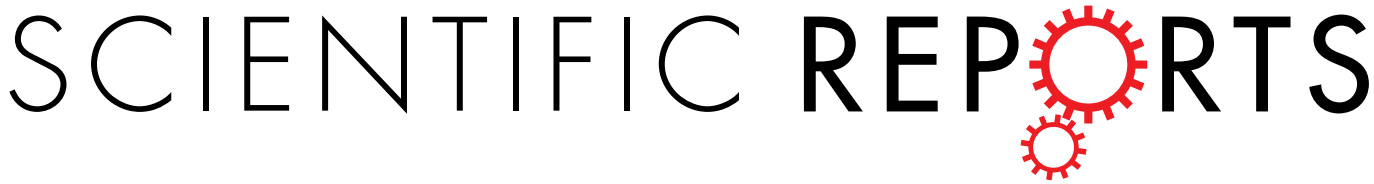

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# Excellent magnetocaloric properties in $RE_2Cu_2Cd$ ($RE$ = Dy and Tm) compounds and its composite materials

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**The magnetic properties and magnetocaloric effect (MCE) of ternary intermetallic $RE_2Cu_2Cd$ ($RE$ = Dy and Tm) compounds and its composite materials have been investigated in detail. Both compounds undergo a paramagnetic to ferromagnetic transition at its own Curie temperatures of $T_C$ ~ 48.5 and 15 K for $Dy_2Cu_2Cd$ and $Tm_2Cu_2Cd$, respectively, giving rise to the large reversible MCE. An additionally magnetic transition can be observed around 16 K for $Dy_2Cu_2Cd$ compound. The maximum values of magnetic entropy change ($-\Delta S_M^{max}$) are estimated to be 17.0 and 20.8 J/kg K for $Dy_2Cu_2Cd$ and $Tm_2Cu_2Cd$, for a magnetic field change of 0–70 kOe, respectively. A table-like MCE in a wide temperature range of 10–70 K and enhanced refrigerant capacity ($RC$) are achieved in the $Dy_2Cu_2Cd$ - $Tm_2Cu_2Cd$ composite materials. For a magnetic field change of 0–50 kOe, the maximum improvements of $RC$ reach 32% and 153%, in comparison with that of individual compound $Dy_2Cu_2Cd$ and $Tm_2Cu_2Cd$. The excellent MCE properties suggest the $RE_2Cu_2Cd$ ($RE$ = Dy and Tm) and its composite materials could be expected to have effective applications for low temperature magnetic refrigeration.**

Magnetic refrigeration technology based on the magnetocaloric effect (MCE) shows superior application potential over conventional gas compression/expansion refrigeration technology because of its environmental friendliness, higher energy efficiency as well as compactness[1–5]. The MCE is an intrinsic thermal response for the application or removal of a magnetic field to a magnetic material, which can be characterized by the coupled variations of two quantities: the adiabatic temperature change ($\Delta T_{ad}$) or/and isothermal magnetic entropy change ($\Delta S_M$). To satisfy practical application, extensive efforts have been carried out to pick out the magnetic materials with large/giant MCE as magnetic refrigerants[1–10].

Recently, the rare-earth ($RE$) based alloys and oxides, which exhibit the large reversible MCEs and refrigeration capacity with small or zero hysteresis have been of great of interest[11–17]. Increasing efforts have been devoted for study of the ternary intermetallic compounds of the $RE_2T_2X$2:2:1 ($T$ = transition metals, and $X$ = III group p-metals). Among of the 2:2:1 system, the $RE_2Cu_2X$ ($X$ = Mg, Cd, Sn or In) crystallized with the tetragonal $Mo_2B_2Fe$-type structure[18], have attracted some attentions because of their unique physical and magnetic properties. The basic crystal chemical data of the different $RE_2T_2X$ series have been reviewed[19,20]. Very recently, Zhang *et al.* and Li *et al.* have reported the large reversible MCEs in $RE_2Cu_2In$ ($RE$ = Dy, Er, and Tm) and $Ho_2T_2In$ ($T$ = Cu and Au) compounds, respectively[21–23]. However, the systems with the p-metals as cadmium are much less known, what besides other reasons could be explained also by the difficulty in materials synthesis due to the high vapour pressure (low boiling point) of cadmium.

To further understand the physical properties of $RE_2T_2X$ system, in this paper, the magnetic properties and MCE in $RE_2Cu_2Cd$ ($RE$ = Dy and Tm) compounds and its composite materials have been investigated systematically. Not only a large reversible MCE was observed in $Dy_2Cu_2Cd$ and $Tm_2Cu_2Cd$ compounds, but also an enhanced refrigerant capacity was found in its composite materials.

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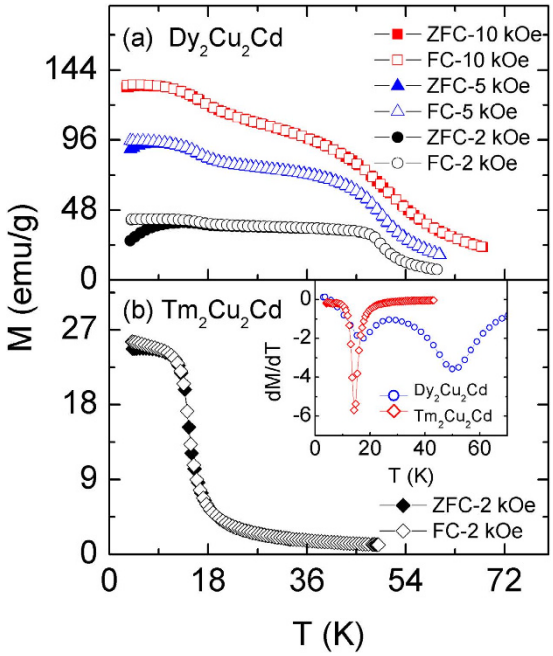


**Figure 1.** Temperature dependence zero-field cooling (ZFC) and field cooling (FC) magnetization ($M$) under different magnetic fields for $Dy_2Cu_2Cd$ (**a**) and the magnetic field of 2 kOe for $Tm_2Cu_2Cd$ (**b**) compounds, respectively. Inset of (**b**) shows the temperature dependence $dM_{FC}/dT$ for $Dy_2Cu_2Cd$ and $Tm_2Cu_2Cd$ compounds under the magnetic field of 2 kOe.

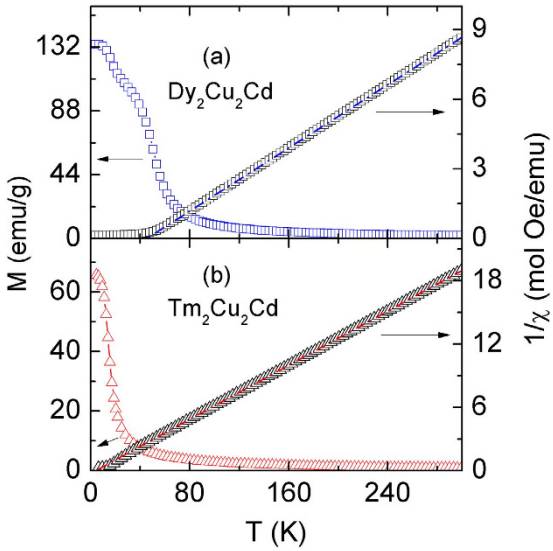


**Figure 2.** Temperature dependence of magnetization ($M$, left scale) and the reciprocal susceptibility ($1/\chi$, right scale) for $Dy_2Cu_2Cd$ (**a**) and $Tm_2Cu_2Cd$ (**b**) compounds under the magnetic field of $H = 10$ kOe, respectively.

## Results and Discussion

Figure 1(a,b) show the temperature dependence of the zero field cooled (ZFC) and field cooled (FC) magnetization $M$ under different magnetic fields for $Dy_2Cu_2Cd$ and a magnetic field of 2 kOe for $Tm_2Cu_2Cd$, respectively. Both compounds display a typical paramagnetic to ferromagnetic (PM-FM) transition, and the Curie temperatures $T_C$, corresponding to the peak of $dM_{FC}/dT$ - $T$ curve [inset of Fig. 1(b)], are determined to be 48.5 K and 15 K for $Dy_2Cu_2Cd$ and $Tm_2Cu_2Cd$, respectively. Another magnetic transition can be observed for $Dy_2Cu_2Cd$ around $T_S \sim 16$ K under low magnetic fields and it shifts to much lower temperatures with increasing magnetic field. Such behaviours may arise from a spin glass transition or spin reorientation phenomenon[24,25], a systematically detail study of the lower temperature magnetic transition will be performed later. The transition temperatures are in good agreement with previously reported values in the literatures[20]. Figure 2(a,b) show the temperature dependence of the magnetization $M$ (left side) and the reciprocal susceptibility $1/\chi$ (right side) for $Dy_2Cu_2Cd$ and

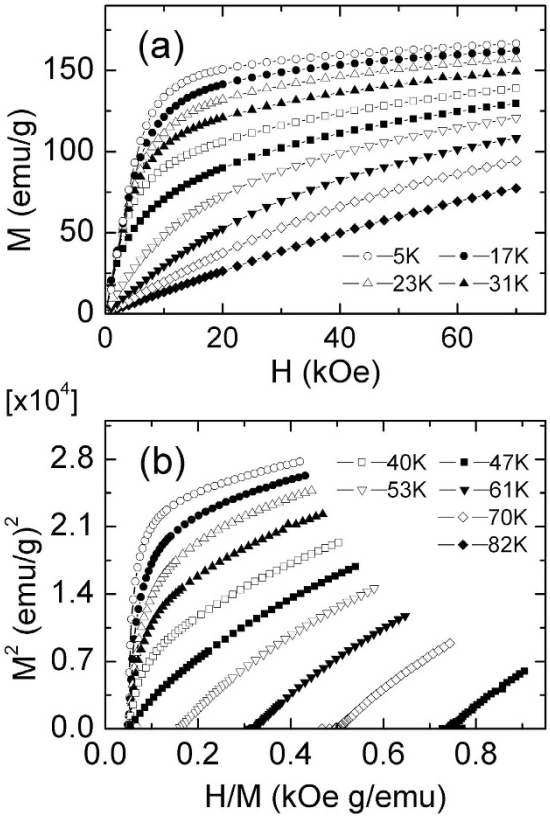


**Figure 3.** (**a**) Magnetic field dependence of the magnetization (increasing field only) for $Dy_2Cu_2Cd$ at some selected temperatures. (**b**) The plots of $H/M$ versus $M^2$ for $Dy_2Cu_2Cd$ at some selected temperatures.

$Tm_2Cu_2Cd$ compounds under a magnetic field of 10 kOe, respectively. The $1/\chi$ in paramagnetic regime from 80 to 298 K obeys the Curie-Weiss law for both compounds. The fitted lines are a guide to the eyes for $Dy_2Cu_2Cd$ and $Tm_2Cu_2Cd$ compounds as shown in the insets of Fig. 2(a,b), respectively. The fit to the Curie-Weiss formula yields positive paramagnetic Curie temperatures ($\theta_P$), $\theta_P = 45.3$ K for $Dy_2Cu_2Cd$ and $\theta_P = 14.1$ K for $Tm_2Cu_2Cd$, respectively, suggesting dominant ferromagnetic interactions. The effective magnetic moments ($\mu_{eff}$) are 10.84 $\mu_B$ and 7.72 $\mu_B$ for $Dy_2Cu_2Cd$ and $Tm_2Cu_2Cd$, respectively. Such moments are close to those of the free ion values of Dy and Tm taking the theoretical $RE^{3+}$ moment of 10.86 $\mu_B$ and 7.56 $\mu_B$, respectively.

The magnetic isothermal $M(H)$ curves of $Dy_2Cu_2Cd$ and $Tm_2Cu_2Cd$ compounds with increasing field around their transition temperatures with increasing magnetic field up to 70 kOe have been measured and some of them are shown in Figs 3(a) and 4(a), respectively. The magnetization below $T_C$ increases rapidly in the low magnetic field range for both compounds, and it tends to saturate for $Dy_2Cu_2Cd$ compound with increasing magnetic field, whereas it is not saturated at 70 kOe for $Tm_2CuCd$ compound. To further understand the magnetic transitions, Arrott plots ($H/M$ vs. $M^2$) of $Dy_2Cu_2Cd$ and $Tm_2Cu_2Cd$ compounds are shown in Figs 3(b) and 4(b), respectively. According to Banerjee criterion[26], the signal (positive and negative) of the slope in Arrott plots has been used to determine the nature of the magnetic phase transition. The negative slopes or inflection points in the Arrott plots often are corresponding to a first order phase transition, whereas the positive slopes are associated to a second order phase transition. By this criterion, neither the inflection points nor negative slopes can be observed in the Arrott plots for $Dy_2Cu_2Cd$ and $Tm_2Cu_2Cd$ compounds, indicating a characteristic of the second order (FM-PM) magnetic phase transition.

Figure 5(a,b) show the temperature dependence of magnetic entropy change $-\Delta S_M$ for $Dy_2Cu_2Cd$ and $Tm_2Cu_2Cd$ compounds which is derived from the temperature and field dependence of the magnetization $M(H, T)$ by using the Maxwell's thermodynamic relation[27], $\Delta S_M(T, \Delta H) = \int_0^{H^{max}} (\partial M(H, T)/\partial T)_H dH$, respectively. It can be found that the maximum value of $-\Delta S_M$ increases monotonically with increasing magnetic field change for both compounds [see insets of Fig. 5(a,b)]. Two successive $-\Delta S_M$ peaks (one at around $T_C$, another at around $T_S$) can be clearly seen even the low magnetic field change for $Dy_2Cu_2Cd$ compound, thus obviously enlarging the temperature range of MCE. Only a pronounced peak in the $-\Delta S_M(T)$ curves is observed around $T_C$ for $Tm_2Cu_2Cd$ compound. For the magnetic field changes of 0–20, 0–50, and 0–70 kOe, the maximum values of the magnetic entropy change ($-\Delta S_M^{max}$) are evaluated to be 7.2, 13.8, and 17.0 J/kg K around $T_C$, and 3.3, 6.6, and 8.3 J/kg K around $T_S$ for $Dy_2Cu_2Cd$ compound; and to be 9.2, 17.3 and 20.8 J/kg K for $Tm_2Cu_2Cd$ compound, respectively.

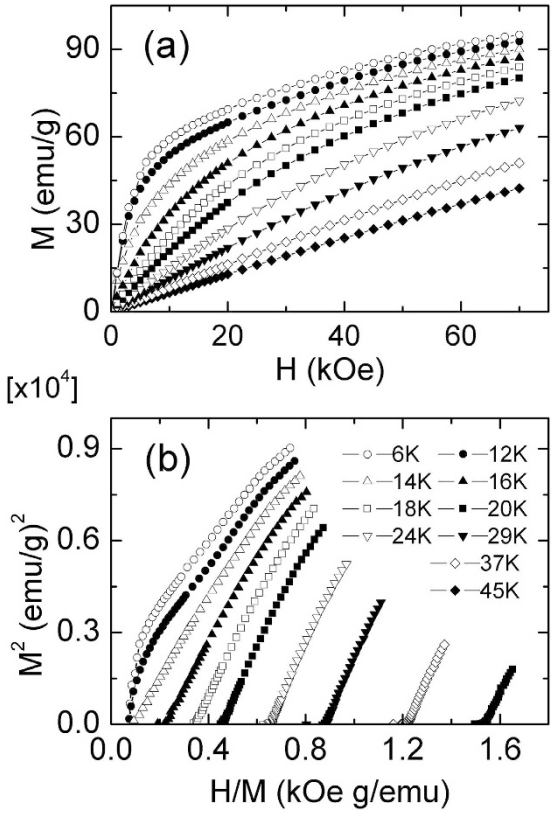


**Figure 4.** (**a**) Magnetic field dependence of the magnetization (increasing field only) for $Tm_2Cu_2Cd$ at some selected temperatures. (**b**) The plots of $H/M$ versus $M^2$ for $Tm_2Cu_2Cd$ at some selected temperatures.

In addition, the $\Delta S_M(T)$ curves for the materials with the second order phase transition can be also described using a universal curve[28,29], which is constructed by normalizing with their respective maximum value $\Delta S_M{}^{max}$ (i. e. $\Delta S' = \Delta S_M(T)/\Delta S_M{}^{max}$) and rescaling the temperature $\theta$, defined as

$$\theta = \begin{cases} -(T - T_C)/(T_{r1} - T_C), & T \le T_C \\ (T - T_C)/(T_{r2} - T_C), & T > T_C, \end{cases} \quad (1)$$

where the $T_{r1}$ and $T_{r2}$ are the temperatures of the two reference points of each curve that correspond to $0.6\Delta S_M{}^{max}$. The transformed $\Delta S'(\theta)$ curves for $Tm_2Cu_2Cd$ and $Dy_2Cu_2Cd$ compounds are displayed in Figs 6 and 7, respectively. We can note that all the rescaled $\Delta S_M$ curves for $Tm_2Cu_2Cd$ are overlapped with each other in the present temperature range, as shown in Fig. 6, proving the occurrence of the second order magnetic phase transition in $Tm_2Cu_2Cd$ compound. In parallel, the curves for $Dy_2Cu_2Cd$ compound are also overlapped with each other around and above $T_C$ (see Fig. 7). Whereas an obvious deviation below $T_C$ for $\theta < -2$ (around $T_S$) can be found which is properly due to the spin reorientation phenomenon or spin glass transition. Therefore, the $\Delta S_M(T)$ around $T_S$ (5–30 K) are rescaled and the results are shown in the inset of Fig. 7. Similarly, the curves around $T_S$ are well overlapped with each other. Furthermore, the rescaled $\Delta S'(\theta)$ curves around $T_C$ and $T_S$ for $Dy_2Cu_2Cd$ compound under various magnetic field changes are summarized together (as given in the Fig. 8). One can find that all the rescaled $\Delta S_M$ curves can collapse onto one universal curve, which is consistent with the previous investigations that the materials with successive magnetic phase transitions[22,24,30,31]. The analysis of the universal behaviour further confirms that the $Dy_2Cu_2Cd$ compound with the second order phase transition.

Another important quality factor of refrigerant materials is the refrigerant capacity [*RC*, defined as numerically integrating the area under the $-\Delta S_M$ - $T$ curve at full width of half maximum ($\delta_{FWHM}$) of the $-\Delta S_M$ peak as the integrating limits]. For the magnetic field changes of 0–20, 0–50, and 0–70 kOe, the values of *RC* are evaluated to be 87, 316, and 495 J/kg for $Dy_2Cu_2Cd$ compound; and to be 60, 165, and 248 J/kg for $Tm_2Cu_2Cd$ compound, respectively. It is well known that magnetic refrigeration systems based on an ideal Ericsson cycle requires a magnetocaloric material with a constant $\Delta S_M$ over an operating refrigeration temperature range[32,33]. Besides the materials with successive magnetic transitions or with a very magnetic field sensitive magnetic phase transitions[22,24,30,31,34], composite materials have been considered to be the most promising method to accomplish the requirement of Ericsson cycle since it can lead to almost constant $\Delta S_M$ with enlarged temperature span[35–38]. An enhanced *RC* have been successfully realized in $Eu_8Ga_{16}Ge_{30}$-EuO[36], amorphous FeZrB(Cu)[37], and ErNiBC-GdNiBC[38] composite materials. We can note that the $Dy_2Cu_2Cd$ and $Tm_2Cu_2Cd$ compounds possess the same crystal structure with similar lattice parameters and similar magnitudes of the magnetic entropy change ($-\Delta S_M$). Therefore, these composite materials could be expected to fulfil the required Ericsson cycle conditions.

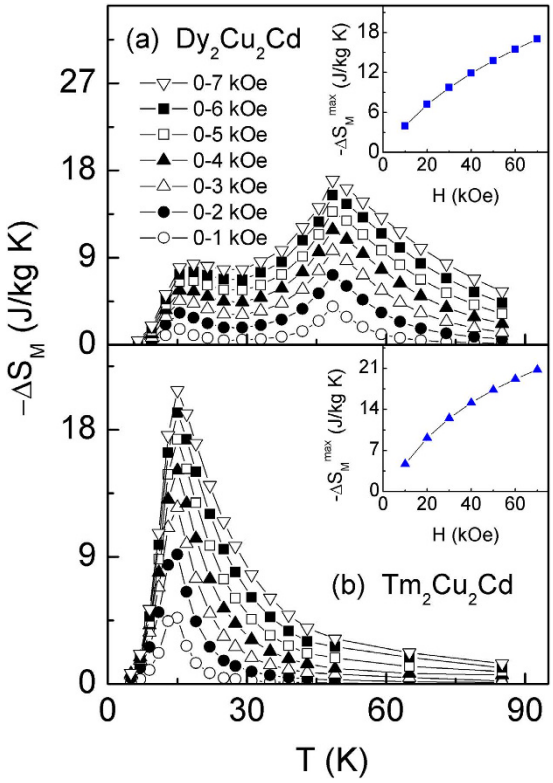


**Figure 5.** The magnetic entropy change $-\Delta S_M$ as a function of temperature for various magnetic field changes $\Delta H$ up to 0–70 kOe for $Dy_2Cu_2Cd$ (**a**) and $Tm_2Cu_2Cd$ (**b**) compounds, respectively. Insets of (**a**,**b**) show the maximum values of magnetic entropy change ($-\Delta S_M^{max}$) as a function of the magnetic field changes for $Dy_2Cu_2Cd$ and $Tm_2Cu_2Cd$ compounds, respectively.

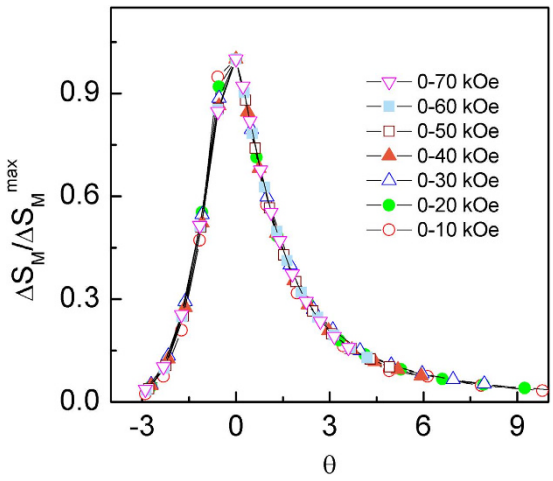


**Figure 6. Normalized magnetic entropy change $\Delta S'$ ($=\Delta S_M/\Delta S_M^{max}$) as a function of the rescaled temperature $\theta$ in the present temperature range for $Tm_2Cu_2Cd$ compound.**

The total magnetic entropy change of $x$ $Dy_2Cu_2Cd + (1-x)$ $Tm_2Cu_2Cd$ composite materials, $\Delta S_{comp}(T, H, x)$, can be calculated theoretically from the individual $\Delta S_M(T)$ curves[35–38],

$$\Delta S_{comp}(T, H, x) = x\Delta S_{Dy}(T, H) + (1 - x)\Delta S_{Tm}(T, H), \quad (2)$$

where $x$ and $1-x$ are the weight amounts of $Dy_2Cu_2Cd$ and $Tm_2Cu_2Cd$, respectively. Based on both compounds, a composite material can be formed and the optimum ratio of $x \sim 0.77$ is determined by using a numerical method. The magnetic entropy change $\Delta S_{comp}(T)$ for $Dy_2Cu_2Cd$ - $Tm_2Cu_2Cd$ composite material at $x \sim 0.77$ under a magnetic field change of 0–50 kOe is shown in Fig. 9. A table-like MCE in a wide temperature span of

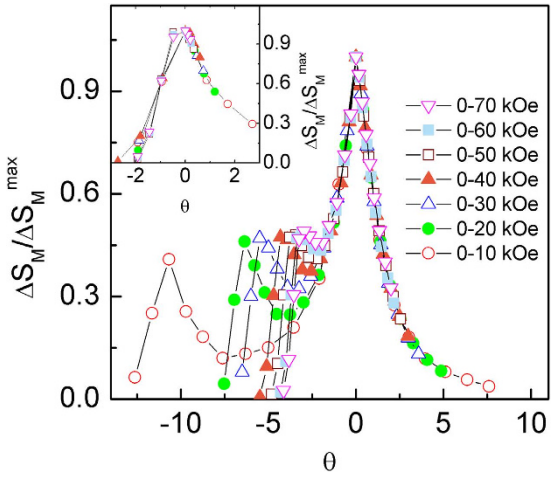


**Figure 7. Normalized magnetic entropy change $\Delta S'$ ($=\Delta S_M/\Delta S_M^{max}$) as a function of the rescaled temperature $\theta$ around $T_C$ for $Dy_2Cu_2Cd$ compound.** Inset shows the normalized magnetic entropy change $\Delta S'$ ($=\Delta S_M/\Delta S_M^{max}$) as a function of the rescaled temperature $\theta$ around $T_S$ for $Dy_2Cu_2Cd$ compound.

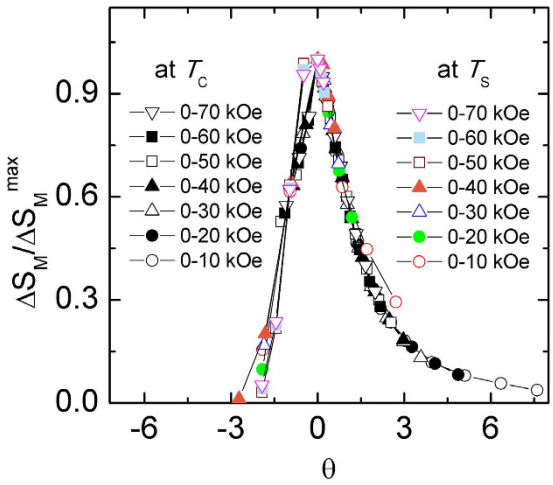


**Figure 8. Normalized magnetic entropy change $\Delta S'$ ($=\Delta S_M/\Delta S_M^{max}$) as a function of the rescaled temperature $\theta$ around $T_C$ and $T_S$ for $Dy_2Cu_2Cd$ compound.**

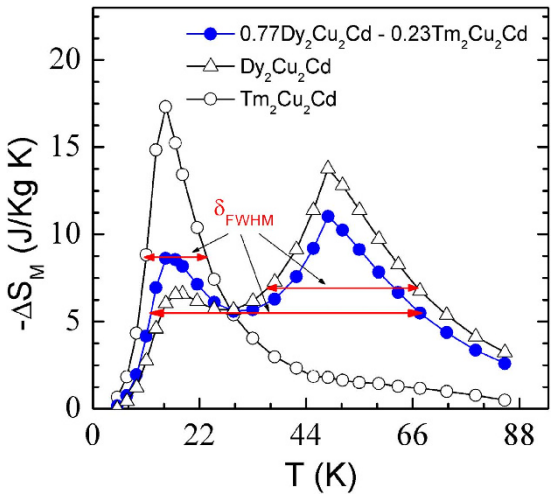


**Figure 9. Temperature dependence of magnetic entropy change $-\Delta S_{comp}$ for the 0.77 $Dy_2Cu_2Cd$ - 0.23 $Tm_2Cu_2Cd$ composite material for the magnetic field change of 0–50 kOe.**

| Material | $T_C$ (K) | $-\Delta S_M^{max}$ (J /kg K) | $RC$ (J/kg) | Ref. |
|---|---|---|---|---|
| $Dy_2Cu_2Cd$ | 48.5/16 | 13.8 | 316 | present |
| $Tm_2Cu_2Cd$ | 15 | 17.3 | 165 | present |
| $0.77Dy_2Cu_2Cd$-$0.23Tm_2Cu_2Cd$ | | 11.0 | 417 | present |
| $DyNi_2B_2C$ | 10 | 17.1 | ~182 | 39 |
| ErAgAl | 14 | 10.5 | ~196 | 40 |
| $Dy_2CoGa_3$ | 17 | 10.8 | 252 | 41 |
| $Ho_2Au_2In$ | 21 | 12.9 | ~261 | 23 |
| HoPdIn | 23 | 14.6 | ~372 | 24 |
| $TbCo_3B_2$ | 28 | 8.7 | ~215 | 42 |
| $Ho_2Cu_2In$ | 30 | 17.4 | ~320 | 23 |
| EuAuGe | 33 | 7.6 | ~269 | 43 |
| $Tm_2Cu_2In$ | 39.4 | 14.4 | 260 | 21 |
| EuAuZn | 52 | 9.1 | ~239 | 44 |
| $Tb_3Ni_6Al_2$ | 57.5 | 9.8 | ~346 | 45 |
| $Dy_{12}Co_7$ | 64 | 10.0 | 299 | 46 |

**Table 1. The transition temperature $T_C$, the maximum values of magnetic entropy change $-\Delta S_M^{max}$ and refrigeration capacity $RC$ under the magnetic field change of 0–50 kOe for $Dy_2Cu_2Cd$ and $Tm_2Cu_2Cd$ as well as the $0.77Dy_2Cu_2Cd$ - $0.23Tm_2Cu_2Cd$ composite material together with some MCE materials with the $T_C$ from 10 to 70 K.**

10–70 K can be observed in $\Delta S_{comp}(T)$ curve which is desirable for an ideal Ericsson-cycle magnetic refrigeration. The corresponding maximum value of $RC_{comp}$ is 417 J/kg, which is 32% and 153% higher than those of $Dy_2Cu_2Cd$ (316 J/kg) or $Tm_2Cu_2Cd$ (165 J/kg). The transition temperature $T_C$, the maximum values of $-\Delta S_M^{max}$ and $RC$ under the magnetic field change of 0–50 kOe for $Dy_2Cu_2Cd$ and $Tm_2Cu_2Cd$ as well as the 0.77 $Dy_2Cu_2Cd$ - 0.23 $Tm_2Cu_2Cd$ composite material together with some MCE materials in the similar working temperature range are listed in Table 1 for comparison. The MCE parameters for the present studied materials are comparable or larger than those of other potential magnetic refrigerant materials in the similar temperature region, suggesting $RE_2Cu_2Cd$ composite materials could be a promising candidate for magnetic refrigeration for Ericsson cycle in the temperature range of 10–70 K. The present results allow for the possibility of using $RE_2Cu_2Cd$ compounds to fabricate composite materials with desirable magnetocaloric properties for active magnetic refrigeration.

## Conclusions

In summary, two single phased $Dy_2Cu_2Cd$ and $Tm_2Cu_2Cd$ compounds have been fabricated and the magnetism and magnetocaloric effect have been investigated experimentally. Both compounds undergo a paramagnetic to ferromagnetic transition at their own Curie temperatures, additionally, another magnetic transition is also observed for $Dy_2Cu_2Cd$ at low temperatures. For a magnetic field change of 0–50 kOe, the maximum values of magnetic entropy change ($-\Delta S_M^{max}$) are 13.8 J/kg K around $T_C$, and 6.6 J/kg K around $T_S$ for $Dy_2Cu_2Cd$; and 17.3 J/kg K for $Tm_2Cu_2Cd$, respectively. The rescaled entropy change $\Delta S_M$ curves around $T_C$ follow a universal behaviour for $Dy_2Cu_2Cd$ and $Tm_2Cu_2Cd$, which further confirm both compounds with the second order phase transition. A table-like MCE from 10 to 70 K and a strong enhancement of $RC$ have been found in theoretically calculated $Dy_2Cu_2Cd$-$Tm_2Cu_2Cd$ composite materials. The maximum value of $RC_{comp}$ is 417 J/kg in the $0.77Er_2Cu_2Cd$ - $0.23Tm_2Cu_2Cd$ composite material for a magnetic field change of 0–50 kOe, which is obviously larger than those for either $Dy_2Cu_2Cd$ (316 J/kg) or $Tm_2Cu_2Cd$ (165 J/kg) compounds. The results indicate that the $RE_2Cu_2Cd$ ($RE$ = Dy and Tm) compounds and its composite materials could be promising candidates for magnetic refrigeration in the temperature range of 10–70 K. Furthermore, the present results may also provide a cost-effective strategy for exploring suitable refrigeration candidates with table-like magnetocaloric feature by a materials composition method, beneficial for Ericsson-cycle in the wide temperature range.

## Methods

The $Dy_2Cu_2Cd$ and $Tm_2Cu_2Cd$ polycrystallize samples were fabricated by induction melting the elements in a sealed quartz crucible. Firstly, high purity Dy, Tm, Cu and Cd with stoichiometric amounts were weighted and placed in the quartz crucible. Secondly, a high vacuum better than $2^*10^{-5}$ mbar was achieved in the crucible. Then the crucible was filled with purified argon gas at pressure of ca. 750 mbar and sealed immediately. Finally, the quartz crucible was placed in an induction furnace and heated at 1100 K for 4 minutes, following by 3 hours annealing at 850 K. The powder X-ray diffraction (Bruker D8 Advance) measurements were carried out at room temperature using Cu $K\alpha$ radiation. Both samples were proved to be single phase, and the lattice parameters were evaluated to be $a = 7.491$ and $c = 3.742$ Å for $Dy_2Cu_2Cd$; and to be $a = 7.439$ and $c = 3.687$ Å for $Tm_2Cu_2Cd$, respectively. The magnetic measurements were performed by using a commercial vibrating sample magnetometer (VSM) which is an option of the physical properties measurement system (PPMS-9, Quantum Design) in the temperature range of 3–298 K with a DC magnetic field from 0 to 7 T, and the samples are small particles of 4.5 and 3.8 mg for $Dy_2Cu_2Cd$ and $Tm_2Cu_2Cd$, respectively.

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## Author Contributions
Y.Z. designed the study. Y.Y., X.X., S.G. and L.H. prepared the samples and preformed the magnetocaloric measurements. Z.R., X.L. and G.W. provided suggestions for the data analyses and the manuscript. Y.Z. prepared the manuscript and all authors reviewed the manuscript.

## Additional Information
**Competing financial interests:** The authors declare no competing financial interests.

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