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Magnetic properties and magnetocaloric effects in $Er_{3-x}Gd_xCo$ intermetallic compounds

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A series of intermetallic $Er_{3-x}Gd_xCo$ ($x = 0.5$–3) compounds were synthesized and their magnetic properties and magnetocaloric effects were investigated. The Neél temperature (T_N) could be tuned from 28 to 129 K by partially replacement of Gd with Er. For a field change of 5 T, the $Er_{1.5}Gd_{1.5}Co$ exhibited a minimum $-\Delta S_M$ of 9.8 J/kg K and maximum refrigerant capacity power (RCP) value of 629 J/kg which originated from an enlarged temperature span of magnetic entropy change in the compound. Results demonstrate that it is a feasible way to search for a large RCP material from the compounds with two magnetic transitions and controlled temperature region. © *2013 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4776742]

I. INTRODUCTION

Magnetic refrigeration based on magnetocaloric effect (MCE) can be a solution to the serious environmental concerns comparison with conventional vapor compression refrigeration, due to its various advantages such as high efficiency, energy saving, and pollution-free.[1] For a long time, to seek for a high value of magnetic entropy change, $-\Delta S_M$ is regarded as the primary task.[2–8] A large number of materials with first-order magnetic transition, such as $LaFe_{13-x}Si_x$,[9,10] $MnAs_{1-x}Sb_x$,[11] $MnFeP_xAs_{1-x}$,[12] and $Mn_{1-x}Fe_xAs$,[13] have been found to exhibit giant MCE due to its large value of magnetic entropy change (ΔS_M) around their transition temperatures. However, $-\Delta S_M$ is not the only parameter to characterize the refrigerant material. A considerable magnetic refrigerant capacity power (RCP) is considered to be an important requirement of a potential magnetic refrigerant.[14,15] It is a measure of the amount of heat transfer between the cold and hot reservoirs in an ideal refrigeration cycle. It is defined as $RCP = -\Delta S_m^{max} \times \delta T$, here the $-\Delta S_m^{max}$ is the maximum magnetic entropy change, δT is the full width of half maximum $-\Delta S_m^{max}$ in the magnetic field changes, respectively. To enhance the RCP, it is effective to broaden the δT span based on the definition of RCP.

R_3Co (R = rare earth, Ho, Er, and Gd)-type compounds with Fe_3C-type orthorhombic crystallographic structure have attracted much attention due to the large and reversible magnetic entropy change ΔS_M arising from the highest rare content and second order magnetic phase transition.[16–19] However, their magnetic properties, such as magnetic transition temperature, are quite different due to various rare earth ions. For instance, Er_3Co exhibits ferromagnetic like (FM-like) magnetic ordering at 14 K (Ref. 20) whereas Gd_3Co shows antiferromagnetic (AFM) transition at 128 K.[19] For field changes (ΔH) of 50 kOe, the maximum values of isothermal $-\Delta S_M$ are found to be 17 and 11 J/kg K for Er_3Co and Gd_3Co compounds, respectively. Accordingly, their RCP values are 450 J/kg for $Er_3Co$and 497 J/kg for Gd_3Co. The large difference of magnetic order transition temperature between Er_3Co and Gd_3Co compounds sheds some lights on the design of intermediate alloy to enlarge the temperature span of the $-\Delta S_M$ peak. If these two magnetic order transition could be stabilized in one compound then the enlarged temperature span of the $-\Delta S_M$ peak could be realized. In the present paper, we report on the magnetic properties and MCE in$Er_{3-x}Gd_xCo$ ($x = 0.5$–3) compounds. A considerable RCP of $Er_{1.5}Gd_{1.5}Co$ originates from the combined contribution from spin-reorientation and AFM-paramagnetism (PM) transitions are obtained.

II. EXPERIMENTAL

The polycrystalline $Er_{3-x}Gd_xCo$ ($x = 0.5$, 1, 1.5, 2, 2.5, 3) samples were synthesized by arc-melting in a water-cooled copper hearth under a purified argon atmosphere using rare-earth metals (99.9%) and Co (99.9%), and Al (99.99%), respectively. The ingots were melted three times with the button being turned over after each melting to ensure the homogeneity. The samples were wrapped by molybdenum foil, sealed in a quartz tube of high vacuum, annealed at 923 K for 7 days, and then quenched to room temperature. Powder X-ray diffraction (XRD) measurements were performed at room temperature by using Cu Kα radiation to identify the crystal structure and the lattice parameters. Magnetizations and ac susceptibility were measured by employing a commercial superconducting quantum interference device (SQUID) magnetometer, model MPMS-7 from Quantum Design Inc.

III. RESULTS AND DISCUSSION

The XRD patterns at room temperature (Fig. 1) indicate that $Er_{3-x}Gd_xCo$ ($x = 0$–3) compounds crystallize in an

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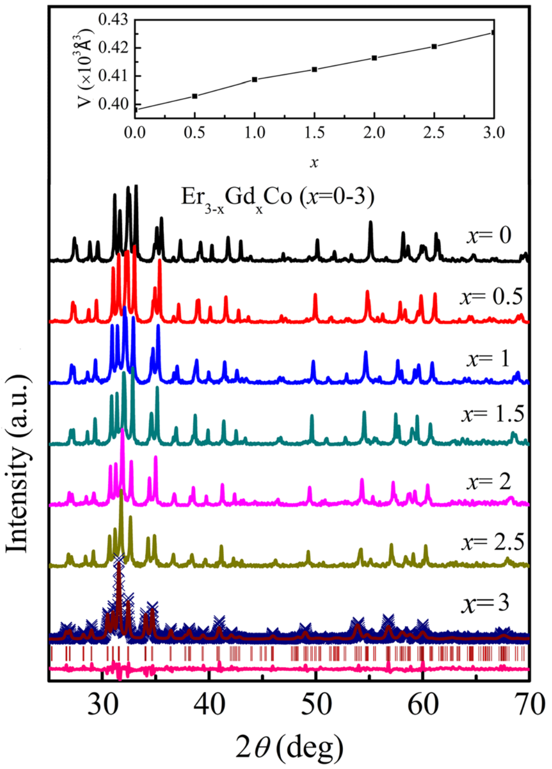

FIG. 1. Powder X-Ray diffraction pattern for the samples of $Er_{3-x}Gd_xCo$ ($x = 0$–3).

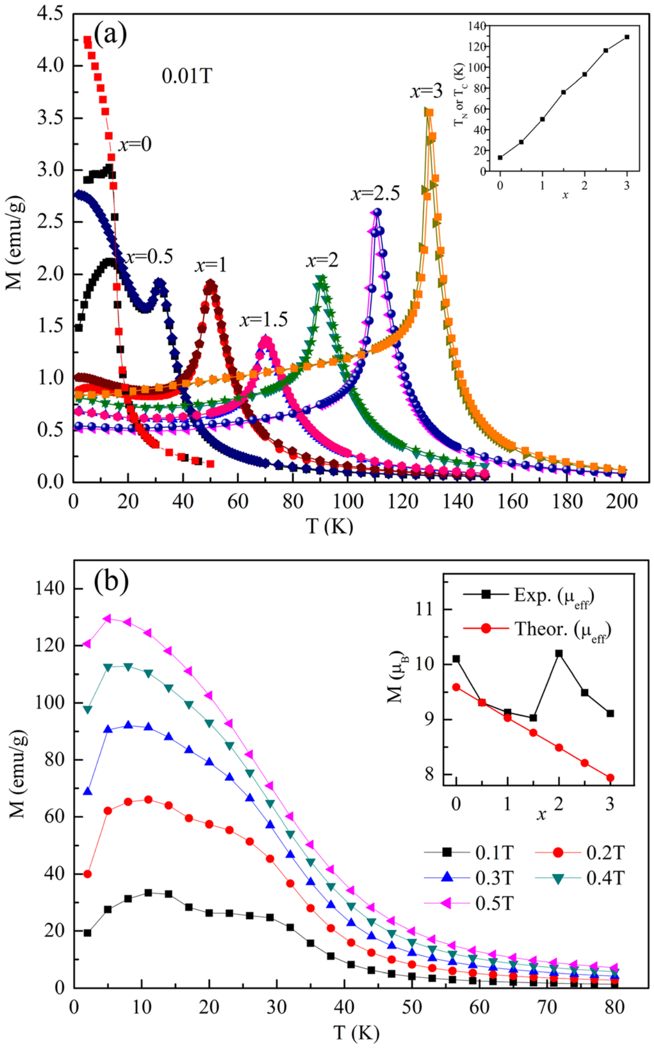

FIG. 2. (a) Temperature dependence of the magnetization of $Er_{3-x}Gd_xCo$ ($x = 0$, 0.5, 1, 1.5, 2, 2.5, 3) compounds measured in a magnetic field of 0.01 T. The inset: transition temperature-x; (b)The temperature dependences of the magnetization for $Er_{2.5}Gd_{0.5}Co$ in different magnetic fields. The inset: The experiment μ_{eff} and theoretical value μ_{eff}–x.

orthorhombic Fe_3C-type crystallographic structure. With increasing Gd concentration, the diffraction peaks move to the left and the unit cell volume increases linearly (see the inset of Fig. 1). It is attributed to the lanthanide contraction law of rare-earth intermetallic compound (the bigger atomic radius of the Gd atom than Er). The data of Gd_3Co are refined by the Rietveld technique using EXPGUI program and the lattice parameters are $a = 7.060$, $b = 9.528$, and $c = 6.326$.

Fig. 2(a) shows the temperature (T) dependence of magnetization (M) data measured in an applied field of 0.01T under zero-field-cooling (ZFC) and field-cooling (FC) conditions for $Er_{3-x}Gd_xCo$ ($x = 0$, 0.5, 1, 1.5, 2, 2.5, 3) compounds. The compound Er_3Co shows a FM-like transition at 13 K due to the thermomagnetic irreversibility between ZFC and FC M (T) curves, which is consistent with the reported data.[18] It is obvious that the compound with $x = 0.5$ shows two successive magnetic transitions at $T_{N1} = 28$ K which shows the transition from PM to AFM, and $T_{N2} = 13$ K which coincides to the transition from AFM to ferromagnetic-like (FM-like) order. However, two transition behaviors seem to disappear instead of a magnetic plateau emerges below T_N for the compounds with $x > 0.05$. Only a sharp AFM transition is observed and T_N linearly shifts to higher temperature with x, as plotted in the inset of Fig. 2(a). No thermal hysteresis is observed between ZFC and FC curves around T_N for the compounds with $x > 0.05$, which is a characteristic of the second-order magnetic transition.

The effective magnetic moment μ_{eff} based on the Curie-Weiss law $\chi_m^{-1} = (T - \theta_p)/C_m$, $\mu_{eff} = \mu_B\ (7.96 \times M/C_m)^{1/2}$, where θ_p is the PM Curie temperature, C_m is the Curie-Weiss constant, and M is the Molar mass relative one Molar of Re ion; the theoretical value $\mu_{eff} = \mu_B\ g(J^2 + J)^{1/2}$ is calculated by the proportion of $Er^{3+}$and Gd^{3+}ions for the $Er_{3-x}Gd_xCo$ compounds, as plotted in the inset of Fig. 1(b). Our obtained μ_{eff} is in a good agreement with the theoretical value at $x = 0.5$, suggesting that the presence of a zero moment on Co. However, for the other compounds with $x \neq 0.5$, the experimental value of μ_{eff} is higher than the theoretic value which should arise from the partial polarization of 3d band by the rare earth exchange field due to the broken high symmetry crystal field.[21]

Fig. 2(b) shows the temperature dependences of the magnetization for $Er_{2.5}Gd_{0.5}Co$ in different magnetic fields. Afield-induced metamagnetic transition from AFM to FM states is clearly observed below T_{N1} and the field-induced modification toward the FM state occurs in a relative low field of 0.4 T.

Magnetization isotherms of $Er_{3-x}Gd_xCo$ ($x = 0.5$–3) compounds were measured in a wide temperature region under applied fields up to 7 T. All the present compounds show similar behaviors, the isothermal magnetization curves for Er_2Gd_1Co with field increasing are shown in Fig. 3(a) as an example. The magnetization of Er_2Gd_1Co below T_N increases linearly with the increase of the magnetic field in low field ranges, while the magnetization increases rapidly with increasing the magnetic field and saturates gradually under high applied field. It confirms the field-induced metamagnetic transition from AFM to FM states and completely transforms into the FM state in end, when the magnetic field approaches about 1.5 T. However, it should be noticed that although persuasive sings of domain saturation are observed at considerably low fields, complete saturation is not observed at 7 T, which likely due to the antiferromagnetic ground. Fig. 3(b) shows the isothermal magnetization curves for Er_2Gd_1Co with field increasing and decreasing in a temperature range 5–35 K. The *M-H* isotherms exhibit a little magnetic hysteresis in 5 K, 15 K, and 25 K magnetization isotherm during the field cycles. However, the *M-H* isotherms do not exhibit magnetic hysteresis at 35 K, revealing the perfect magnetic reversibility of the second-order magnetic transitions around T_N. As is known, a completely reversible MCE requires no hysteresis in magnetization as a function of magnetic field. For the present sample, such a case is advantageous to practical applications of the materials. Further analysis on magnetization data, critical magnetic field (H_c) is shown in the inset of Fig. 3(c). The H_c monotonically increases with the decrease of temperature and reaches a value of 0.45 T at 5 K. It suggests that a small magnetic field can destroy the AFM structure of Er_2Gd_1Co and induce a FM state and implies the dominant fraction of FM than that of AFM state after the field-induced metamagnetic transition.

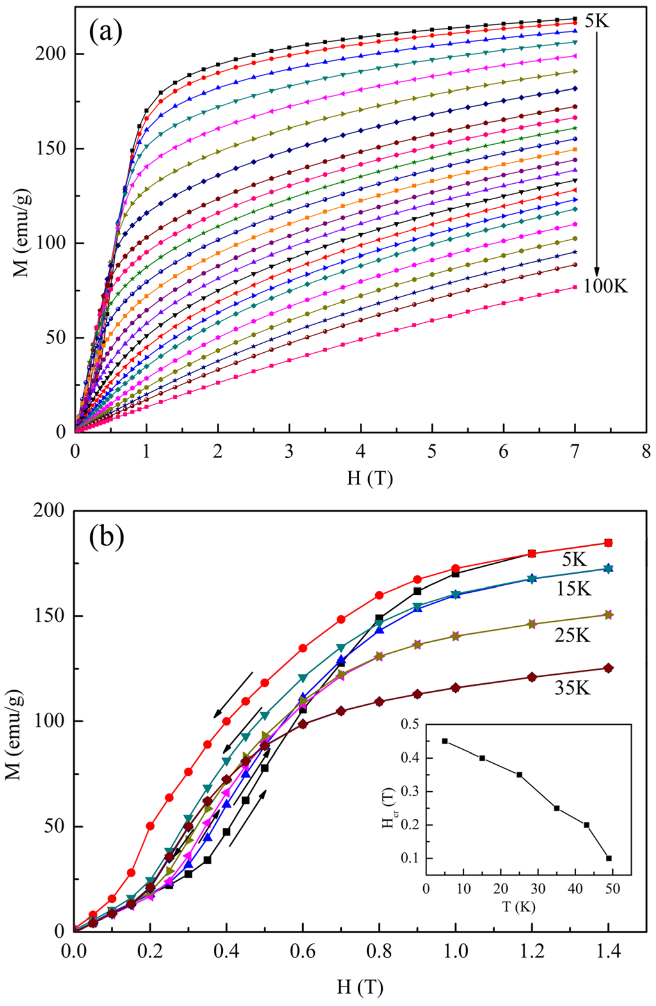

FIG. 3. Magnetization isotherms of Er_2Gd_1Co compound, (a) in a temperature range of 20–110 K with different temperature step sunder applied fields 0–7 T. (b)in a temperature range of 5–35 K with field increasing and decreasing under applied fields 0–1.4 T. Inset: the critical magnetic field-T.

The isothermal magnetic entropy changes ($-\Delta S_M$) of $Er_{3-x}Gd_xCo$ are obtained from the experimental isothermal magnetization data by using the Maxwell relation $\Delta S(T,H) = \int_0^H (\partial M/\partial T)_H dH$. Fig. 4 shows the temperature dependences of $-\Delta S_M$ for magnetic field changes 5 T. It can be noted from the $-\Delta S_M - T$ curves that $-\Delta S_M$ does not die out even at temperature well above the T_N. This may be attributed to the short range magnetic correlations associated with spin fluctuations.[21] Since the Er_3Co undergoes a magnetic transition from PM to FM state, and at the same situation, the Gd_3Co undergoes a magnetic transition from PM to AFM state, the interaction between the Er^{3+} and Gd^{3+} results in a spin-reorientation transition at lower temperature. Therefore, two obviously peaks of Er_2Gd_1Co can be clearly visualized.

Fig. 5 shows the $-\Delta S_M - T$ curves of $Er_{3-x}Gd_xCo$ ($x = 0.5$–2.5) compounds under magnetic field changes 5 T by bimodal lorentzian fitting. It reveals all these series of compounds have two peaks. Two successive ΔS_M peaks are overlapping each other even the first peak was submerged, because the first peak was quickly reduced with the increase of Gd content. The first peak results from spin-reorientation transition; the second comes from the magnetic transition FM-PM. It is noteworthy that the temperature of two peaks (T_1 is the lower peak; T_2 is the higher peak) rises with increase of Gd content, but the T_1 increases slowly than T_2, so ΔT also rises, as shown in Fig. 5(f). In addition, the nature of magnetic ordering can get from MCE. The negative value

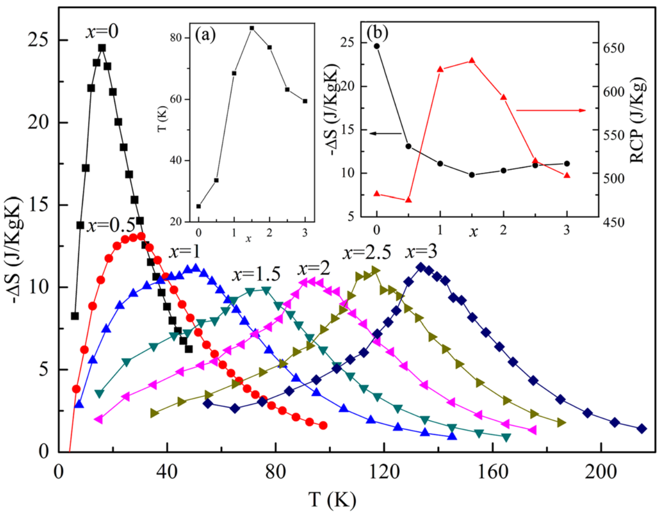

FIG. 4. The magnetic entropy change $-\Delta S_M$ as a function of temperature for the $Er_{3-x}Gd_xCo$ compounds under 0–5 T. The inset (a)the full width of half maximum $-x$; (b)$-\Delta S_{Max} - x$ and RCP-x in 0–5 T.

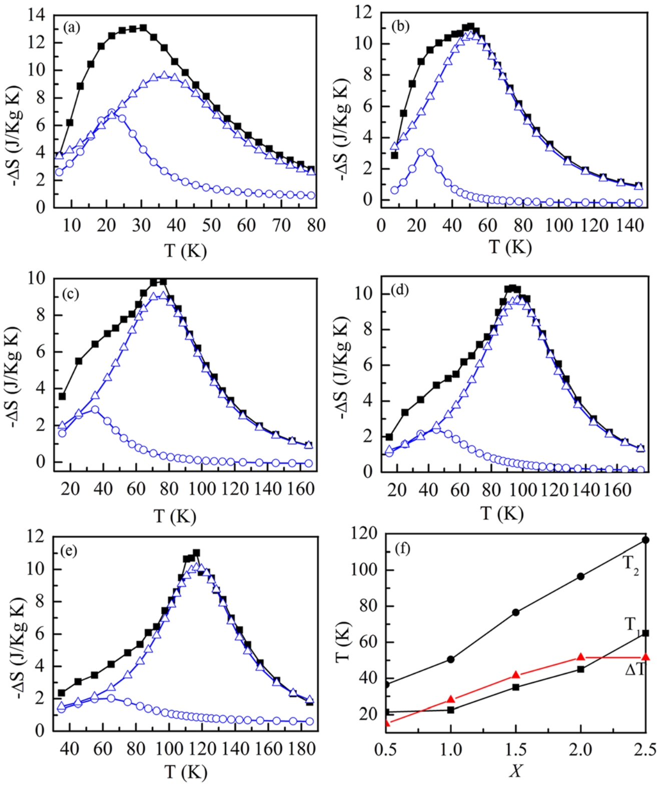

FIG. 5. (a-e) Temperature dependences of magnetic entropy changes $-\Delta S_M$ for the $Er_{3-x}Gd_xCo$ ($x = 0.5$–2.5) compounds for 0–5 T by bimodal lorentzian fitting. (f) temperature of two peaks$-x$.

of $-\Delta S_M$ is observed in the case of AFM ordering due to disorderedness of the magnetic sublattice antiparallel to the applied magnetic field.[22] However, the value of $-\Delta S_M$ is positive in the case of FM and paramagnetic state because of magnetically more ordered configuration with the application of external magnetic field.[23] The values of $-\Delta S_M$ for $Er_{3-x}Gd_xCo$ are negative at relative low temperatures and low magnetic field, and the values are changed to positive with the increase of applied field. Take the $Er_{1.5}Gd_{1.5}Co$ for instance, Fig. 6(a) shows that the $-\Delta S_M$ curve of $Er_{1.5}Gd_{1.5}Co$ is negative below the transition temperature for a low magnetic field change. When the value of $-\Delta S_M$ is negative, the negative value first decreases and then increases with the increase of magnetic field, as shown in Fig. 6(b). It indicates the magnetic transition from AFM to FM states. The $-\Delta S_M$ changes to a positive value with the increase of the magnetic field, corresponding to the magnetic transition from FM to PM states. A large magnetic entropy change results from the field-induced metamagnetic transition of FM-PM in $Er_{1.5}Gd_{1.5}Co$. This phenomenon results from the mixed exchange interaction, and the applied magnetic field leads to a further spin-disordered state near the transition temperature, thereby increasing the configurational entropy.[24] Temperature is another important parameter for magnetic transition. Fig. 6(b) shows the values of $-\Delta S_M$ for different temperature changes as a function of magnetic field. With increase in the temperature, the negative value of $-\Delta S_M{}^{min}$ increases and changes to positive, and the magnetic field of negative value of $-\Delta S_M{}^{min}$ increases to zero. These indicate that enhanced molecular thermal motion that results in a low magnetic field can make metamagnetic transition from AFM to FM.

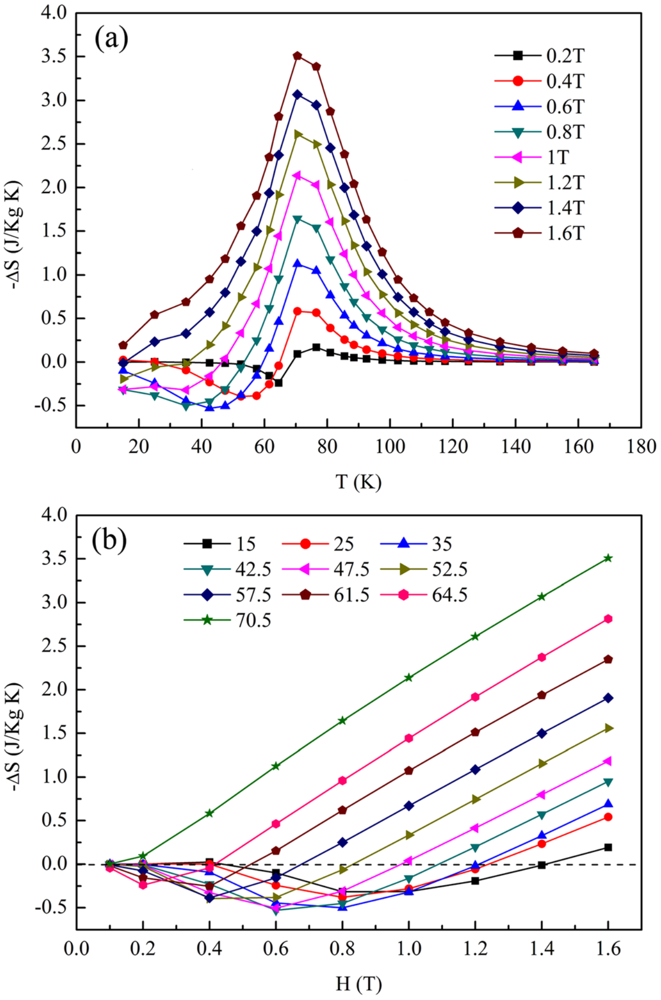

FIG. 6. (a) Temperature dependences of magnetic entropy change in $Er_{1.5}Gd_{1.5}Co$ for different magnetic field changes. (b)Magnetic field dependences of magnetic entropy change in $Er_{1.5}Gd_{1.5}Co$ for different temperature changes.

The maximum of $-\Delta S_M$ and *RC* values at their T_N for a field change of 0–5 T of $Er_{3-x}Gd_xCo$ ($x = 0$, 0.5, 1, 1.5, 2, 2.5, 3) compounds are plotted in the inset of Fig. 4. It is observed that the $-\Delta S_M$ decreases from 24.6 ($x = 0$) to 9.8 J/kg K ($x = 1.5$) with x, then increases from 9.8 ($x = 1.5$) to 11.1 J/kg K ($x = 3$) for $\Delta H = 5$ T. However, the RCP shows a contrasting behavior. The RCP value increases with x showing a maximum value of 629 J/kg for $\Delta H = 5$ T at intermediate content of $x = 1.5$, which is ∼37.6% and ∼24.5% higher than that of Er_3Co and Gd_3Co, respectively.[20] Then, the RCP value decreases with x above 1.5. This phenomenon is attributed to the trend of temperature span δT with x based on the definition of RCP, as shown in the inset of Fig. 4.The δT closely relates to ΔT. The increasing of ΔT expands the temperature span of δT result in large RCP as $x \leq 1.5$. When x is bigger than 1.5, although the ΔT continue increasing, the $-\Delta S_M$ of first peak is too small that no contribution for expand the span of δT. It shows a widest temperature span of 83.2 K of $-\Delta S_M$ in $Er_{1.5}Gd_{1.5}Co$ compound due to the most preferred chemical proportion with intermediate substitution of $x = 1.5$.

Evidently, the large *RC* of $Er_{1.5}Gd_{1.5}Co$ results from the combined contribution of two submerged successive magnetic transitions, which overlap and lead to a wide temperature span of large MCE. The $Er_{3-x}Gd_xCo$ compounds can cover the temperature range of 10–150 K with considerable MCE properties by changing the rare earth. The large values of $-\Delta S_M$ and RCP indicate that the $Er_{3-x}Gd_xCo$ compounds could be competitive candidates for active magnetic refrigeration.

IV. CONCLUSION

In conclusion, a series of Gd substituted Er_3Co garnets have been prepared by arc-melting under ultra-pure argon atmosphere. Their magnetic and magnetocaloric characterizations were investigated. The temperature dependence of magnetization showed that the introduction of Gd caused an increase in T_N. With the increase of Gd content from 0 to 3, the maximum value of $-\Delta S_M$ reduced from 16.1 J/kg K to 9.8 J/kg K and increased to 11.1 J/kg K for a magnetic field change of 5 T. However, the RCP shows a contrasting change from 469 J/kg to 629 J/kg and reduced to 497 J/kg. The highest RCP value of 629 J/kg for a magnetic field change of 5 T $Er_{1.5}Gd_{1.5}Co$ is due to a combined contribution from two submerged successive transitions. Our study demonstrates that the δT, $-\Delta S_M$, and RCP of magnetocaloric materials with two successive magnetic transition can be easily tuned.

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