Anomalous magnetocaloric effect and magnetoresistance in Ho(Ni,Fe)₂ compounds

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Magnetic, magnetocaloric, and magnetoresistance studies have been carried out on polycrystalline samples of Laves phase compounds Ho(Ni₁₋ₓFeₓ)₂ [x=0, 0.05, and 0.1]. The magnetocaloric effect in HoNi₂ is found to be maximum near the ordering temperature with values of 7 J mol⁻¹ K⁻¹ and 10.1 K for the isothermal magnetic entropy change and the adiabatic temperature change, respectively, for a field of 50 kOe. With Fe substitution, the temperature variation of magnetocaloric effect shows an additional peak at low temperatures, which is much more pronounced than the peak at the ordering temperature. The origin of the low temperature peak is attributed to the field-induced metamagnetic transition. The magnetoresistance data also seem to support the occurrence of the metamagnetic transition.

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I. INTRODUCTION

Rare earth (R)-transition metal (TM) intermetallic compounds belonging to the Laves phase family have attracted considerable attention owing to their magnetic and related physical properties, which enable them to be suitable candidates for fundamental studies as well as for various applications. Many compounds of this family are well known for large magnetostriiction, magnetocaloric effect (MCE), and magnetoresistance (MR). The property of magnetic materials to heat up or cool down when they are subjected to a varying magnetic field in an adiabic process is known as magnetocaloric effect and is intrinsic to all magnetic materials. Materials with large MCE are used as active materials in magnetic refrigerators. Recently, the search for potential magnetic refrigerants has resulted in an intensive research in the field of magnetocaloric effect. MCE can be measured either in terms of isothermal magnetic entropy change or adiabatic temperature change. Generally, the MCE shows a maximum at temperatures at which a magnetic transition, such as an order-disorder transition, occurs. The materials should show considerably broad MCE peak near the operating temperature of the refrigerator. Therefore, for refrigeration purposes, materials which exhibit “tablelike” MCE, or composite materials with distributed magnetic ordering temperatures (Tₘ), are of importance.

As part of our efforts to develop novel magnetic refrigerant materials suitable for different temperature ranges, we have been concentrating our studies on a variety of Laves phase systems of the type RCo₂. Many of these systems have been found to exhibit considerable MCE by virtue of the itinerant electron metamagnetism of the Co sublattice. Another class of Laves phase compounds, which possesses some similarities with RCo₂, but which has not been subjected to a detailed investigation of MCE and MR is RNi₂ compounds. Recently, theoretical studies on the MCE of RNi₂ (R=Er, Ho, Dy, Tb, and Gd) compounds have been reported, which suggests that the maximum MCE occurs in HoNi₂. Experimental investigations carried out in HoNi₂ are in close agreement with the theoretically predicted results. These reports have motivated us to focus our studies on the HoNi₂-based system. With the aim of achieving a composite material with distributed Tₘ, we have partially substituted nominal concentrations of Fe for Ni in HoNi₂ which is intended to increase the magnetic ordering temperature. Since a change in the magnetic state often leads to a change in the electrical resistivity, we have carried out magnetoresistance measurements on these compounds, in addition to the MCE studies.

II. EXPERIMENTAL DETAILS

Ho(Ni₁₋ₓFeₓ)₂ compounds [x=0, 0.05, and 0.1] were prepared by arc melting the constituent elements (of at least 99.9% purity) in high purity argon atmosphere. The ingots were melted several times to ensure homogeneity. The alloy buttons were subsequently annealed in argon atmosphere at 800 °C for a week. The powder x-ray diffraction patterns were taken using Cu-Kα radiation at room temperature. Lattice parameters were calculated from the Rietveld analysis (using Fullprof program). Magnetization measurements, in the temperature range 2–200 K and up to a maximum field of 50 kOe, were performed using a vibrating sample magnetometer (VSM, Oxford instruments). Heat capacity measurements, in the temperature range 2–200 K and in a field up to 50 kOe, were performed using the relaxation method (PPMS, Quantum Design). While the isothermal magnetic entropy change has been calculated independently using the magnetization isotherms as well as the heat capacity data, the adiabatic temperature change has been estimated using the heat capacity data. The magnetoresistance has been calculated by measuring the electrical resistivity in fields up to 50 kOe in the temperature range 2–300 K, using the linear four-probe technique (PPMS, Quantum Design).

III. RESULTS AND DISCUSSION

Figure 1 shows the Rietveld refinement of the powder x-ray diffractogram for the Ho(Ni₁₋ₓFeₓ)₂ compound with x
At 500 Oe, the compounds with $x = 0.05$ and 0.1 show an anomaly, at about 19 K for $x = 0.05$ and 23 K for $x = 0.1$. In the former case, the anomaly is in the form of a minimum, while in the latter it is in the form of a small drop in the magnetization. This suggests that there is some other contribution to the reduction in the magnetization at these temperatures, in addition to what is expected from the domain wall pinning effect.

The variation of heat capacity ($C$) as a function of temperature for HoNi$_2$ in fields $H=0$ and 50 kOe is shown in Fig. 3. The zero-field heat capacity data shows a peak, which thereby reducing the spontaneous cooperative alignment of the majority of the spins near the “zero-field $T_C$” (i.e., the ordering temperature observed in the absence of the field). This results in the smearing out of the heat capacity peak as the temperature is lowered, which is attributed to the domain wall pinning effect. Since the width of the domain wall is directly proportional to $T_C$, these systems have relatively narrow domain walls. It is seen that narrow domain wall systems show considerable pinning effect, at low temperatures. As the sample is cooled from above the ordering temperature in the ZFC state, the domain walls become frozen (pinned) and less mobile. This gives rise to a reduction in the magnetization at low temperatures. As the temperature increases, the mobility of the domain walls increases due to the increase in the thermal energy and hence the magnetization increases. By comparing the $M$-$T$ plots at 500 Oe and at 20 kOe, it is evident that the domain wall pinning effect is absent at 20 kOe. Furthermore, as can be seen from Fig. 2, the $M$-$T$ data of iron-substituted compounds at 500 Oe show an anomaly, at about 19 K for $x = 0.05$ and 23 K for $x = 0.1$. In the former case, the anomaly is in the form of a minimum, while in the latter it is in the form of a small drop in the magnetization. This suggests that there is some other contribution to the reduction in the magnetization at these temperatures, in addition to what is expected from the domain wall pinning effect.

The variation of heat capacity ($C$) as a function of temperature for HoNi$_2$ in fields $H=0$ and 50 kOe is shown in Fig. 3. The zero-field heat capacity data shows a peak, which nearly coincides with the $T_C$ observed from the temperature dependence of magnetization data. A gradual rise in heat capacity below $T_C$ and a sharp drop close to $T_C$ with a slight high temperature tail, characteristic of a second order transition ($\lambda$-transition) is observed in the $C$-$T$ plot. The high temperature tail is due to the onset of magnetic order in the paramagnetic state as the magnetic interaction between the spins starts to overcome the thermal energy. At the ordering temperature, there is a sudden change in magnetic entropy due to ferromagnetic ordering of the moments. When a constant magnetic field is applied to the sample, the ordering process is modified. The presence of field assists in the ferromagnetic coupling of the spins at temperatures above $T_C$, thereby reducing the spontaneous cooperative alignment of the majority of the spins near the “zero-field $T_C$” (i.e., the ordering temperature observed in the absence of the field). This results in the smearing out of the heat capacity peak.
This is clearly evident in the heat capacity plot at 50 kOe, in Fig. 3. However, in the iron substituted compounds no peak in heat capacity could be seen even in zero field (inset in Fig. 3). Since the ordering temperatures of the iron-substituted compounds are considerably higher than that of HoNi$_2$, the relatively larger lattice and electronic contributions to the total heat capacity would mask any weak peak due to the magnetic contribution.

The isothermal magnetic entropy change ($\Delta S_M$) and adiabatic temperature change ($\Delta T_{ad}$) for all the compounds have been calculated from the heat capacity data using the methods reported by Pecharsky and Gschneidner$^8$ [i.e., using Eqs. (1) and (2), respectively]. The entropy change has been calculated for formula unit of the corresponding compounds throughout this paper,

$$\Delta S_M(T, \mathcal{H}) = \int_0^T \left( \frac{C(T', \mathcal{H}) - C(T', 0)}{T'} \right) dT',$$

$$\Delta T_{ad}(T, 0) = \left[ T(S)_{H=\mathcal{H}} - T(S)_{H=0} \right],$$

$$\left( \frac{\partial S(T, \mathcal{H})}{\partial \mathcal{H}} \right)_T = \left( \frac{\partial M(T, \mathcal{H})}{\partial T} \right)_H,$$

$$\Delta S_M(T_{av,i},0) = \frac{1}{T_{i+1} - T_i} \int_{T_i}^{T_{i+1}} \left( M(T_{i+1}, \mathcal{H}) - M(T_i, \mathcal{H}) \right) dH,$$

where $T_{av,i}$ is the average of $T_i$ and $T_{i+1}$.

The entropy change has also been calculated from the $M$-$\mathcal{H}$ data [using Eqs. (3) and (4), Ref. 8] collected below $T_C$ with a temperature interval of 4 K, up to a maximum field of 50 kOe. It is found that the entropy change calculated from the magnetization data is in close agreement with that calculated from the capacity data, for all the compounds studied.

Figures 4 and 5 show the temperature variation of $\Delta S_M$ and $\Delta T_{ad}$, respectively, in Ho(Ni$_{1-x}$Fe$_x$)$_2$. It can be seen from Figs. 4 and 5 that $\Delta S_M$ and $\Delta T_{ad}$ for HoNi$_2$ show a maximum near $T_C$, as expected. The maximum values of $\Delta S_M$ and $\Delta T_{ad}$ are about 7 J mol$^{-1}$ K$^{-1}$ and 10.1 K, respectively. These values compare reasonably well with the theoretically predicted$^{15}$ values of $\sim$9 J mol$^{-1}$ K$^{-1}$ and 14 K, respectively. Theoretical calculations also show a weak low temperature peak in MCE below 2 K. As our measurements were down to 2 K only, we could not detect this peak in the present study.

In sharp contrast, the iron-substituted compounds show two MCE peaks, a weak one near $T_C$, and a prominent one at low temperatures. We call the peak near $T_C$ as the primary peak and the low temperature peak as the secondary peak. It is of interest to note that the temperatures corresponding to the secondary MCE peak and the anomaly in the $M$-$\mathcal{H}$ plot (at 500 Oe) nearly coincide, in both the iron-substituted compounds. To the best of our knowledge, there are only very few materials, typical examples being Gd$_3$Al$_2$ (Ref. 19) and GdMn$_2$, in which such a double peak MCE behavior has been reported. However, there is a difference in the structure of the double peak in the present case compared to that of Gd$_3$Al$_2$ and GdMn$_2$. In the latter two compounds, the two peaks in the MCE are quite distinguishable with a well-defined valley separating them. But in Ho(Ni$_{1-x}$Fe$_x$)$_2$ compounds, the entropy change in the temperature range separating the two peaks is not small and therefore, the two peaks are not well-distinguishable. This suggests that considerable contribution to the magnetic entropy change exists in the region between the two peaks.

The presence of the secondary peak indicates that there is an increase in the strength of magnetic order with increase of applied field, at low temperatures. Therefore, it is reasonable to assume that at low temperatures, in the absence of an external field, some kind of randomness associated with the magnetic moments exists in the iron-substituted compounds. Since Ni is known to possess zero magnetic moment, one cannot attribute the randomness with the Ni sublattice. The amount of Fe is quite small and therefore, it is hard to believe that the randomness associated with the Fe moments would give rise to a pronounced peak in MCE at such low temperatures. Even if one does not ignore this contribution it can be shown that such a large change in entropy could not be ascribed to the Fe moments. By taking into account the molar concentration of Fe and using the relation $R \ln (2J + 1)$, the theoretical magnetic entropy is found to be $\sim$0.6 J mol$^{-1}$ K$^{-1}$ for $J=1/2$ and 1.5 J mol$^{-1}$ K$^{-1}$ for $J = 5/2$ (maximum J for Fe), for the compound with $x=0.05$. For the compound with $x=0.1$, the corresponding values are $\sim$1.2 J mol$^{-1}$ K$^{-1}$ and 3 J mol$^{-1}$ K$^{-1}$, respectively. On the
FIG. 6. Variation of isothermal entropy change as a function of temperature for $\Delta H=10$ and 50 kOe. The inset shows the corresponding adiabatic temperature change.

other hand, the observed entropy changes associated with the secondary peak are $\sim 2.7$ J mol$^{-1}$ K$^{-1}$ and $1.7$ J mol$^{-1}$ K$^{-1}$, respectively for the compounds with $x=0.05$ and 0.1. Comparing the theoretical and the observed entropy changes and taking into account the fact that in a magnetocaloric process the real utilization of entropy ranges from $\sim 20\%$ to $\sim 50\%$ of the theoretical value$^{21}$ (for field changes as high as 75 kOe), it can be seen that the observed values are higher than the values expected from the Fe sublattice, in both the iron-substituted compounds. Therefore, the randomness occurring at low temperatures must be associated with the Ho moments only.

In order to understand the low temperature peak in detail, we have also calculated the magnetic entropy change and the adiabatic temperature change for a field of 10 kOe as well, as shown in Fig. 6. The entropy change for a field of 10 kOe becomes considerable at about 20 K and remains constant till the ordering temperature. On the other hand, when the field is increased to 50 kOe, two peaks develop, the prominent one at low temperature and the weaker one at $T_C$. The fact that the $\Delta S_M - T$ (and $\Delta T_{ad} - T$) plot does not show the low temperature peak prominently at 10 kOe suggests that a critical field (more than 10 kOe in the present case) exists, which orders the random moments of Ho.

To further probe the magnetic entropy contribution, we have also tried to analyze the weak primary MCE peak near $T_C$ in the iron-substituted compounds. The $\Delta S_M$ value at $T_C$, for the compound with $x=0.05$, is found to be $\sim 1.4$ J mol$^{-1}$ K$^{-1}$. This value is higher than that of the theoretical value (with $J=1/2$) associated with the Fe sublattice in this compound, which is $\sim 0.6$ J mol$^{-1}$ K$^{-1}$. The experimental value for the compound with $x=0.1$ is found to be $0.8$ J mol$^{-1}$ K$^{-1}$, whereas the theoretical value is about $1.2$ J mol$^{-1}$ K$^{-1}$. Considering the fact that the entropy change that can be realized in a real process is only a small fraction of the theoretical value, it can be inferred that the MCE peak near $T_C$ in both the Fe-substituted compounds has a contribution from the Ho sublattice as well. Therefore, it seems that the randomization of Ho ions, which started at low temperature, is completed only near $T_C$. The fact that the $M-T$ plot at 20 kOe shows a rather faster decrease may be a consequence of the randomness associated with the Ho sublattice. In fact, a similar behavior has been reported in $RFe_2H_x$ compounds, in which hydrogen insertion causes randomization of $R$ moments.$^{22}$ However, due to the dominant domain wall pinning effect, this trend is not visible in the $M-T$ plot at 500 Oe for the present compounds. In addition, the randomization of the Ho sublattice at low temperatures may also be the reason for the absence of a peak at $T_C$ in the zero-field $C$ vs $T$ plot of the iron-substituted compounds.

As mentioned earlier, the peculiar MCE behavior of these iron-substituted compounds is similar to that of Gd$_3$Al$_2$ and GdMn$_2$. It has been reported that a field-induced metamagnetic transition and a spin reorientation transition are responsible for the low temperature MCE peak in Gd$_3$Al$_2$ and GdMn$_2$, respectively. It is possible that a metamagnetic transition occurs for the randomized Ho moments at low temperatures in these iron-substituted compounds as well, when the applied field is more than the critical value. Such a transition has indeed been observed in the $M-H$ data obtained at 13 K in the Ho(Ni$_{0.95}$Fe$_{0.05}$)$_2$ compound, as shown in Fig. 7. The $M-H$ isotherm at 2 K is shown in the inset of this figure. It is also found that the magnetization at 13 K is more than that at 2 K for the same field, which suggests the existence of a ferrimagnetic ordering at 2 K. This is expected because the $R$-Fe coupling is known to be antiferromagnetic in the case of heavy rare earths like Ho. Though Fe concentration is very low, it gives rise to a reasonable exchange coupling at temperatures as low as 2 K. A similar trend has been observed in the compound with $x=0.1$ as well.

The double peak behavior of MCE in the present case results in significant values of entropy change and the temperature change over a wide range of temperature, resulting in a “tablelike” MCE behavior. This makes the present system comparable to the well known systems like (Gd,Er)NiAl.$^{23}$

In view of the anomalous behavior seen in the MCE of these compounds, we have studied their electrical resistivity as a function of applied field at various temperatures. The zero field electrical resistance (normalized to the value at 300 K) shows anomalies corresponding to the magnetic ordering temperatures in all the three compounds. While HoNi$_2$ shows a dip in the normalized resistance vs $T$ plot, the other two compounds show a clear change of slope, close to $T_C$.

The magnetoresistance, defined as
for all the compounds have been calculated. Here $R(0)$ and $R(H)$ refer to the resistance in zero field and in presence of the applied field, respectively. Figure 8 shows the field dependence of MR at temperatures close to $T_C$, for the compounds with $x=0$ and 0.05. In HoNi$_2$, the MR is very small and almost field-independent below $T_C$, but becomes positive and field-dependent above $T_C$. The positive MR at temperature above $T_C$ may be due to the dominant contribution arising from the Lorentz force,$^{5,14,24}$ since there are no major negative contributions to MR in the paramagnetic state. However, at temperatures above their ordering temperature, the compound with $x=0.05$ shows negative MR of about 1% for a field of 50 kOe, whereas it is about 9% in the compound with $x=0.1$. The large MR may be due to the quenching$^{5,14}$ of spin fluctuations associated mainly with the Fe moments. It is well known that transition metal systems show spin fluctuations, which give rise to additional contribution to the resistivity. Application of a magnetic field causes quenching of spin fluctuations, thereby reducing the resistivity.

In the iron-substituted compounds, we have also measured MR in the low temperature region where the secondary peak in MCE has been observed. Figure 9 shows the variation of MR in Ho(Ni$_{0.95}$Fe$_{0.05}$)$_2$ at low temperatures. A similar plot has been observed for Ho(Ni$_{0.9}$Fe$_{0.1}$)$_2$ as well. It is of interest to note that these compounds show strong field dependence of MR at temperatures below $T_C$, unlike HoNi$_2$. It is also quite evident from Fig. 9 that in fields up to about 10 kOe, the MR tends to be positive. However, for higher fields, there is a tendency for the MR to become negative. A negative MR implies that the applied field suppresses the magnetic disorder contribution to the electrical resistivity. Hence, it may be inferred that the metamagnetic transition is responsible for changing the sign of MR from positive to negative with increase in field. The fact that considerable hysteresis exists between the MR measured during increasing and decreasing fields, lends additional credence to the proposition of the metamagnetic transition. Nigam et al. have reported a similar effect of metamagnetic transition on the magnetoresistance in UCu$_2$Ge$_2$. Therefore, it is interesting to note that in the present case, MR variations also seem to suggest the existence of the metamagnetic transition, at low temperatures.

IV. SUMMARY

The magnetic, magnetoresistance, and magnetocaloric behavior of Ho(Ni$_{1-x}$Fe$_x$)$_2$ compounds with $x=0.05$ and 0.1 suggest the occurrence of a field-induced metamagnetic transition at low temperatures. Though double peak MCE behavior has been observed in compounds like Gd$_3$Al$_2$ and GdMn$_2$, a satisfactory explanation has not been reported. In Gd$_3$Al$_2$, the metamagnetic transition is expected to be responsible for the low temperature MCE peak, while in GdMn$_2$, it is a spin reorientation transition that gives rise to the low temperature peak. The main reason for the metamagnetic transition in the present case may be due to the presence of some degree of randomness in the Ho sublattice, even at low temperatures ($T < T_C$) for low fields (less than 10 kOe). On the application of a field above a critical value, magnetic order sets in, resulting in a metamagnetic transition. We feel that the randomness is due to the local anisotropy variations as a result of substitution of very low concentration of magnetic Fe for nonmagnetic Ni. It has indeed been reported that in $R$Fe$_2$ compounds, hydrogen insertion causes a randomization of the rare earth moments.$^{22}$ Therefore, the results obtained in the present series of compounds along with those of Gd$_3$Al$_2$ and GdMn$_2$ show that, though the exact low temperature magnetic structures are different, the magnetic transitions occurring at temperatures below the ordering temperatures could give rise to MCE peaks which...
are much more pronounced than those at the ordering temperatures, at least in certain compounds.

V. CONCLUSIONS

In conclusion, our studies show that HoNi₂ possesses very large MCE values, which enable it to become an active magnetic refrigerator at low temperatures. The compounds Ho(Ni₀.₉₆Fe₀.₀₄)₂ and Ho(Ni₀.₉₄Fe₀.₀₆)₂ exhibit double-peak MCE behavior, with the magnetic entropy distributed over a wide range of temperatures. The field dependence of magnetoresistance also shows a peak at low temperatures in these two latter compounds. Magnetic, magnetocaloric and magnetoresistance results seem to suggest the existence of some degree of randomness in the Ho sublattice at temperatures well below the ordering temperatures, in the iron-substituted compounds. The field-induced metamagnetic transition, which suppresses the randomization, may be responsible for the anomalous behavior of both the magnetocaloric effect and the magnetoresistance.

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