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Citation: Appl. Phys. Lett. **99**, 132504 (2011); doi: 10.1063/1.3643142
View online: http://dx.doi.org/10.1063/1.3643142
View Table of Contents: http://apl.aip.org/resource/1/APPLAB/v99/i13
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Magnetic properties and magnetocaloric effects in R_3Ni_2 (R = Ho and Er) compounds

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(Received 7 July 2011; accepted 3 September 2011; published online 26 September 2011)

Magnetic and magnetocaloric properties of R_3Ni_2 (R = Ho and Er) compounds have been investigated. Both Ho_3Ni_2 and Er_3Ni_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_3Ni_2 and 19.5 J kg^{-1} K^{-1} for Er_3Ni_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_3Ni_2 (R = 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.[1,2] 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.[3,4] Large isothermal magnetic entropy change (ΔS), as an important parameter for evaluating the amount of the MCE, has been found in materials with a first-order or second-order phase transition, such as $Gd_5(Si, Ge)_4$,[5] $La(Fe, Si)_{13}$,[6,7] MnAs,[8,9] MnFe(P, As),[10] Ni_2MnGa,[11] and Gd.[4] Researches are still in progress for exploring new materials which have large MCE at low fields near room temperature for the refrigeration technological application. However, systems exhibiting large MCE at low temperature are also important for basic research as well as special technological applications such as space science and liquefaction of hydrogen in fuel industry.[3,4] Therefore, it is desirable to explore magnetocaloric materials applicable in the low temperature range.

It was found that only rare earth atoms carry out magnetic moment, whereas Ni atoms remain nonmagnetic in the intermetallic compounds R_3Ni and RNi series (R is heavy rare earth) with different crystal structure.[12,13] Ho_3Ni and Er_3Ni compounds crystallize in the orthorhombic Fe_3C-type structure. The compounds HoNi and ErNi crystallize in the orthorhombic FeB-type structure. The magnetic properties of two series have been investigated in detail. The Er_3Ni compound exhibits an antiferromagnetic (AFM) state below Néel temperature T_N (=7 K). The spin freezing phenomenon occurs in the temperature range between T_N and spin freezing temperature T_{sf} (=12 K).[12] The similar situation has been observed in Ho_3Ni compound with $T_N = 15.5$ K and $T_{sf} = 34$ K.[12] However, the HoNi and ErNi compounds display ferromagnetic (FM) state below their respective Curie temperature T_C. A noncollinear arrangement of magnetic moment in rare earth sublattices has been confirmed. Moreover, HoNi and ErNi compounds have different arrangement of moments.[13,14] In one word, R_3Ni and RNi series with R = Ho, Er have complicated magnetic structures.

The R_3Ni_2 series (R = Ho and Er) are the only kind of compounds between R_3Ni and RNi series with R = Ho, Er. The crystalline structure of Er_3Ni_2 is rhomb-centered rhombohedral (space group $R\bar{3}$).[15] 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_3Ni_2 is isotypic with Er_3Ni_2.[16] Based on their complicated crystalline structure, Ho_3Ni_2 and Er_3Ni_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_3Ni_2 (R = 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_3Ni_2 (R = 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_3Ni_2 and 873 K for 30 days for Ho_3Ni_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_3Ni_2 (R = Ho and Er) compounds. Almost all the diffraction peaks can be indexed to a rhomb-centered rhombohedral Er_3Ni_2-type structure. The lattice parameters obtained from the refinement are $a = 8.523(5)$ Å and $c = 15.758(6)$ Å for Ho_3Ni_2 compound, $a = 8.486(0)$ Å and $c = 15.704(1)$ Å for Er_3Ni_2 compound, which almost accord with the previous reports.[15,16]

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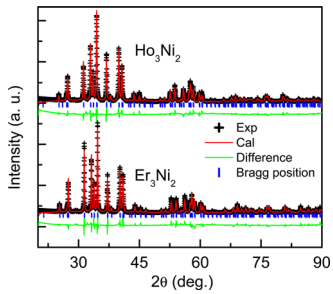

FIG. 1. (Color online) Rietveld refined powder XRD patterns of Ho_3Ni_2 and Er_3Ni_2 at room temperature. The observed data are indicated by crosses, and the calculated profile is the continuous line overlying them. The short vertical lines indicate the angular positions of the Bragg peaks of Ho_3Ni_2 and Er_3Ni_2. The lower curve shows the difference between the observed and calculated intensity.

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 ~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 χ^{-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 be also 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 R atom 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 μ_B and 9.9 μ_B, which are close to the free ion values (10.6 μ_B for Ho ion and 9.5 μ_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_3Ni and RNi compounds.[12,13] 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

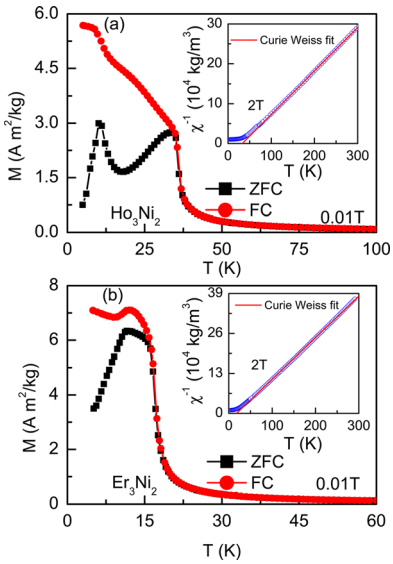

FIG. 2. (Color online) Temperature dependences of ZFC and FC magnetizations of Ho_3Ni_2 (a) and Er_3Ni_2 (b) under 0.01 T. The insets of (a) and (b) show the temperature variations of the ZFC inverse susceptibility fitted to the Curie-Weiss law under 2 T for Ho_3Ni_2 and Er_3Ni_2, respectively.

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[17] 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 ΔS of R_3Ni_2 (R = Ho and Er) compounds can be calculated from isothermal magnetization data by using Maxwell relation $\Delta S = \int_0^H (\partial M/\partial T)_H dH$. Figure 4(a) displays the values of ΔS 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 ΔS-T curve, which is in accord with the results of magnetic and specific capacity (see Fig. 4(b)) measurements. Another peak centers at T_C in every ΔS-T curve. For a field change of 0-5 T, the peak values of ΔS 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),[18] DyCoAl (16.3 J kg^{-1} K^{-1} at 37 K),[19] HoNi (14.5 J kg^{-1} K^{-1} at 36 K),[13] $TbCoC_2$ (15.3 J kg^{-1} K^{-1} at 28 K),[20] DyCuAl (20.4 J kg^{-1} K^{-1} at 28 K),[21] and ErGa (21.3 J kg^{-1} K^{-1} at 30 K).[22]

One can find from Fig. 4(a) that the peak values of ΔS 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

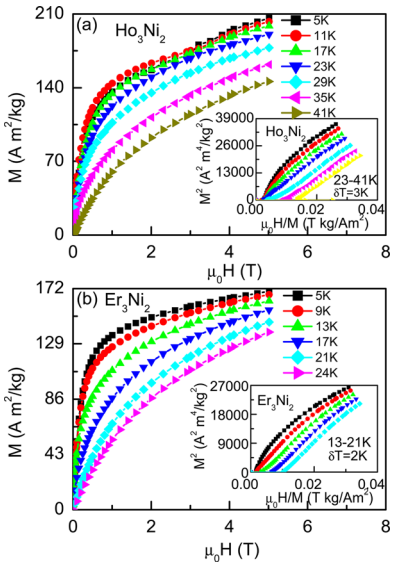

FIG. 3. (Color online) Typical magnetic isothermals of Ho_3Ni_2 (a) and Er_3Ni_2 (b) measured during field increasing. The insets of (a) and (b) show the Arrott-plots of Ho_3Ni_2 and Er_3Ni_2 around T_C, respectively.

of ΔS is observed. The inset of Fig. 4(a) displays the temperature dependence of ΔS 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 ΔS-T curve, with the temperatures at half maximum of the peak used as the integration limits.[23] The large RC attributes to the appreciably large values of ΔS 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 ΔT_{ad} based on the data of Figs. 4(a) and 4(b) by using

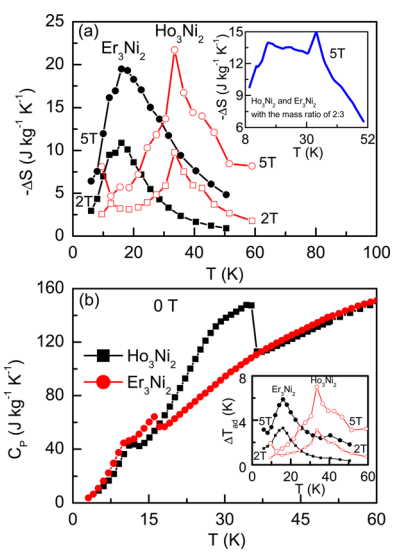

FIG. 4. (Color online) (a) Magnetic entropy change as a function of temperature for Ho_3Ni_2 and Er_3Ni_2 for magnetic field changes of 0-2 T and 0-5 T, where the inset shows the temperature dependence of magnetic entropy change for the composite material for a field change of 0-5 T. (b) Temperature dependences of the specific capacities for Ho_3Ni_2 and Er_3Ni_2 under zero field, where the inset shows the adiabatic temperature change curves for field changes of 0-2 T and 0-5 T.

$\Delta T_{ad} = -\Delta S(T,H) \times T/C_P(T,H_0)$, where $C_P(T,H_0)$ is zero-field specific heat. The inset of Fig. 4(b) shows the temperature dependences of ΔT_{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 ΔT_{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 $DyNi_2$,[18] DyCuAl,[21] and DyNiAl.[24]

In summery, 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 ΔS 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 ΔT_{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.

This work is supported by the National Natural Science Foundation of China (Grant Nos. 50731007, 11004204 and 51001077), the Hi-Tech Research and Development program of China, and the Knowledge Innovation Project of the Chinese Academy of Sciences.

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