Effect of Dy substitution on magnetic properties and magnetocaloric effects of $Tb_6Co_{1.67}Si_3$ compounds*

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The magnetic and magnetocaloric properties of $(Tb_{1-x}Dy_x)_6Co_{1.67}Si_3$ ($0 \le x \le 0.8$) have been experimentally investigated. The compounds exhibit a $Ce_6Ni_2Si_3$-type hexagonal structure and undergo a second-order magnetic transition. The Curie temperature decreases from $\sim$ 187 K to 142 K as the content of Dy grows from 0 to 0.8. The maximal magnetic entropy change, for a field change of 0–5 T, varies between $\sim$ 6.2 and $\sim$ 7.4 J/kg·K, slightly decreasing when Dy is introduced. The substitution of Dy leads to a remarkable increase in refrigeration capacity (RC). A large RC value of $\sim$ 626 J/kg is achieved for $x = 0.4$ under a field change of 0–5 T.

Keywords: magnetic properties, magnetic entropy change, refrigerant capacity

PACC: 7530S, 7550C

1. Introduction

The ternary silicides $R_6Ni_2Si_3$ (R= La, Ce, Pr and Nd), which exhibit a hexagonal structure with the space group $P6_3/m$, were obtained by Bodak *et al.* in the 1970s.[1] Recently, Co-based silicides of $R_6Co_{1.67}Si_3$ (R=Ce, Nd, Gd, Tb and Dy), which possess the same structure as $Re_6Ni_2Si_3$, were reported by Chevalier *et al.*,[2] and an intensive study on their structural and magnetic properties has been performed.[3,4] The rare earth atoms were found to have two different crystallographic sites in the compounds, and several different magnetic states were available as the temperature decreased.[5,6] Due to the oscillatory Ruderman–Kittel–Kasuya–Yosida (RKKY) interaction between magnetic atoms, a compound with rare-earth moments at nonequivalent crystallographic sites may exhibit a complex magnetic behaviour. Due to the similarity of the rare earths in many aspects, the intermetallics obtained by simply changing the rare earth elements may exhibit a systematic variation in both the crystal structure and the magnetic property.[7] Recently, the magnetocaloric effects (MCEs) of the $R_6Co_{1.67}Si_3$ (R= Pr, Gd, Nd, Tb) compounds were reported.[8−14] A large refrigeration capacity (RC) was observed in $Gd_6Co_2Si_3$ near room temperature.[13,14] In the present paper, we perform a further study on the magnetic and magnetocaloric properties of $(Tb_{1-x}Dy_x)_6Co_{1.67}Si_3$ (x = 0, 0.2, 0.4, 0.6 and 0.8), focusing on the effect of Dy substitution on the MCE.

2. Experiments

The $(Tb_{1-x}Dy_x)_6Co_{1.67}Si_3$ (x = 0, 0.2, 0.4, 0.6, 0.8 and 1.0) compounds were prepared by arc melting the appropriate amounts of Tb, Dy, Co, and Si in a high-purity argon atmosphere. The purities are 99.9% for Tb, Dy and Co, and 99.999% for Si. To ensure homogeneity, the samples were repeatedly melted with several intermediate turnovers. Ingots thus obtained were first wrapped by molybdenum foil sealed in a quartz tube with high vacuum, and annealed at 1073 K for 30 days, then quenched to room temperature. The x-ray diffraction (XRD) measurements were performed to check phase purity and crystal structure.

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Magnetic measurements were performed using a superconducting quantum interference device (SQUID) magnetometer in a temperature range of 4.2–470 K and magnetic fields up to 5 T. By using the Maxwell relation, the magnetic entropy change was calculated based on the isothermal magnetization around the Curie temperature.

3. Results and discussion

Figure 1 displays the room-temperature powder XRD patterns of $(Tb_{1-x}Dy_x)_6Co_{1.67}Si_3$ (x = 0, 0.2, 0.4, 0.6 and 0.8). All the diffraction peaks, except for those of the minor impurity phases, can be indexed based on the hexagonal $Ce_6Ni_2Si_3$-type structure (space group $P6_3/m$).[3] The $Dy_6Co_{1.67}Si_3$ compound exists but it is not obtainable as a single phase. This shows the dependence of the thermal stability of these compounds on the nature of the rare earth elements. The XRD peak of the $(Tb_{1-x}Dy_x)_6Co_{1.67}Si_3$ compounds shifts to large angles with the increase of the content of Dy, which indicates the reduction of the lattice constants. The Rietveld refinement was done to get more information about the unit cell parameters. As the Dy content grows from 0 to 0.8, the lattice constant a, which is governed by the Co–Si sublattice, decreases from 1.1678 nm to 1.1637 nm; the lattice constant c, which is influenced by the size of the R^{3+} ions,[2] grows from 0.4128 nm to 0.4108 nm. Figure 2 shows the unit cell volume as a function of Dy content for $(Tb_{1-x}Dy_x)_6Co_{1.67}Si_3$. The decrease in unit cell volume indicates lattice contraction due to the introduction of smaller Dy atoms, similar to what happens when R varies in the sequence R=Pr, Nd, Gd and Tb for the $R_6Co_{1.67}Si_3$ compounds (see the inset of Fig. 2).

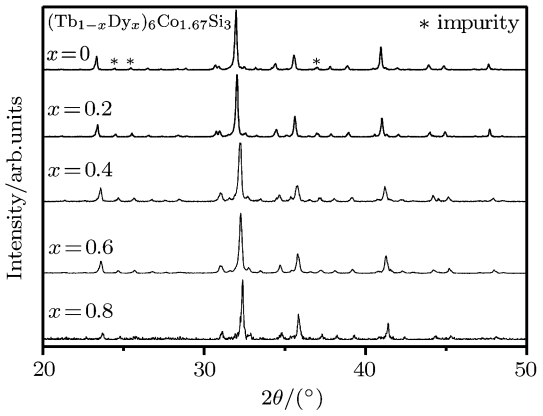


Fig. 1. The room-temperature x-ray diffraction patterns of $(Tb_{1-x}Dy_x)_6Co_{1.67}Si_3$ with x = 0, 0.2, 0.4, 0.6 and 0.8. The impurity phase is indicated by ∗.

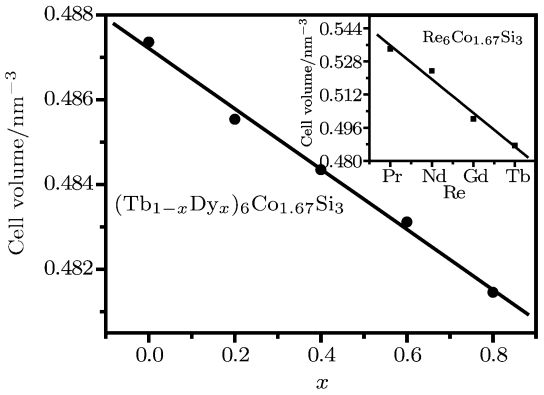


Fig. 2. The unit cell volumes as a function of Dy content obtained by Rietveld refinement for $(Tb_{1-x}Dy_x)_6Co_{1.67}Si_3$ compounds with x = 0, 0.2, 0.4, 0.6 and 0.8. The inset shows the unit cell volumes of $R_6Co_{1.67}Si_3$ (R=Pr, Nd, Gd and Tb) compounds.

The lattice shrinkage and thus the change in atomic distance will certainly produce a strong effect on the interaction. As we know, the phase transition temperature has a close relation with the magnetic interaction between magnetic atoms. It is therefore anticipated that the phase transition will be affected by substituting Dy for Tb.

Figure 3(a) shows the temperature dependence of the magnetization of $(Tb_{1-x}Dy_x)_6Co_{1.67}Si_3$ (x = 0, 0.2, 0.4, 0.6 and 0.8), measured under a field of 0.01 T. It is obvious that $(Tb_{1-x}Dy_x)_6Co_{1.67}Si_3$ experiences four successive transitions at T_C, T_{SR}, T_1 and T_2 with the decrease of temperature (as shown in Table 1). The complex magnetic behaviour of $(Tb_{1-x}Dy_x)_6Co_{1.67}Si_3$ can be ascribed to the existence of two crystallographic sites, namely R_1 and R_2, for the rare earth atoms.[2] The magnetic moments of R at the two sites are different because of the different environments around R_1 and R_2. As is well established, R_1 has 10 R, 3 Co and 3 Si as close neighbours. In contrast, R_2 is surrounded by 10 R, 2 Co and 5 Si.[3,4] The first transition is a transition of the two rare earth sublattices from a paramagnetic order to a canted ferromagnetic order.[5] The Curie temperatures T_C, defined as the temperature corresponding to the maximal slope of the thermal magnetization curve, decreases linearly from 187 K to 142 K with increasing Dy concentration from 0 to 0.8. As was suggested by Chevalier *et al.*,[2] Co is non-magnetic in $R_6Co_{1.67}Si_3$ and the lanthanide is the origin of the magnetism. The magnetic properties of the ternary silicides are associated with the RKKY-type indirect exchange interaction between the 4f electrons. So, the depression of T_C after the replacement of Tb by Dy is due to the difference of the de Gennes values of Tb and Dy, as one might expect.

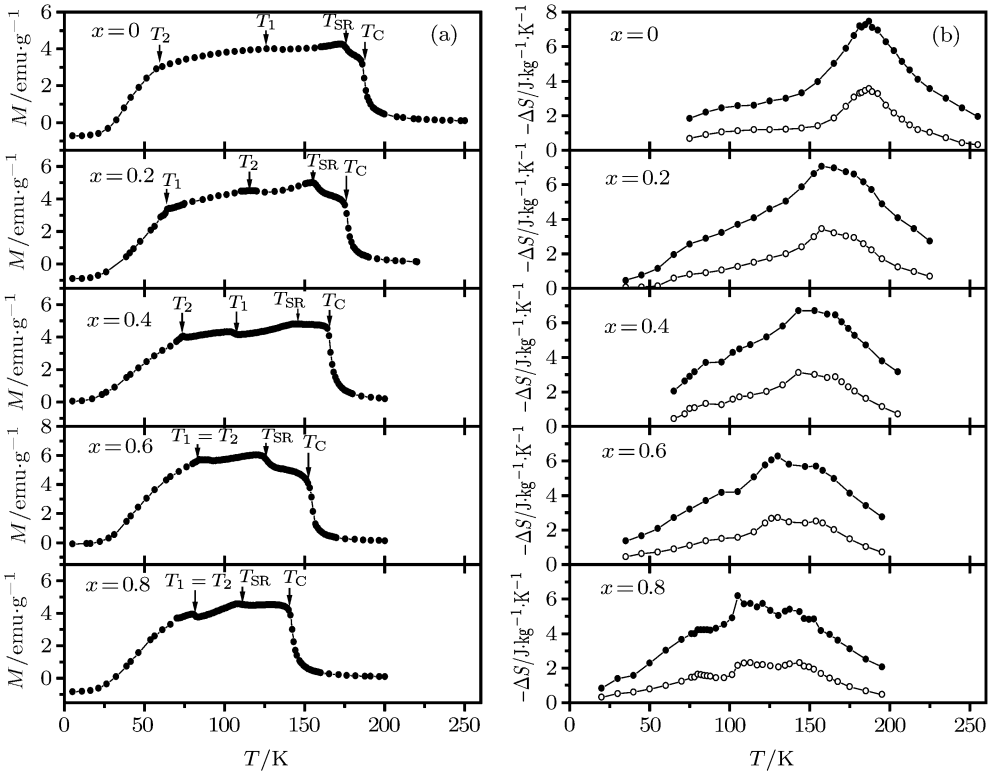


Fig. 3. Temperature dependence of magnetization measured under a field of 0.01 T (a), and temperature dependence of magnetic entropy change for the magnetic field changes from 0 to 2 T and from 0 to 5 T for $(Tb_{1-x}Dy_x)_6Co_{1.67}Si_3$ compounds with $x = 0$, 0.2, 0.4, 0.6 and 0.8, respectively (b).

The second transition is a spin reorientation according to the literature.[5] The critical temperature T_{SR} is found to decrease with the increase of Dy content. The more rapid decrease of T_{SR} with x, compared with T_C, may indicate a stronger effect of the element substitution on spin reorientation. According to Fig. 3, the remaining two phase transitions at T_1 and T_2 exhibit a systematic variation with x. This indicates an intrinsic origin of T_1 and T_2, rather than the effect of impurities. They may originate from the complex magnetic structures of the compounds, due to the different coordination of the rare earths. A neutron diffraction study is required to get a deep understanding of the magnetic structure of the compounds.

The isothermal magnetization curves of $(Tb_{1-x}Dy_x)_6Co_{1.67}Si_3$ ($x = 0$, 0.2, 0.4, 0.6 and 0.8) were measured under different temperatures (not shown here). The magnetization was measured in both the field ascending and descending modes at temperatures near the critical temperatures, while only the data for the field ascending mode were recorded at temperatures far away from the phase transition temperatures. There is no obvious magnetic hysteresis because of the second-order nature of the phase transition. The magnetic entropy change of the compound was further calculated based on the magnetization data, employing the well-known Maxwell relation. The magnetic entropy change (ΔS_M) as a function of temperature for $(Tb_{1-x}Dy_x)_6Co_{1.67}Si_3$ compounds is shown in Fig. 3(b), for the field changes of 0–2 T and 0–5 T. A careful analysis of the $\Delta S_M - T$ indicates the presence of ΔS_M peaks corresponding to each phase transition, leading to a broad temperature span of ΔS_M. It is noteworthy that the maximum values of ΔS_M show a small decrease with increasing Dy concentration as can be seen in Table 1, probably due to the small difference in the magnetic moments of Tb and Dy.

The refrigeration capacity (RC) of $(Tb_{1-x}Dy_x)_6$ $Co_{1.67}Si_3$ is calculated by integrating numerically the area below the ΔS_M–T curve over the temperature interval that corresponds to half maximum of the ΔS_M peak.[15] Table 1 shows the RC values of $(Tb_{1-x}Dy_x)_6Co_{1.67}Si_3$ for a field change of 0–5 T. The maximal value of RC first increases rapidly with increasing Dy content, reaches a maximum at $x = 0.4$, then decreases. It is interesting to note that a very large RC is obtained for $(Tb_{0.6}Dy_{0.4})_6Co_{1.67}Si_3$ and its value is as high as 626 J/kg ($\Delta S_M = 6.7$ J/kg·K at $T_C = 166$ K) for a field change of 0–5 T. This is much larger than those of

some magnetocaloric materials with a second-order magnetic transition in a similar temperature range, such as $GdAl_2$ ($\sim$ 504 J/kg, ΔS_M = 7.6 J/kg·K at T_C = 167 K),[16] Tb_2In ($\sim$ 490 J/kg, ΔS_M = 6.6 J/kg·K at T_C=165 K),[17] $Dy(Co_{0.925}Si_{0.075})_2$ ($\sim$ 185 J/kg, ΔS_M = 6.6 J/kg·K at T_C = 164 K),[18] $(Ho_{0.4}Tb_{0.6})Co_2$ ($\sim$ 245 J/kg, ΔS_M = 7.3 J/kg·K at T_C = 182 K),[19] and $(Er_{0.7}Gd_{0.3})Co_2$ ($\sim$ 230 J/kg, ΔS_M = 4.5 J/kg·K at T_C = 167 K).[20] The RC values listed above are estimated from the ΔS_M–T data in the literature. A broad distribution of the ΔS_M peak leads to a large RC value. As the Dy concentration increases from 0 to 0.8, the width of the ΔS_M peak at half maximum of $(Tb_{1-x}Dy_x)_6Co_{1.67}Si_3$ increases from 81.5 K for $x = 0$, approaches a maximal value of 116.9 K for x = 0.4, then decreases to 115 K for x=0.8 under a field change of 0–5 T. Therefore, it is apparent that the large RC of $(Tb_{1-x}Dy_x)_6Co_{1.67}Si_3$ originates from the combined effect of the multiple magnetic transitions, which enlarge the temperature span of the ΔS_M–T curves.

Table 1. Curie temperature T_C, spin reorientation temperature T_{SR}, magnetic phase transitions T_1 and T_2 at low temperature, magnetic entropy changes ΔS_M under a field change of 0–5 T, and refrigeration capacity RC for $(Tb_{1-x}Dy_x)_6Co_{1.67}Si_3$ compounds with x = 0, 0.2, 0.4, 0.6 and 0.8, respectively.

compounds $(Tb_{1-x}Dy_x)_6Co_{1.67}Si_3$	T_C/K	T_{SR}/K	T_1/K	T_2/K	$-\Delta S$(0–5 T)/(J/kg·K)	RC (0–5 T)/(J/kg)
$x = 0$	187	176	132	56	7.4	399
$x = 0.2$	177	158	120	64	7.0	596
$x = 0.4$	166	142	104	74	6.7	626
$x = 0.6$	154	126	84		6.3	547
$x = 0.8$	142	110	79		6.2	527

4. Conclusion

The study on magnetic properties and MCEs of $(Tb_{1-x}Dy_x)_6Co_{1.67}Si_3$ shows that the existence of two crystallographic sites R_1 and R_2 for rare earth atoms leads to complex magnetic transitions. With increasing Dy concentration x from 0 to 0.8, the Curie temperatures T_C decrease linearly from $\sim$ 187 K to 142 K, but the maximum values of ΔS_M decrease slightly from $\sim$ 7.4 to 6.2 J/kg·K under a magnetic field change of 0–5 T. The large RC value is observed due to a broad distribution of the ΔS_M peak caused by successive multiple magnetic transitions. As x is equal to 0.4, the maximal value of RC is estimated to be $\sim$ 626 J/kg for a field change of 0–5 T, which is much larger than that of most potential magnetic refrigerant materials with similar magnetic transition temperatures.

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