with a much lower magnitude when a field larger than 1 T is applied, and it almost disappears under a field of 5 T. It may also be noted from Fig. 3 that the values of heat capacity in applied fields above  $T_C$  are much larger than those at zero-field in a wide temperature range. Similar behavior has been reported in many rare-earth based compounds, such as HoNiAl,<sup>18</sup> ErNiAl,<sup>22</sup> Gd<sub>3</sub>Al<sub>2</sub>,<sup>23</sup> and Gd<sub>3</sub>Co,<sup>24</sup> however, the origin of such behavior has not been provided. The abnormal heat capacity of ErGa may be related to the existence of short-range FM correlations in the PM state as has been revealed by the  $M$ - $H$  curvatures above  $T_C$ .

The magnetic entropy change of ErGa was calculated from magnetization isotherms by using the Maxwell relation  $\Delta S_M = \int_0^H (\partial M / \partial T)_H dH$  (Ref. 25) and from the heat capacity data through the expression  $\Delta S_M = \int_0^T \{ [C(T, H) - C(T, 0)] / T \} dT$  as well.<sup>25,26</sup> The temperature dependences of  $\Delta S_M$  calculated from magnetizations and heat capacity data for field changes of 0–2 and 0–5 T are shown in Fig. 4, respectively, for a comparison. The results obtained by using the two techniques are in good agreement with each other. Two peaks, comparable with each other in magnitude, are centered at  $T_{SR}$  and  $T_C$ , respectively, corresponding to the double transitions detected in magnetic and thermal measurements. The maximal values of  $-\Delta S_M$  are 10.9 and 21.3 J/kg K at  $T_C$  for field changes of 0–2 and 0–5 T, respectively, comparable with or much larger than those of some best known magnetic refrigerant materials with second-order

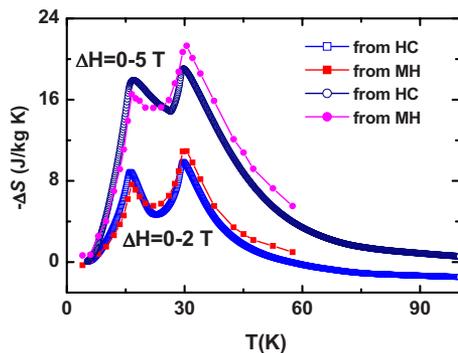


FIG. 4. (Color online) Temperature dependences of magnetic entropy change  $\Delta S_M$  calculated from magnetizations and heat capacity data for field changes of 0–2 and 0–5 T, respectively.

magnetic transition in a similar temperature range, such as  $\text{DyNi}_2$  (21.3 J/kg K at 20 K),<sup>27</sup>  $\text{TbCoC}_2$  (15.3 J/kg K at 28 K),<sup>28</sup> and  $\text{DyCoAl}$  (16.3 J/kg K at 37 K),<sup>29</sup> for the field change of 0–5 T. On the other hand, the maximal values of  $-\Delta S_M$  observed at  $T_{SR}$  are 7.6 and 16.5 J/kg K for field changes of 0–2 and 0–5 T, respectively. The  $-\Delta S_M$  value that is caused by the SR transition has been rarely reported in polycrystalline compounds previously. Only in  $\text{HoAl}_2$  (Ref. 30) and  $\text{Gd}_4\text{Co}_3$  (Ref. 31) can the SR transition bring about a visible peak on their  $\Delta S_M$ - $T$  curves, with values of  $\sim 15$  and  $\sim 4.6$  J/kg K for a field change of 0–5 T, respectively. Mössbauer spectroscopic measurements show that  $\text{Er}^{3+}$  spins deviate from the  $a$ -axis toward the  $bc$ -plane with temperature increasing due to the competition between the exchange interaction and the interaction of the crystalline electric field at low temperatures.<sup>15,17</sup> Neutron diffraction measurements<sup>32</sup> revealed that  $\text{ErGa}$  had a noncollinear magnetic structure. The sudden axis-plane change in easy magnetization direction of  $\text{ErGa}$  with the noncollinear magnetic structure is undoubtedly accompanied by the change in the order of  $\text{Er}^{3+}$  spins, and thus results in the noticeable magnetic entropy changes around  $T_{SR}$ .

To evaluate the applicability of  $\text{ErGa}$  as a magnetic refrigerant material in a reasonable way, we have estimated the RC by using the approach suggested by Gschneidner *et al.*<sup>33</sup> The RC is defined as  $\text{RC} = \int_{T_1}^{T_2} |\Delta S_M| dT$ , where  $T_1$  and  $T_2$  are the temperatures corresponding to both sides of the half-maximum value of  $-\Delta S_M$  peak, respectively. Calculations show that the maximal value of RC for  $\text{ErGa}$  is 494 J/kg for a magnetic field change of 0–5 T, which is larger than those for  $\text{DyNi}_2$  (349 J/kg),<sup>27</sup>  $\text{TbCoC}_2$  (354 J/kg),<sup>28</sup> and  $\text{DyCoAl}$  (485 J/kg) (Ref. 29), where the RC values are estimated from the temperature dependence of  $\Delta S_M$  in the literature, respectively. Evidently, the large RC of  $\text{ErGa}$  originates from the combined contribution from SR and FM-PM transitions, which enlarge the temperature span of large MCE.

In summary,  $\text{ErGa}$  possesses a large reversible MCE, characterized by two  $\Delta S_M$  peaks, i.e.,  $-\Delta S_M = 21.3$  J/kg K at  $T_C$  and 16.5 J/kg K at  $T_{SR}$  for a field change of 0–5 T. The value of RC is estimated to be as large as 494 J/kg for a field change of 0–5 T. The excellent magnetocaloric performance indicates the applicability of  $\text{ErGa}$  to the liquefaction of hydrogen gas.

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