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Effect of Fe substitution on magnetocaloric effect in borocarbide superconductor Dy(Ni$_{1-x}$Fe$_x$)$_2$B$_2$C

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Abstract

The magnetic properties and magnetocaloric effect (MCE) in antiferromagnetic superconductor Dy(Ni$_{1-x}$Fe$_x$)$_2$B$_2$C ($x = 0, 0.1,$ and 0.2) has been studied. The magnetic transition temperature $T_M$ as well as the temperature at the maximum of magnetic entropy change ($-\Delta S_M^{\text{max}}$) slightly shift to low temperature with increasing $x$. An inverse MCE was observed, which is attributed to the nature of antiferromagnetic state under low magnetic field and at low temperatures for the present Dy(Ni$_{1-x}$Fe$_x$)$_2$B$_2$C compounds. A normal large MCE was observed under higher magnetic field changes, which is related to a field-induced first order metamagnetic transition from antiferromagnetic to ferromagnetic state. Under a magnetic field change of 7 T, the values of $-\Delta S_M^{\text{max}}$ reach 22.1, 16.6, and 14.8 J Kg$^{-1}$ K$^{-1}$ for $x = 0$, 0.1, and 0.2, respectively. The corresponding values of relative cooling power are 464, 332 and 295 J/kg. The observed large magnetic entropy is related to a field-induced first order metamagnetic transition from antiferromagnetic to ferromagnetic state.

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1. Introduction

The rare-earth nickel boroncarbide RNi$_2$B$_2$C compounds crystallized in the LuNi$_2$B$_2$C-type crystal structure have attracted much attention because of the interplay of superconductivity and magnetic ordering phenomena [1-8]. According to previous reported results [1-4], the Y, Lu, and Sc systems exhibit superconductivity without magnetic ordering. For the Dy, Ho, Er and Tm systems, superconductivity coexists with magnetic order. For the quaternary parent compounds, $T_c$ as well as $T_N$ can be well scaled with the de Gennes factor $(g_J-1)^2 J(J+1)$, where $g_J$ is the Landé $g$ factor and $J$ is the total angular moment of the R$^{3+}$ ion estimated for the Hund's rule ground-state [1-4]. The linear dependence of $T_c$ on the de Gennes (DG) factor is consistent with the predictions of the Abriskov-Gor'kov (AG) theory [6] of the pair-breaking effect by magnetic impurities. The scaling of $T_N$ can be understood in terms of the conduction electron-mediated Ruderman – Kittel – Kasuya – Yosida (RKKY) coupling between rare earth ions, which is an exchange interaction between localized magnetic spins and conduction electrons [3, 4].

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The magnetocaloric effect (MCE) in various materials has been extensively studied, not only because of their great potential for magnetic refrigeration applications but also for further understanding the fundamental properties of the materials [9-16]. The MCE manifests as an isothermal magnetic entropy change ($\Delta S_M$) or an adiabatic temperature change ($\Delta T_{ad}$) when the magnetic material is exposed to a varying magnetic field. The MCE in single crystalline HoNi$_2$B$_2$C has been studied theoretically and experimentally, respectively by Oliveira et al [11] and Massalami et al [12]. Very recently, a giant/large MCEs in Dy$_{0.9}$Tm$_{0.1}$Ni$_2$B$_2$C [13], RNi$_2$B$_2$C ($R$= Dy, Ho, and Er) [14], and Dy$_{1-x}$Ho$_x$Ni$_2$B$_2$C compounds [15] have been reported by us. The magnetism and superconductivity has also been reported in RNi$_2$B$_2$C compounds. A rapid decrease of $T_c$ and almost unchanged $T_N$ with Fe-substitution for Ni were observed [16, 17]. To search new MCE materials and further understand the physical properties of AFM boroncarbide RNi$_2$B$_2$C superconductors, in this work, the magnetic and MCE properties in Dy(Ni$_{1-x}$Fe$_x$)$_2$B$_2$C compounds were studied.

2. Experimental

Polycrystalline samples of Dy(Ni$_{1-x}$Fe$_x$)$_2$B$_2$C (x = 0, 0.1, and 0.2) were prepared by the arc melting method using a tungsten electrode under an argon atmosphere. The samples were finally annealed at 1323 K for 72 h in evacuated quartz tubes. All the samples were proved to be single phase by X-ray powder diffraction (XRD) analysis. The electrical resistivity measurements were carried out using a standard four-probe technique using the physical property measurement system (PPMS-9, Quantum Design). The magnetization measurements were done using a superconducting quantum interference device magnetometer (Quantum Design, MPMS-7). The specific heat measurements were carried out by the adiabatic heat relaxation method using the PPMS-9.

3. Results and Discussion

The temperature dependence of normalized zero field electrical resistivity $\rho(T)/\rho(20)$, DC magnetization $M$ ($H = 1$ T), and zero field specific heat $C$ for Dy(Ni$_{1-x}$Fe$_x$)$_2$B$_2$C (x = 0, 0.1, and 0.2) are shown in Fig. 1 (a), (b), and (c), respectively. For DyNi$_2$B$_2$C, the magnetic phase transition $T_M$ and superconducting transition temperature $T_c$ are 10.5 and 6 K, respectively, which are consistent with those previously reported results [3, 4, 8]. No superconductivity can be observed above 2 K for the doped samples. The sudden changes in the temperature dependence of resistivity around 10.5, 9.2, and 8 K for $x = 0, 0.1$, and 0.2, respectively, were originated from the magnetic ordering. The large peaks of $C$ are ascribed to the contributions from the magnetic transitions. The peak heights decrease and their position shift toward lower $T$ with increasing $x$. Figure 2 shows the magnetic isothermals on increasing (open symbols) and decreasing (filled symbols) field for Dy(Ni$_{1-x}$Fe$_x$)$_2$B$_2$C (x = 0, 0.1, and 0.2) at 2 K. We can note that the saturation magnetization decreases gradually with increasing Fe content $x$. A large magnetic hysteresis can be observed for DyNi$_2$B$_2$C, it decreases obviously for $x = 0.1$ and becoming ignorable for $x = 0.2$. The feature of low magnetic field magnetization indicates antiferromagnetic ordering, whereas a field-induced metamagnetic transition from AFM to FM phase has been observed with the application of higher magnetic field.

![Fig. 1. Temperature dependence of normalized zero field electrical resistivity $\rho(T)/\rho(20)$, DC magnetization $M$ ($H = 1$ T), and zero field specific heat $C$ for Dy(Ni$_{1-x}$Fe$_x$)$_2$B$_2$C (x = 0, 0.1, and 0.2)](image-url)

A set of selected magnetic isothermals with increasing and decreasing field for Dy(Ni$_{1-x}$Fe$_x$)$_2$B$_2$C (x = 0, 0.1, and 0.2) are measured with the temperature range from 2 to 36 K up to 7 T. Although a hysteresis of $M(H)$ was noticeable for DyNi$_2$B$_2$C at low temperatures, it gradually became smaller with increasing temperature, and almost disappeared above 5 K. To ensure the readability of the figure, only several isotherms with increasing field for $x = 0.1$ and 0.2 are presented in Fig. 3(a) and (b), respectively. A large reversible MCE is expected around the transition temperature where the magnetization rapidly changes with varying temperature. According to Banerjee criterion [18], the magnetic transition is of the second order if all the $H/M$ versus $M^2$ curves (also named Arrott plots) have a positive slope. On the
other hand, if the $H/M$ versus $M^2$ curves shows a negative slope at some point, the magnetic transition is of the first order. To clarify the order of the magnetic transition in Dy(Ni$_{1-x}$Fe$_x$)$_2$B$_2$C, the measured $M$-$H$ isotherms were converted into $H/M$ versus $M^2$ plots. The measured $M$-$H$ isotherms of Dy(Ni$_{1-x}$Fe$_x$)$_2$B$_2$C ($x = 0, 0.1$, and $0.2$) were converted into $H/M$ versus $M^2$ plots, and the curves are shown in Fig. 3 (c) and (d). A clear negative slope at low temperature and low magnetic field region can be observed, indicating the first order magnetic phase transition for Dy(Ni$_{1-x}$Fe$_x$)$_2$B$_2$C ($x = 0, 0.1$, and $0.2$) compounds, which is similar to those reported in Dy$_{1-x}$Ho$_x$Ni$_2$B$_2$C ($x = 0$-$1$) and RNi$_2$B$_2$C ($R =$ Dy, Ho, and Er) systems.

The magnetic entropy change $\Delta S_M$ was calculated from magnetization isotherm $M(H, T)$ curves using an integral version of Maxwell’s thermodynamic relation [9]:

$$\Delta S_M(T, \Delta H) = \int_{T}^{\infty} \left( \frac{\partial M(H, T)}{\partial T} \right)_H dH.$$  

The resulting temperature dependence of $-\Delta S_M$ with the magnetic field changes of 1, 2, 5, and 7 T are shown in Fig. 4 for Dy(Ni$_{1-x}$Fe$_x$)$_2$B$_2$C ($x = 0$, 0.1, and 0.2). For magnetic field changes of 1 and 2 T, $-\Delta S_M$ is negative (inverse MCE) below the transition temperature, and changes to positive with increasing temperature, this behaviour is similar to that of the recently reported Dy$_{1-x}$Ho$_x$Ni$_2$B$_2$C [15], RNi$_2$B$_2$C ($R = $ Dy, Ho, and Er) [14], and Tb$_2$Ni$_2$Sn [19] compounds which can be understood in terms of the FM-AFM phase coexistence and the variation in the ratio of these phases under different magnetic fields. For the magnetic field changes of 5 and 7 T, a positive $-\Delta S_M$ (i.e., conventional MCE) with a broad peak can be observed. Under a magnetic field change of 5 T, the values of $-\Delta S_M^{\text{max}}$ reach 17.1, 11.7, and 11.3 J Kg$^{-1}$K$^{-1}$ for $x = 0$, 0.1, and 0.2, respectively. The large magnetic entropy changes in Dy(Ni$_{1-x}$Fe$_x$)$_2$B$_2$C are believed to be related to the field-induced first-order magnetic transition from AFM to FM, similar to those observed in Dy$_{0.9}$Tm$_{0.1}$Ni$_2$B$_2$C and RNi$_2$B$_2$C ($R = $ Dy, Ho, and Er) systems. The reduction in the MCE of Dy(Ni$_{1-x}$Fe$_x$)$_2$B$_2$C system was due to the decreases of saturation magnetization upon Fe doping. Another important parameter for the MCE materials is the relative cooling power ($RCP$) which is a measure of the amount of heat transfer between the cold and hot reservoirs in an ideal refrigeration cycle. The $RCP$ is defined as the product of the maximum magnetic entropy...
change $\Delta S_M^{\text{max}}$ and full width at half maximum in $\Delta S_M(T)$ curve $\delta T_{\text{FWHM}}$. With the magnetic field changes of 5 and 7 T, the values of $RCP$ are evaluated to be 255 and 464 J/kg for $x = 0$; 228 and 332 J/kg for $x = 0.1$; 220 and 295 J/kg for $x = 0.2$, respectively.

![Graph showing temperature dependence of magnetic entropy change $-\Delta S_M$ for Dy(Ni$_{1-x}$Fe$_x$)$_2$B$_2$C ($x = 0, 0.1$, and 0.2).](image)

**Fig. 4.** Temperature dependence of magnetic entropy change $-\Delta S_M$ for Dy(Ni$_{1-x}$Fe$_x$)$_2$B$_2$C ($x = 0, 0.1$, and 0.2).

### 4. Conclusions

In summary, a large magnetic entropy change was observed in the Dy(Ni$_{1-x}$Fe$_x$)$_2$B$_2$C ($x = 0, 0.1$, and 0.2), which is related to a field-induced first order metamagnetic transition from AFM to FM state. The Fe dopant reduces the magnetic hysteresis and lowers the magnetic transition temperature $T_M$. The maximum values of $-\Delta S_M^{\text{max}}$ 17.1, 11.7, and 11.3 J Kg$^{-1}$ K$^{-1}$ with a magnetic field change of 5 T for $x = 0, 0.1$, and 0.2, respectively. The reduction in the MCE of Dy(Ni$_{1-x}$Fe$_x$)$_2$B$_2$C system was due to the decreases of saturation magnetization upon Fe doping. The present results may give some clue for searching proper materials for active magnetic refrigeration.

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