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Magnetic properties and magnetocaloric effects in $R_3\mathrm{Ni}_2$ ($R=\text{Ho and Er}$) compounds

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Magnetic and magnetocaloric properties of $R_3\mathrm{Ni}_2$ ($R=\text{Ho and Er}$) compounds have been investigated. Both Ho$_3\mathrm{Ni}_2$ and Er$_3\mathrm{Ni}_2$ compounds undergo two successive phase transitions: spin reorientation transition and second-order ferromagnetic-paramagnetic transition. The maximal values of magnetic entropy change are achieved to be 21.7 J kg$^{-1}$ K$^{-1}$ for Ho$_3\mathrm{Ni}_2$ and 19.5 J kg$^{-1}$ K$^{-1}$ for Er$_3\mathrm{Ni}_2$ for a field change of 0-5 T. A large refrigerant capacity (RC) of 496 J kg$^{-1}$ in the composite material is also obtained. Large reversible magnetocaloric effect and RC indicate the potentiality of $R_3\mathrm{Ni}_2$ ($R=\text{Ho and Er}$) compounds as candidates for low-temperature magnetic refrigerant. © 2011 American Institute of Physics. [doi:10.1063/1.3643142]

Magnetic refrigeration based on magnetocaloric effect (MCE) of solid-state working substances has been widely employed in ultra-low temperature. Recently, it has been anticipated to be a promising alternative technology available at high temperature and even room temperature, due to its higher energy-efficient and environment-friendly features as compared with the common gas-compression refrigeration technology that is used currently. Large isothermal magnetic entropy change compared with the common gas-compression refrigeration technology that is used currently. Large isothermal magnetic entropy change is anticipated to be a promising alternative technology available in the near future.

$T_N$ and $T_C$ are the Curie temperature for the refrigeration technological application. How- ever, the increased magnetic moment in rare earth sublattices has been confirmed. Moreover, HoNi and ErNi compounds have different arrangement of moments. In one word, $R_3\mathrm{Ni}$ and $R\mathrm{Ni}$ series with $R=\text{Ho, Er}$ have complicated magnetic structures.

The $R_3\mathrm{Ni}_2$ series ($R=\text{Ho and Er}$) are the only kind of compounds between $R_2\mathrm{Ni}$ and $R\mathrm{Ni}$ series with $R=\text{Ho, Er}$. The crystalline structure of Er$_3\mathrm{Ni}_2$ is rhomb-centered rhombohedral (space group R3$\overline{3}$). Er atoms occupy three nonequivalent sites, 3b site for Er(1), 6c site for Er(2), and 18f site for Er(3). Although Ni atoms also occupy 18f site, their positions are different from those of Er(3). The high-temperature phase of Ho$_3\mathrm{Ni}_2$ is isotypic with Er$_3\mathrm{Ni}_2$. Based on their complicated crystalline structure, Ho$_3\mathrm{Ni}_2$ and Er$_3\mathrm{Ni}_2$ compounds may have interesting magnetic structure. Large MCEs in them can be also expected due to the large rare earth content. Nevertheless, no reports on magnetic properties and MCEs of $R_3\mathrm{Ni}_2$ ($R=\text{Ho and Er}$) compounds are found up to now. So in this paper, we present a study on the magnetic properties and MCEs of $R_3\mathrm{Ni}_2$ ($R=\text{Ho and Er}$) compounds.

The samples were prepared by arc melting the constituent elements with the purity better than 99.9% in high-purity argon atmosphere. The obtained ingots were sealed in a high-vacuum quartz tube, annealed at 1023 K for 3 days for Er$_3\mathrm{Ni}_2$ and 873 K for 30 days for Ho$_3\mathrm{Ni}_2$, and then quenched into liquid nitrogen. Powder x-ray diffractometer was performed to characterize the crystal structure of the samples. Magnetic measurements were carried out on a commercial MPMS-7 superconducting quantum interference device magnetometer. Heat capacity was measured by using a commercial PPMS-14H physical property measurement system.

Figure 1 shows the Rietveld refined powder x-ray diffraction patterns of $R_3\mathrm{Ni}_2$ ($R=\text{Ho and Er}$) compounds. Almost all the diffraction peaks can be indexed to a rhombohedral structure. The lattice parameters obtained from the refinement are $a = 8.523(5)$ Å and $c = 15.758(6)$ Å for Ho$_3\mathrm{Ni}_2$ compound, $a = 8.486(0)$ Å and $c = 15.704(1)$ Å for Er$_3\mathrm{Ni}_2$ compound, which almost accord with the previous reports.15,16

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The low-field temperature-dependence of magnetization has been measured in order to determine magnetic state, phase transition temperature, and the nature of the transition. Figures 2(a) and 2(b) display the zero-field cooling (ZFC) and field-cooling (FC) magnetization curves of $R_3Ni_2$ ($R=Ho$ and Er) compounds under a field of $0.01 T$, respectively. It is found that there are two successive magnetic transitions in the $M-T$ curves for these compounds. For $Er_3Ni_2$ compound (see Fig. 2(b)), the anomaly at low temperature may be a spin-reorientation (SR) transition. The SR transition temperature, $T_{SR}$, is decided to be $\sim 12 K$. The authentic evidence needs to be supplied by neutron diffraction study in the future work. The transition at higher temperature corresponds to a change from FM to paramagnetic (PM) state with increasing temperature. The Curie temperature, $T_C$, corresponding to the maximum slope of $M-T$ curve under a field of $0.01 T$, is determined to be $17 K$. The reciprocal magnetic susceptibility $\chi^{-1}$ versus temperature for $Er_3Ni_2$ under a field of $2 T$ is shown in the inset of Fig. 2(b). The magnetic susceptibility above $50 K$ obeys the Curie-Weiss law, and a positive PM Curie temperature is obtained, further confirming that a FM-PM phase transition takes place around $T_C$ for $Er_3Ni_2$. It can also be seen from Fig. 2(b) that the ZFC and FC curves are completely reversible around $T_C$, which is a characteristic of a second-order transition. $Ho_3Ni_2$ compound shows similar phenomena, as shown in Fig. 2(a) and its inset. $T_{SR}$ and $T_C$ are decided to be $10 K$ and $36 K$, respectively.

Given that Ni atoms are nonmagnetic in $R_3Ni_2$ ($R=Ho$ and Er) compounds, the effective magnetic moments per unit cell of $R_3Ni_2$ ($R=Ho$ and Er) compounds, evaluated from the slope of $1/\chi$ in the PM region under the field of $2 T$ (see the insets of Figs. 2(a) and 2(b)), equal to $10.9 \mu_B$ and $9.9 \mu_B$, which are close to the free ion values ($10.6 \mu_B$ for Ho ion and $9.5 \mu_B$ for Er ion), respectively. This illustrates that the hypothesis about the non-magnetism of Ni atoms in $R_3Ni_2$ ($R=Ho$ and Er) compounds is correct, which is similar to the case in $R_2Ni$ and $RNI$ compounds. The PM Curie temperatures obtained by fitting the susceptibility data under the field of $2 T$ are $33 K$ and $18 K$ for $Ho_3Ni_2$ and $Er_3Ni_2$ compounds, respectively.

The isothermal magnetization curves as a function of magnetic field for $R_3Ni_2$ ($R=Ho$ and Er) compounds were measured in applied fields of up to $5 T$ in a wide temperature range. Fig. 3(a) shows the typical magnetization curves of $Ho_3Ni_2$ in the temperature range of $5-41 K$. It can be seen from Fig. 3(a) that there is a considerable difference in the $M-H$ characteristics in different temperature ranges. The $Ho_3Ni_2$ compound shows a metamagnetic transition at about $3.2 T$ below $17 K$, whereas it shows typical FM nature in the temperature range of $17-35 K$. The selective isothermal magnetization curves of $Er_3Ni_2$ compound in the temperature range of $5-24 K$ are presented in Fig. 3(b). One can find that the $Er_3Ni_2$ exhibits typical FM nature at temperatures lower than $T_C$. The Arrott plots around $T_C$ for $R_3Ni_2$ ($R=Ho$ and Er) compounds are shown in the insets of Figs. 3(a) and 3(b), respectively. The positive slope of the Arrott plots confirms a characteristic of the second-order FM-PM transition, which accords well with the case mentioned based on Fig. 2 where thermal hysteresis around $T_C$ is absent.

The magnetic entropy change $\Delta S$ of $R_3Ni_2$ ($R=Ho$ and Er) compounds can be calculated from isothermal magnetization data by using Maxwell relation $\Delta S = \int_H^L (\partial M/\partial T)_{H} dH$. Figure 4(a) displays the values of $\Delta S$ for $R_3Ni_2$ ($R=Ho$ and Er) compounds as a function of temperature for the field changes of $0-2 T$ and $0-5 T$. A broad cusp around $T_{SR}$ is observed in each $\Delta S-T$ curve, which is in accord with the results of magnetic and specific capacity measurements. Another peak center at $T_C$ in every $\Delta S-T$ curve. For a field change of $0-5 T$, the peak values of $\Delta S$ for $Ho_3Ni_2$ and $Er_3Ni_2$ reach to $21.7 J kg^{-1} K^{-1}$ and $19.5 J kg^{-1} K^{-1}$, respectively, which are comparable with or much larger than those of some magnetic refrigerant materials with a similar phase temperature, such as DyNi$_2$ (21.3 J kg$^{-1}$ K$^{-1}$ at 20 K), DyCoAl (16.3 J kg$^{-1}$ K$^{-1}$ at 37 K), HoNi (14.5 J kg$^{-1}$ K$^{-1}$ at 36 K), TbCoC$_2$ (15.3 J kg$^{-1}$ K$^{-1}$ at 28 K), DyCuAl (20.4 J kg$^{-1}$ K$^{-1}$ at 28 K), and ErGa (21.3 J kg$^{-1}$ K$^{-1}$ at 30 K).

One can find from Fig. 4(a) that the peak values of $\Delta S$ around $T_C$ for $Ho_3Ni_2$ and $Er_3Ni_2$ compounds approximately equal each other and the corresponding temperature span is only $17 K$. So when $Ho_3Ni_2$ and $Er_3Ni_2$ compounds with the mass ratio of 2:3 are mixed together, the best quasi-platform
of $\Delta S$ is observed. The inset of Fig. 4(a) displays the temperature dependence of $\Delta S$ for the composite material for a field change of 0-5 T. A large RC value of 496 J kg$^{-1}$ is thus obtained, which is calculated by numerically integrating the area under the $\Delta S$-$T$ curve, with the temperatures at half maximum of the peak used as the integration limits.\(^2\) The large RC attributes to the appreciably large values of $\Delta S$ around $T_C$ for $R_3Ni_2 (R = Ho$ and Er) compounds.

In order to get better comprehension of the application potential of $R_3Ni_2 (R = Ho$ and Er) compounds, we have also calculated the MCE in terms of adiabatic temperature change $\Delta T_{ad}$ based on the data of Figs. 4(a) and 4(b) by using

$$\Delta T_{ad} = -\Delta S(TH_0) \times \frac{1}{C_p(TH_0)},$$

where $C_p(TH_0)$ is zero-field specific heat. The inset of Fig. 4(b) shows the temperature dependences of $\Delta T_{ad}$ of the $Ho_3Ni_2$ and $Er_3Ni_2$ compounds for field changes of 0-2 T and 0-5 T. The maximum values of $\Delta T_{ad}$ are found to be 3.2 and 7.0 K for $Ho_3Ni_2$, 3.3 and 5.9 K for $Er_3Ni_2$, respectively. They are comparable well with those of $DyNi_2$, $DyCuAl$, and $DyNiAl$.\(^4\) In summary, from the magnetization and heat capacity measurements, it is found that $R_3Ni_2 (R = Ho$ and Er) compounds undergo two successive phase transitions at low temperatures. Large $\Delta S$ of 21.7 J kg$^{-1}$ K$^{-1}$ for $Ho_3Ni_2$ and 19.5 J kg$^{-1}$ K$^{-1}$ for $Er_3Ni_2$ are obtained for a field change of 0-5 T. The maximum values of $\Delta T_{ad}$ for $Ho_3Ni_2$ and $Er_3Ni_2$ reach to 7.0 and 5.9 K for the same field change, respectively. For the composite material formed by $Ho_3Ni_2$ and $Er_3Ni_2$ with the mass ratio of 2:3, a large RC of 496 J kg$^{-1}$ is achieved for a field change of 0-5 T. The excellent magnetocaloric properties indicate the applicability of $R_3Ni_2 (R = Ho$ and Er) compounds to the liquefaction of hydrogen gas.

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\(^1\)W. F. Giauque and D. P. MacDougall, Phys. Rev. 43, 0768 (1933).