First- and second-order phase transitions in RE$_6$Co$_2$Ga (RE = Ho, Dy or Gd) cryogenic magnetocaloric materials

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**ABSTRACT** Rare-earth (RE) rich intermetallics crystallizing in orthorhombic Ho$_6$Co$_2$Ga-type crystal structure exhibit peculiar magnetic properties that are not widely reported for their magnetic ordering, order of magnetic phase transition, and related magnetocaloric behavior. By tuning the type of RE element in RE$_6$Co$_2$Ga (RE = Ho, Dy or Gd) compounds, metamagnetic anti-to-paramagnetic (AF to PM) phase transitions could be tuned to ferro-to-paramagnetic (FM to PM) phase transitions. Furthermore, the FM ground state for Gd$_6$Co$_2$Ga is confirmed by density functional theory calculations in addition to experimental observations. The field dependence magnetocaloric and Banerjee’s criteria demonstrate that Ho$_6$Co$_2$Ga and Dy$_6$Co$_2$Ga undergo a first-order phase transition in addition to a second-order phase transition, whereas only the latter is observed for Gd$_6$Co$_2$Ga. The two extreme alloys of the series, Ho$_6$Co$_2$Ga and Gd$_6$Co$_2$Ga, show maximum isothermal entropy change (|ΔS$_{iso}$|$^{max}$ (5 T)) of 10.1 and 9.1 J kg$^{-1}$K$^{-1}$ at 26 and 75 K, close to H$_2$ and N$_2$ liquefaction, respectively. This outstanding magnetocaloric effect performance makes the RE$_6$Co$_2$Ga series of potential for cryogenic magnetic refrigeration applications.

**Keywords:** RE$_6$Co$_2$Ga compounds, magnetic phase transitions, magnetocaloric effect, rare-earth

**INTRODUCTION**

The pursuit of energy conservation and environmental protection has become the mainstream of modern society. The vapor-compression refrigeration, a widely used technology in transportation, and residential, commercial, and industrial refrigeration, can no longer meet the current development needs due to its low efficiency, adverse environmental impact, and noise of the compressor. Several researchers have shifted their focus to magnetic refrigeration (MR) based on the magnetocaloric effect (MCE) of magnetic materials due to their distinguished performance without relying on any hazardous or ozone-depleting refrigerant gas and noise-free advantage [1–7]. The use of natural gas as well as H$_2$, He, N$_2$, and O$_2$, is widely extended with several scientific, industrial, and commercial purposes. Moreover, their consumption is expected to increase in future years. For better gas storage and transport, gas liquefaction is required despite being a complex process [8]. In recent years, it has been shown that MR technology could overcome some of the issues related to conventional methods [9,10]. Therefore, it is of significance to search for MCE materials suitable for cryogenic MR applications. The performance of MCE materials can be evaluated by the magnetic entropy change in an isothermal process (ΔS$_{iso}$) and/or temperature change in an adiabatic process (ΔT$_{ad}$), which are correlated to thermomagnetic phase transitions of the materials. In general, MCE materials are classified into the order of thermomagnetic phase transitions they undergo. For those undergoing first-order phase transition (FOPT), they usually exhibit large ΔS$_{iso}$ values, but their accompanying thermal and magnetic hystereses can affect their cyclicality. On the other hand, for those exhibiting...
second-order phase transition (SOP), while they exhibit no hysteresis, their $\Delta S_{\text{iso}}$ values may be lower than those of FOPT materials [11–13].

In the past decade, a large number of MCE materials have been reported [14–20], among which rare-earth (RE) based alloys show great significance for MR applications at cryogenic temperatures. In particular, those crystallizing in orthorhombic Ho$_6$Co$_2$Ga-type structures (space group $Immm$) could exhibit both inverse (positive $\Delta S_{\text{iso}}$ under magnetization process) and direct MCE (negative $\Delta S_{\text{iso}}$ under magnetization process) despite showing peculiar and complex magnetic behavior [21–36]. For example, S-shaped curves of magnetization versus magnetic field $M(H)$ were reported for Re$_6$Co$_2$(Al/Sn)$_y$ ($x = 2.2–2.5$ and $y = 0.5–0.8$), whereby all of them adopted the Ho$_6$Co$_2$Ga-type structure [21–23]. Inverse and direct MCE were then reported for isostructural Dy$_6$Co$_2$Sn$_{0.5}$ [21] and Re$_6$Co$_2$Al$_{1.8}$ (RE = Dy or Tb) [22], in which authors suggested that the magnetic ordering of Ho$_6$Co$_2$-Ga-type compounds is determined by the orthohombically distorted octahedral RE sublattice, which in turn can yield similar magnetic structure and properties for such compounds despite their selection for the elements. Overall, these investigations centered on using compositions that can crystallize into orthorhombic Ho$_6$Co$_2$Ga-type structure; nevertheless, the studies on nominal Re$_6$Co$_2$Ga compositions, which are directly adopted from the structure itself, are less reported [24,25] and mainly on their crystal structures while their thermomagnetic and MCE properties have not been explored.

Hence, in this paper, we aim to systematically investigate the influence of various RE elements on the structures, thermomagnetic phase transitions, and magnetocaloric properties of Re$_6$Co$_2$Ga-type compounds by changing RE from Ho to Dy and Gd. Using the recently developed criterion based on MCE [37] and the conventional Banerjee’s criterion [38], we report the nature of the order of magnetic phase transition undergone by these compounds. It is found that the Ho- and Dy-containing compounds exhibit low-temperature FOPT while the Gd-containing one exhibits SOPT. Density functional theory (DFT) calculations are performed for these compounds, further supporting the magnetic ordering observed from the experimental results.

**EXPERIMENTAL AND SIMULATION DETAILS**

Polycrystalline samples with nominal compositions of Re$_6$Co$_2$Ga (RE = Ho, Dy or Gd) were synthesized by arc melting from raw pure materials RE (99.9 %), Co (99.9 %) and Ga (99.999 %) in an argon atmosphere. Since RE elements could be easily volatilized during melting, 2 wt.% excess was added to ensure the nominal stoichiometry. The ingots were re-melted four times for good compositional homogeneity. They were sealed in a quartz tube filled with argon and then annealed in a muffle furnace at 600°C for seven days, followed by quenching with ice water. X-ray diffraction (XRD) patterns of the samples at room temperature were collected by a Bruker D8 diffractometer (Cu-Kα radiation) for studying their microstructures. Magnetization measurements were carried out using the vibrating sample magnetometer (VSM) option of the physical properties measurement system (PPMS-9). $\Delta S_{\text{iso}}$, one of the parameters to quantify the MCE of materials, was indirectly determined from the measured magnetic isotherms using thermodynamic Maxwell relation:

$$\Delta S_{\text{iso}}(T, H) = \mu_0 \int_0^H \frac{\partial M(T, H)}{\partial T} \, dH,$$  \hspace{1cm} (1)

where $M$, $H$, and $T$ represent the magnetization, magnetic field, and temperature, respectively. In order to investigate the order of the phase transition by the novel MCE criterion, the field-dependent exponent of $\Delta S_{\text{iso}}$ was calculated from the following formula [37]:

$$n(T, H) = \frac{\partial \ln |\Delta S_{\text{iso}}|}{\partial \ln H}.$$  \hspace{1cm} (2)

In addition, DFT calculations were performed for unveiling the magnetic behavior of Re$_6$Co$_2$Ga compounds, whereby we exclusively focused on Gd$_6$Co$_2$Ga as the latest and the most sophisticated DFT methods are limited in accurately describing the complex magnetic behavior of some RE elements, such as Ho and Dy. For this purpose, we employed the standard Vienna Ab-initio Simulation Package (VASP) 5.4.1 [39], using plane waves to reproduce the one-electron wave functions with a kinetic energy cutoff of 400 eV for constructing the basis set and projected augmented wave pseudopotentials [40,41] for all the species involved. In particular, the valence electrons excluded in the pseudopotentials were $3d^{4}4s^{1}$ (9) in Co, $4s^{2}4p^{4}$ (3) in Ga and $5s^{2}5p^{6}$ $4f^{3}$ $5d^{1}6s^{2}$ (18) in Gd. Thus, the f electrons of Gd were explicitly considered to properly describe its magnetism. The electronic exchange and correlation were modeled using a hybrid functional, namely the HSE06, which contained 25% of exact Hartree-Fock as exchange, following the implementation of the VASP code [42,43]. As a start, the standard Perdew-Burke-Ernzerhof (PBE) functional [44] was used but it was later found insufficient for such a complex system. In particular, it failed when resolving the on-site magnetism...
of the compound. As spin polarization was required for all calculations, we used the Vosko-Wilk-Nusair interpolation [45] for this task.

Using the geometry provided by XRD data [24] for the analysis of the compound, structural optimizations using a conjugate gradient algorithm, sampling the reciprocal space with a 4 × 4 × 4 Monkhorst-pack grid, were performed until forces upon atoms were smaller than 0.01 eV Å⁻¹, and each self-consistent electronic loop converged to a tolerance better than 10⁻⁴ eV [46]. At PBE level, the obtained structure remains very similar to the experimental configuration with minimal displacement in atomic coordinates (only up to 0.1 Å in the worse scenario). This relaxed structure was further analyzed using the HSE06 hybrid functional. In all cases, we deal with a primitive 18-atom cell, which corresponds to a Niggli reduced cell. This is a quasi-rhombohedral unit cell (with \(a = 8.323\,\text{Å}, \alpha = 107.25^\circ, \beta = 109.96^\circ, \) and \(\gamma = 111.23^\circ\) ) generated using the VESTA software [47]. It possesses a unit cell volume and a number of atoms that are small enough to allow calculations with hybrid functionals despite the high proportion of RE metals. Even in that case, we had to reduce the k-point grid to a 2 × 2 × 2 mesh due to the enormous computational demand.

RESULTS AND DISCUSSION

Crystal structure

XRD patterns for the RE₆Co₂Ga (RE = Ho, Dy or Gd) series at room temperature and their corresponding Rietveld refinement results are shown in Fig. 1. The results show that all the samples successfully crystallize into a single phase Ho₆Co₂Ga-type structure. Details of the refined lattice parameters and the refinement factors are tabulated in Table 1, which shows that the cell volume and lattice parameters increase as RE changes from Ho to Dy and Gd. The \(c\) cell parameter for Dy₆Co₂Ga (9.8153 Å) is smaller than those for Dy₆Co₂Sn₀.₅ (9.8754 Å) and Dy₆Co₂Al (9.9265 Å), which is in line with Ref. [22] whereby authors predicted that lattice parameter \(c\) increases from Ga to Sn and Al in RE₆Co₂X compounds. Fig. 2a and b illustrate the detailed crystal structures of the RE₆Co₂Ga compounds and the atomic environments of RE1, RE2, RE3, Co1, Co2, Ga1, and Ga2 sites. The Wyckoff sites of RE1, RE2, RE3 atoms are 8l, 8m, and 8n with the ..m, .m., and m. point symmetry, respectively. Co1 and Co2 atoms occupy the Wyckoff sites of 4i and 4h with the mmm and m2m point symmetry, respectively. Ga1 occupies the 2b sites with the mmm point symmetry and Ga2 occupies the 2d sites with the mmm point symmetry.

Magnetic properties

Fig. 3 displays the \(M(T)\) curves and their reciprocal susceptibility (\(1/\chi = H/M\)) under a magnetic field of 0.5 T. Ho₆Co₂Ga (Fig. 3a) shows a magnetic phase transition from antiferromagnetic to paramagnetic (AF to PM) at around 16 K and a plateau at 16–25 K, followed by a paramagnetic behavior. For Dy₆Co₂Ga in Fig. 3b, a phase transition from AF to PM is noticed at ~47 K, with the subsequent paramagnetic behavior at higher temperatures. Gd₆Co₂Ga shows three consecutive features at around 55, 78, and 129 K (pointed by the arrows), indicating three thermomagnetic phase transitions (Fig. 3c). The effective magnetic moment values (\(\mu_{\text{eff}}\)) and paramagnetic Curie temperature (\(\theta_P\)) were deduced by the fittings of the linear part of the \(1/\chi-T\) plots, yielding:

![Figure 1](image-url)
$\mu_{\text{eff}}/\text{f.u.} = 29.105 \pm 0.006 \mu_B$, 29.629 $\pm 0.007 \mu_B$, and 21.635 $\pm 0.020 \mu_B$ for Ho$_6$Co$_2$Ga, Dy$_6$Co$_2$Ga, and Gd$_6$Co$_2$Ga, respectively. Assuming the effective magnetic moment of Co atoms is 1.8 $\mu_B$, the effective magnetic moment per RE atom for all three compounds can be calculated from $\mu_{\text{eff}} = \sqrt{6 \times \mu_{\text{eff}}^2(\text{RE}) + 2 \times \mu_{\text{eff}}^2(\text{Co})}$, resulting in $\mu_{\text{eff}}(\text{Ho}) = 11.837 \pm 0.002 \mu_B$, $\mu_{\text{eff}}(\text{Dy}) = 12.051 \pm 0.003 \mu_B$, and $\mu_{\text{eff}}(\text{Gd}) = 8.771 \pm 0.008 \mu_B$. The calculated $\theta_P$ values are $\sim 1.5$, $\sim 3.2$, and $\sim 99.1$ K for Ho$_6$Co$_2$Ga, Dy$_6$Co$_2$Ga, and Gd$_6$Co$_2$Ga, respectively. In the cases of Ho$_6$Co$_2$Ga and Dy$_6$Co$_2$Ga, the $\theta_P$ values are close to zero, which indicates that there are almost no ferromagnetic (FM) interactions in PM regions.

The zero-field-cooled (ZFC) and field-cooled (FC) $M(T)$ curves for $H = 0.05$ T of Ho$_6$Co$_2$Ga, Dy$_6$Co$_2$Ga, and Gd$_6$Co$_2$Ga are shown in Fig. S1. A small splitting in FC and ZFC $M(T)$ curves for Gd$_6$Co$_2$Ga and Dy$_6$Co$_2$Ga is detected at low temperatures, which could probably be due to the domain wall pinning effects [48]. At higher temperatures, the ZFC and FC curves are well overlapped with each other for all the compounds, demonstrating no thermal hysteresis during their magnetic phase transitions. Such absence/negligible thermal hysteresis even in the first-order transformations for RE-based alloys makes these materials highly interesting from a technical point of view [49–51].

Fig. 4 displays the field dependence of magnetization measured at 3 K. Weak magnetic hysteresis can be observed in Ho$_6$Co$_2$Ga and Dy$_6$Co$_2$Ga, which is common in FOPT materials. For Gd$_6$Co$_2$Ga, there is no hysteresis, which is beneficial to practical applications. It can be seen
that the magnetization isotherms for Ho₆Co₂Ga and Dy₆Co₂Ga compounds show a significant increase for certain applied magnetic fields (fields between 2 and 4.5 T for Ho₆Co₂Ga and Dy₆Co₂Ga, respectively), indicating the existence of metamagnetic transitions. This is in agreement with the S-shaped $M(H)$ curves previously reported for isostructural Dy₆Co₂Al and Er₆Co₂Al compounds [23]. On the other hand, for Gd₆Co₂Ga, the $M(H)$ shape indicates the FM character at 3 K.

In addition to experimental observations, DFT calculations enable the determination of the distribution of the magnetic moments in Gd₆Co₂Ga by using hybrid functional (the standard generalized gradient approximation fails to describe this issue). In particular, a reasonable geometry very similar to the experimental result is successfully obtained from the calculations using the PBE functional, which suggests a strong FM ground state, or at least, a configuration with a high total magnetic moment. However, if we try to resolve the on-site magnetism, this simple approximation does not lead to a reasonable value for the magnetic moments of Gd atoms, being too small compared with the experimental observations. In addition, the spin moments associated with the Co atoms get unstable, assuming that they have some magnetic moments that are ferro- or antiferromagnetically coupled to the RE elements in the compound. Conversely, more advance functionals, such as the HSE06, which includes 25% of exact Hartree-Fock exchange, could properly reproduce the magnetic behavior of complex Gd₆Co₂Ga compound. Namely, we confirm that the magnetic ground state of Gd₆Co₂Ga corresponds to a state in which all Gd atoms have a strong magnetic moment of about 7.5 $\mu_B$ pointing in the same direction whereas Co atoms couple in the opposite direction with a magnetic moment of around 1.8 $\mu_B$. No magnetic moment is observed for Ga atoms. Only a minimal difference among Gd atoms belonging to different Wyckoff sites is found: the exact values are 7.49–7.51 $\mu_B$ (8l), 7.64–7.65 $\mu_B$ (8m), and 7.47 $\mu_B$ (8n). The same trend is also observed for Co atoms, whose magnetic moments are within the range of 1.77–1.78 $\mu_B$. We have also calculated the spin-resolved projected density of states of the different species present in the Gd₆Co₂Ga compound as shown in Fig. 5. The strong magnetic moments observed for Gd atoms are reflected in their densities of states as strong localized states, mainly appearing around ~4 eV spin up below the Fermi level. These states arise from the Gd f orbitals, resembling the fingerprint of the FM phase of pure Gd [52].

In the cases of Ho and Dy in RE₆Co₂Ga compounds, it is not possible to assume any trivial magnetic moment distribution for the constituent atoms that can be compatible with the experimental magnetic moments of RE.

**Figure 3** Temperature dependence of magnetization (left-axis) and reciprocal susceptibility (right-axis) under a field of 0.5 T for Ho₆Co₂Ga (a), Dy₆Co₂Ga (b), and Gd₆Co₂Ga (c).

**Figure 4** The field dependence of magnetization measured at 3 K.
The calculated total magnetic moment of Gd₆Co₂Ga lies between 41–45 μB per f.u., in good agreement with the experimental saturation magnetization values (43.35 μB per f.u. for Gd₆Co₂Ga at 7 T obtained from Fig. 4). It is worth noting that the estimated value is 45 μB per f.u., while the summation over the individual contributions of the constituent atoms leads to 41.6 μB per f.u. The first estimation is supposed to be a more accurate value for the total magnetic moment.

A large number of possible magnetic configurations as starting guesses for the electronic self-consistency calculation were performed but only two stable configurations were obtained. One is described above, and the second stable configuration is with the total FM solution, which is less energetically favorable. Other explored configurations include possible AFM couplings among Gd atoms belonging to different crystallographic sites, but none of them remain stable. It is interesting to note that the 18-atom primitive cell could still contain an even number for all species in all Wyckoff sites, which is a useful condition needed to properly study possible FM or AFM configurations. We did not find any other stable solution considering AFM couplings among Gd atoms. A similar analysis was also made at PBE level, without finding any reasonable conclusion.

Overall, the results of DFT calculations are in good agreement with the experimental observations of Gd₆Co₂Ga. DFT reveals that the compound exhibits a relatively simple magnetic moment distribution (i.e., parallel Gd atoms with the FM ground state), which agrees with the significant and positive θₑ value (~99.1 K) of Gd₆Co₂Ga. Furthermore, the effective magnetic moment of Gd atoms determined by DFT and experimental results is in reasonable agreement with the theoretical value (7.94 μB).

The temperature-averaged magnetic entropy change (TEC), an appropriate parameter to evaluate the MCE materials, has been introduced by Griffith et al. [53] and can be calculated by the following equation:

\[ \Delta S_{\text{iso}} = N \frac{k_B}{H} \ln \left( \frac{H_{\text{ap}}}{H_{\text{int}}} \right) \]

where \( \Delta S_{\text{iso}} \) is the temperature-averaged magnetic entropy change, \( k_B \) is the Boltzmann constant, \( H_{\text{ap}} \) is the applied magnetic field, and \( H_{\text{int}} \) is the internal magnetic field. The maximum values of \( \Delta S_{\text{iso}} \) under \( 
\Delta H \) of 0–7 T are 15.8, 4.8, and 12.6 J kg⁻¹ K⁻¹ for Ho₆Co₂Ga, Dy₆Co₂Ga, and Gd₆Co₂Ga, respectively. It is worth noting that the peak temperatures of \( \Delta S_{\text{iso}} \) for the Ho₆Co₂Ga and Gd₆Co₂Ga compounds, 26 and 75 K, respectively, coincide with the desired range for H₂ and N₂ liquefaction. To check the effect of the demagnetizing field on \( \Delta S_{\text{iso}} \), we considered a demagnetizing factor (N) of 1/3 due to the shape of our samples. The maximum values of isothermal entropy change (\( \Delta S_{\text{iso max}} \)) as a function of the applied field (\( H_{\text{ap}} \)) and the internal field (\( H_{\text{int}} = H_{\text{ap}} - N M \)) for all the compounds are plotted in Fig. S2.

More detailed studies are needed to identify the origin of that feature. The maximum values of \( \Delta S_{\text{iso}} \) under \( \Delta H \) of 0–7 T are 15.8, 4.8, and 12.6 J kg⁻¹ K⁻¹ for Ho₆Co₂Ga, Dy₆Co₂Ga, and Gd₆Co₂Ga, respectively. It is worth highlighting that the peak temperatures of \( \Delta S_{\text{iso}} \) for the Ho₆Co₂Ga and Gd₆Co₂Ga compounds, 26 and 75 K, respectively, coincide with the desired range for H₂ and N₂ liquefaction. To check the effect of the demagnetizing field on \( \Delta S_{\text{iso}} \), we considered a demagnetizing factor (N) of 1/3 due to the shape of our samples. The maximum values of isothermal entropy change (\( \Delta S_{\text{iso max}} \)) as a function of the applied field (\( H_{\text{ap}} \)) and the internal field (\( H_{\text{int}} = H_{\text{ap}} - N M \)) for all the compounds are plotted in Fig. S2.
where $\Delta T_{\text{lift}}$ is temperature span and $T_{\text{mid}}$ is the central temperature whereby the TEC ($\Delta T_{\text{lift}}$) gets the maximum value for the given $\Delta T_{\text{lift}}$. The values of TEC ($10\Delta T_{\text{lift}}$) under field change of 0–7 T are 14.9 J kg$^{-1}$ K$^{-1}$ for Ho$_6$Co$_2$Ga, 4.7 J kg$^{-1}$ K$^{-1}$ for Dy$_6$Co$_2$Ga and 12.5 J kg$^{-1}$ K$^{-1}$ for Gd$_6$Co$_2$Ga, which are close to those of $|\Delta S_{\text{iso}}|_{\text{max}}$.

Another magnetocaloric parameter for a figure of merit is the relative cooling power (RCP), which is used to evaluate the cooling efficiency of MCE materials. It can be calculated by the following formula:

$$\text{RCP} = -\Delta S_{\text{iso}}^{\text{max}} \times \delta T_{\text{FWHM}},$$

where $\delta T_{\text{FWHM}}$ is the full width at half maximum of $|\Delta S_{\text{iso}}|$. The calculated values of RCP under $\Delta H$ of 0–7 T are 532.6 J kg$^{-1}$ for Ho$_6$Co$_2$Ga, 256.9 J kg$^{-1}$ for Dy$_6$Co$_2$Ga, and 945.3 J kg$^{-1}$ for Gd$_6$Co$_2$Ga. Due to the three continuous phase transitions in Gd$_6$Co$_2$Ga, its refrigerant capacity is significantly higher than those of RE-based compounds reported in the literature. Assuming no interactions among the phases, the total values of $\Delta S_{\text{iso}}$ for $x$Ho$_6$Co$_2$Ga + $(1-x)$Gd$_6$Co$_2$Ga composite ($x$ is the mass fraction of Ho$_6$Co$_2$Ga with $0 \leq x \leq 1$) for $\Delta H$ of 0–5 T were estimated as shown in Fig. 7. The optimal table-like MCE is found for $x = 0.2$, obtaining an RCP of 640 J kg$^{-1}$, which is larger than those of Ho$_6$Co$_2$Ga and Gd$_6$Co$_2$Ga. In addition, the maximum temperature span has been found for $x = 0.4$, improving $\delta T_{\text{FWHM}}$ up to 90 K, which is much larger than that of single Ho$_6$Co$_2$Ga and Gd$_6$Co$_2$Ga (29 and 68 K, respectively). Such a wide working temperature range (covering the H$_2$ and N$_2$ liquefaction temperature ranges) makes it

Figure 6 The isothermal magnetization curves at selected temperatures for Ho$_6$Co$_2$Ga (a), Dy$_6$Co$_2$Ga (b), and Gd$_6$Co$_2$Ga (c). The isothermal magnetic entropy changes ($\Delta S_{\text{iso}}$) for Ho$_6$Co$_2$Ga (d), Dy$_6$Co$_2$Ga (e), and Gd$_6$Co$_2$Ga (f). The inset of (f) shows the $\Delta S_{\text{iso}}$–$T$ curve in the range of 0–1 T for Gd$_6$Co$_2$Ga.
suitable for cryogenic refrigeration applications. In addition, these estimated phase fractions showing MCE optimization are in agreement with the reports of Ref. [67] in which the larger phase proportion of the higher $T_C$ phase will lead to RCP enhancement.

Fig. 8a and b display the temperature dependence of $\Delta S_{iso}$ (under $\Delta H$ of 0–1.5 and 0–2.0 T) and exponent $n$ (under $\Delta H$ of 0–1.75 T) for the Ho$_6$Co$_2$Ga. It has been reported that the overshoot of $n$ above 2 near the transition temperature should be observed in the $n(T)$ curves for FOPT materials [12]. For Ho$_6$Co$_2$Ga, it can be observed that $n$ shows large values at low temperatures and in the region that MCE switches from inverse to direct (marked by the cyan box). For the former, the typical whole overshoot is not observed (due to the low transition temperature of Ho$_6$Co$_2$Ga), but still, $n$ shows an increase above 2 within the inverse MCE region (below the transition temperature at 0 field), indicating the first-order character of the AF-PM transition [68]. On the other hand, in the shadowed region, the large $n$ values are due to the change of $\Delta S_{iso}$ signs, unrelated to the order of phase transitions. In addition, the observed features marked by the gray box are related to the plateau observed in Fig. 3. The temperature dependence of $\Delta S_{iso}$ and $n$ for Dy$_6$Co$_2$Ga under the same field change as Ho$_6$Co$_2$Ga are shown in Fig. 8c and d. The overshoot feature ($n$ above 2) can also be clearly observed at low temperatures, which indicates the FOPT nature. Fig. 8e and f show the temperature dependence of $\Delta S_{iso}$ (under $\Delta H$ of 0–3.0 and 0–4.0 T) and exponent $n$ (under $\Delta H$ of 0–3.5 T) for Gd$_6$Co$_2$Ga. The $n(T)$ curve shows three minima, which correspond to the three phase transitions aforementioned in the $M(T)$ results (Fig. 3c). Gd$_6$Co$_2$Ga does not show any overshoot of $n > 2$ near the transition temperatures (except the shadowed region where MCE switches signs),

![Figure 7](image_url) Temperature dependence of $\Delta S_{iso}$ for the hypothetical $x$Ho$_6$Co$_2$Ga + $(1-x)$Gd$_6$Co$_2$Ga composite for $\Delta H$ of 0–5 T.

| Material                  | $T_t$ (K) | $|\Delta S_{iso, max}|$ (J kg$^{-1}$ K$^{-1}$) | RCP (J kg$^{-1}$) | Refs.      |
|---------------------------|-----------|-----------------------------------------------|-------------------|------------|
| Ho$_6$Co$_2$Ga            | 16        | 10.1                                         | 4.1               | 292        | Present work |
| Dy$_6$Co$_2$Ga            | 47        | 2.8                                          | 1.6               | 131        | Present work |
| Gd$_6$Co$_2$Ga            | 55/78/129 | 9.1                                          | –                 | 618        | Present work |
| Dy$_6$Co$_2$Al$_{0.8}$    | 30        | 2.8                                          | 3.9               | –170       | [22]        |
| Gd$_6$Co$_2$Al$_{0.8}$    | 26/59/80  | 10.9                                         | –                 | –760       | [22]        |
| Dy$_6$Co$_2$Sn$_{0.5}$    | 42        | 2.3                                          | 6.5               | –          | [21]        |
| Gd$_{12}$Ni$_{2}$In$_9$   | 41/92/135 | 2.8                                          | –1.0              | 171        | [14]        |
| DyNiSi$_2$                | 25        | 4.4                                          | 3.6               | –70        | [54]        |
| GdCo$_2$B$_2$C             | 17        | 10.3                                         | –                 | 238        | [55]        |
| Ho$_2$CoGa$_3$            | 10        | 13.8                                         | –                 | –383       | [56]        |
| Tm$_2$Co$_3$Ga            | 12        | 11.3                                         | –                 | 152        | [57]        |
| EuAgCd                    | 27        | 13.5                                         | –                 | 321        | [58]        |
| HoCo$_5$Ni$_{17}$         | 27        | 18.6                                         | –                 | –628       | [59]        |
| GdZn$_2$                  | 85        | 8.8                                          | –                 | 530        | [60]        |
| GdPdIn                    | 90        | 4.64                                         | –                 | 464        | [61]        |
| GdNi$_2$                  | 70        | 10.8                                         | –                 | –518       | [62]        |
indicating that the nature of the phase transitions is of second-order. Near the peaks of $\Delta S_{iso}$, $n$ does not show deep minima values below 1 as typically observed at the transition temperatures of single magnetic phase materials, which can be attributed to the mixed phase transitions present in the sample [12].

In addition, the field dependence of $\Delta S_{iso}$ and the exponent $n$ were also investigated, as shown in Fig. S3. For Ho$_6$Co$_2$Ga and Dy$_6$Co$_2$Ga, we chose two temperatures below the inverse MCE peak: 9.5 and 9.0 K, respectively. An obvious overshoot of $n$ above 2 can be found for Ho$_6$Co$_2$Ga, evidencing that an AF-PM first-order metamagnetic phase transition occurred [68]. After the phase transition, $n$ decreases down to negative values due to the influence of the direct MCE associated with the FM phase [68]. It is worth noting that an overshoot (slightly above 2) can also be observed for Dy$_6$Co$_2$Ga at field changes around 3–4 T, also indicating the first-order character of the AF-PM transition. In the case of Gd$_6$Co$_2$Ga, two temperatures after the first two main $\Delta S_{iso}$ peaks were chosen: 63 and 87 K. For both temperatures, the values of $n$ are between 1 and 2 due to the coexistence of FM and PM phases. As the transformation begins (see the curve for 63 K), $n$ increases up to 2 followed by decreasing down to values close to 1, indicating the major FM contribution. No overshoot is observed for either temperature, reconfirming the second-order nature of both transitions.

To further evaluate the nature of phase transition, we also studied the Arrott-plots ($M^2/H/M$) for the three compounds, which are displayed in Fig. 9a–c. Negative slopes are observed for Ho$_6$Co$_2$Ga and Dy$_6$Co$_2$Ga (being more evident for the former), indicating FOPTs according to Banerjee’s criterion [38], which is in agreement with the exponent $n$ criterion. Whereas for Gd$_6$Co$_2$Ga, no negative slope or inflection point is observed, demonstrating the second-order nature of the phase transitions. It should be highlighted that there is good agreement between the analyses based on the exponent $n$ criterion and the conventional Banerjee’s criterion for this particular series of compounds.

CONCLUSIONS

The structural, magnetic, thermomagnetic, and magnetocaloric properties of RE$_6$Co$_2$Ga (RE = Ho, Dy or Gd) compounds were investigated. Rietveld refinement proved the compounds crystallize in single phase Ho$_6$Co$_2$Ga-type crystal structure ($Immm$ space group). They exhibit complex and interesting magnetic behavior similar to literature work of isostructural RE$_6$Co$_x$A$_y$ compounds (A = Al/Sn, $x = 2.2–2.5$, and $y =0.5–0.8$). Using the conventional Banerjee’s criterion, novel MCE field dependence $n$ fingerprint and DFT studies, the nature of the order of phase transitions, type of phase transitions, and magnetic ordering of such compounds are revealed. Ho$_6$Co$_2$Ga and Dy$_6$Co$_2$Ga are found to undergo a field-induced first-order AF to PM transition. Gd$_6$Co$_2$Ga exhibits FM to PM transition, with three consecutive features found to be of the second-order type. Its DFT calculations unveil its strong FM ground state in agreement with the obtained positive $\theta_P$ value and the observed saturated magnetization. By tuning Ho $\rightarrow$ Gd in RE$_6$Co$_2$Ga compounds, FOPT can be obtained in addition to the second-order FM-PM phase transitions: 1st and
2nd order for Ho and Dy, and only 2nd order for Gd. This leads to the compounds exhibiting significant MCE performance tunable from 26 to 75 K which falls in the range of H₂ and N₂ liquefaction, indicating their potential applications in cryogenic MR.

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Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Supporting data are available in the online version of the paper.

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RE₆Co₂Ga (RE = Ho, Dy or Gd) 低温磁制冷材料的一级相变和二级相变

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摘要 具有正交Ho₆Co₂Ga型晶体结构的富稀土金属间化合物因其具备独特的磁性能而被关注，但它们的磁有序、磁相变类型以及磁热性能尚未见系统报道。本文通过对RE₆Co₂Ga化合物中的稀土元素类型的调控，实现了材料相变类型从反铁磁(AF)到顺磁(FM)的转变。利用磁热效应的场依赖性结合Banerjee准则的判断标准研究发现，Ho₆Co₂Ga和Dy₆Co₂Ga同时具备二级相变和一级相变特征，而Gd₆Co₂Ga中则仅存在二级相变。在0–5 T的磁场变化下，Ho₆Co₂Ga和Gd₆Co₂Ga的磁熵变分别在26和75 K附近达到最大值10.1和9.1 J kg⁻¹ K⁻¹，而这两个温度分别接近于H₄液化和H₄液化温度。优异的磁热性能使得RE₆Co₂Ga体系在低温磁制冷领域具有潜在的应用前景。