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Structure and magnetic properties of intermetallic compounds $Gd_5Si_{2-x}Ge_{2-x}M_{2x}$

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Abstract: The effects of substituting stable elements of M(M=Mn, Mo, Al, V) for nonmagnetic Si and Ge on the structure and magnetic properties of $Gd_5Si_2Ge_2$ were investigated by means of X-ray powder diffraction and magnetic measurements. The experimental results show that there is no effect on the structure of parent phase $Gd_5Si_2Ge_2$ compound when being substituted by small amount of stable elements. The measurements of magnetic properties show that the Curie temperatures of $Gd_5Si_{2-x}Ge_{2-x}M_{2x}$ (M=Mn, Mo, Al and V) compounds have no obvious change before annealing, but they increase obviously with x increasing after annealing. Annealing can affect the crystalline microstructure and surface microstructure of the alloy after substitution.

Key words: Curie temperature; annealing; magnetic refrigeration; crystal structure

1 Introduction

Nowadays, there is much interest in magnetic refrigeration materials, as they offer the prospect of an energy-efficient and environment friendly alternative for the traditional vapour cycle refrigeration technique. Magnetic refrigeration is based on the magnetocaloric effect of magnetic materials[1−3]. The magnetocaloric effect is the change of temperature of magnetic materials under influence of the magnetic field in the adiabatic conditions. When magnetic materials containing atoms that carry magnetic moments are placed in an external magnetic field, the magnetic field forces magnetic moments to align, reducing the magnetic entropy, which makes magnetic materials heat up. Conversely, when the materials are taken out of the magnetic field, the magnetic moments randomize again and magnetic entropy increases, which makes the materials cool down to a lower temperature. But the using of magnetic refrigeration is limited in low temperature zone in a long time. The technology of magnetic refrigeration below 20 K is fully developed, which becomes the standard method of getting low temperature. The research of magnetic materials in room temperature zone is carried out much later, but gains much progress in recent years[4−7]. PECHARSKY and GSCHNEIDNER reported the giant magnetocaloric effect in $Gd_5(Si_xGe_{1-x})_4$ ($0<x<0.5=$ in 1997, which made an important break-through in the research of room temperature magnetic refrigeration[8,9]. But their Curie temperature was only 276 K, and the giant magnetocaloric effect decreased vastly during the very wide range of nearby Curie temperature[10,11]. After that, they substituted some metals for Si and Ge in $Gd_5Si_2Ge_2$ compound, and found that $Gd_5Si_{1.985}Ge_{1.985}Ga_{0.03}$ could increase the Curie temperature to 286 K, and the giant magnetocaloric effect kept unchanged[12,13]. The ΔS_{mag} of $Gd_5S_{i2}Ge_2$ when being substituted by appropriate contents of Fe, Co, Ni, Cu and Al is the same as that by substituting for Gd.

This work investigated the crystal structure and magnetic properties of $Gd_5Si_{2-x}Ge_{2-x}M_{2x}$ (M=Mn, Mo, Al and V) compound, analyzed the effect of Curie temperature and crystal structure when low content of thermal stability elements such as Mn, Mo, Al and V

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replace (Si+Ge) in $Gd_5Si_2Ge_2$ and Mn and V substitute for (Si+Ge) after annealing.

2 Experimental

Samples $Gd_5Si_{2-x}Ge_{2-x}Mn_{2x}$, $Gd_5Si_{2-x}Ge_{2-x}Al_{2x}$, $Gd_5Si_{2-x}Ge_{2-x}V_{2x}$ and $Gd_5Si_{2-x}Ge_{2-x}Mo_{2x}$ ($x\leqslant0.04$) with over 99.9% starting materials, were prepared by arc-melting method in an argon atmosphere. The alloys were arc-melted three times with the bottom being turned over after each re-melting to improve the homogeneity of alloys. Then the samples were sealed up to quartz tube with a 10^{-3} Pa vacuum, annealed for 7 d at 1 100 K, rapidly cooled for 3.5 h to 900 K in the stove, and cooled to room temperature in the water at last. The X-ray powder diffraction data were collected on an RINT 3000 diffractometer using Cu K_α radiation. The Curie temperature of the sample was measured by vibrating sample magnetometer with magnetic field of 3.98×10^4 A·m. The crystalline microstructure and surface appearance were analyzed by high performance microscope (MEF-3) and scanning electron microscope(S-750).

3 Results and discussion

From the results of ICP, it can be found that the composition of the sample $Gd_5(Ge_{2-x}Si_{2-x}M_{2x})$(M=Mn, Mo, Al and V) ($x\leqslant0.04$) is nominal composition. From Ref.[3], we know that the crystal structure of $Gd_5Si_2Ge_2$ is monoclinic structure, and the space group is P2 1/*a*, with lattice parameters a=0.777 99(5) nm, b=1.480 2(1) nm, c=0.777 99(5) nm, γ=93.190(4)°. It can be concluded from the powder X-ray diffraction results of the sample that the crystal structure of $Gd_5Si_{2-x}Ge_{2-x}Mo_{2x}$, Gd_5Si_{2-x}-$Ge_{2-x}Al_{2x}$, $Ga_5Si_{2-x}Ge_{2-x}Mn_{2x}$ and $Gd_5Si_{2-x}Ge_{2-x}V_{2x}$ is the same as the parent phase-monoclinic structure.

Fig.1 shows the powder X-ray diffraction patterns of each sample. It can be confirmed that there is no abnormal peak when substituting small amount of Mn, Al and Mo, V for (Si+Ge) in Gd_5 Si_2Ge_2 compound. That is to say, small amount of Mn, Al and Mo, V replace for the hypo-lattice of (Si+Ge) in the unit cell parameters of the parent phase, but the crystal structure of the parent phase keeps unchanged, which is still the same as the crystal structure of the parent phase. The M-T relation curves of the samples $Gd_5Si_{2-x}Ge_{2-x}Mn_{2x}$ (x=0, 0.01, 0.015, 0.02, 0.025, 0.03), $Gd_2Si_{2-x}Ge_{2-x}Mo_{2x}$ (x=0, 0.01, 0.015, 0.02, 0.025, 0.03, 0.04), $Gd_5Si_{2-x}Ge_{2-x}Al_{2x}$ (x=0, 0.01, 0.015, 0.02, 0.025, 0.03, 0.04), $Gd_5Si_{2-x}Ge_{2-x}V_{2x}$ (x=0, 0.01, 0.015, 0.02, 0.025, 0.03) (external magnetic field is 3.98×10^4 A·m) were measured by the vibrating sample magnetometer, by which the Curie temperature

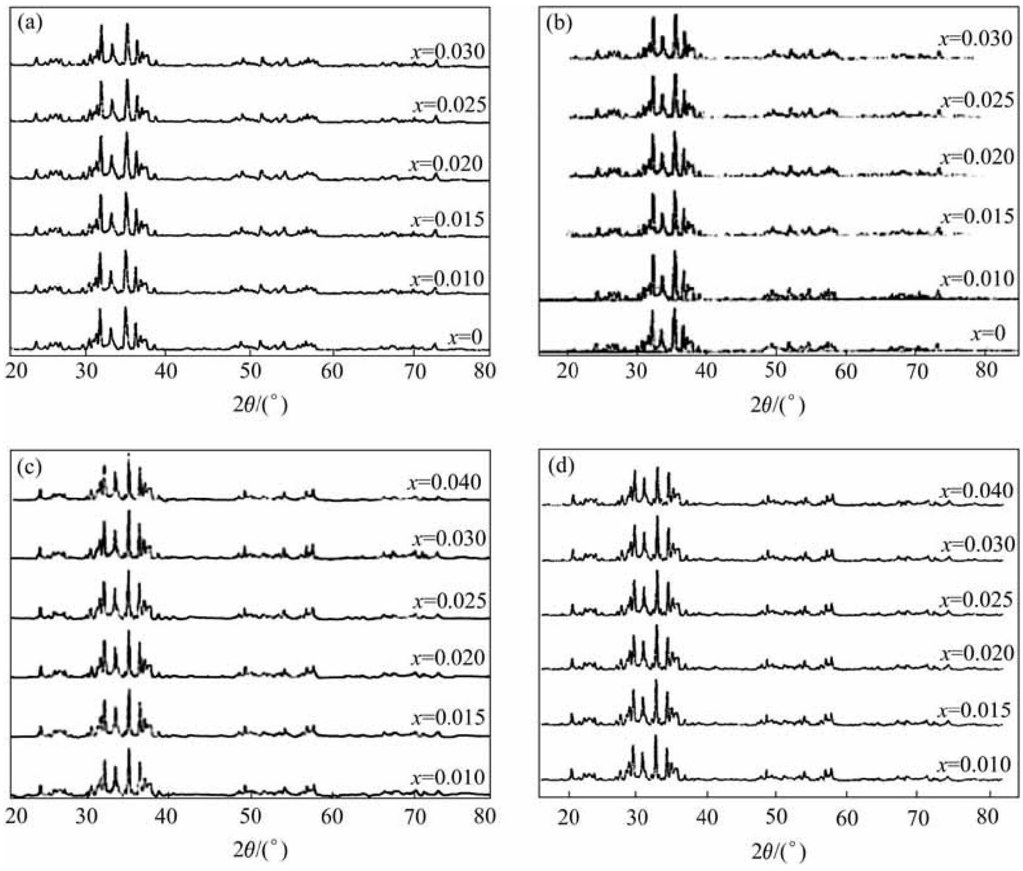

Fig.1 Powder X-ray diffraction patterns of $Gd_5Si_{2-x}Ge_{2-x}M_{2x}$ (M=V, Mn, Mo): (a) $Gd_5Si_{2-x}Ge_{2-x}V_{2x}$; (b) $Gd_5Si_{2-x}Ge_{2-x}Mn_{2x}$; (c) $Gd_2Si_{2-x}Ge_{2-x}Mo_{2x}$; (d) $Gd_5Si_{2-x}Ge_{2-x}Al_{2x}$

of the sample was calculated. Then the samples Gd_5Si_{2-x}-$Ge_{2-x}Mn_{2x}$ (x=0, 0.01, 0,015, 0.02, 0.025, 0.03) and Gd_5Si_{2-x}- $Ge_{2x}V_{2x}$ (x=0, 0.01, 0.015, 0.02, 0.025, 0.03) were annealed to measure the M-T relation curve and calculate the Curie temperature.

Fig.2 shows the relation curve of content x of M (M=Mn, Mo, Al, and V) and Curie temperature T_c before annealing. It can be proved that the Curie temperature of the sample decreases when the added amount of element M rises in a certain range (V is excluded, whose curve of Curie temperature and content was not measured at the content point of 0.02). But in the other range of content of M, the Curie temperature of the sample rises when the content of M rises. The Curie temperature of $Gd_5Si_2Ge_2$ rises when elements Mn, Mo, Al and V are added, except when the content of Mn is at the point of 0.015, and the Curie temperature changes obviously when element Al is added in $Gd_5Si_2Ge_2$. The Curie temperature of $Gd_5Si_{1.97}Ge_{1.97}Al_{0.06}$ can reach 295.52 K. The Curie temperature has no obvious change when other elements are added (the range of Curie temperature is between 3−4 K).

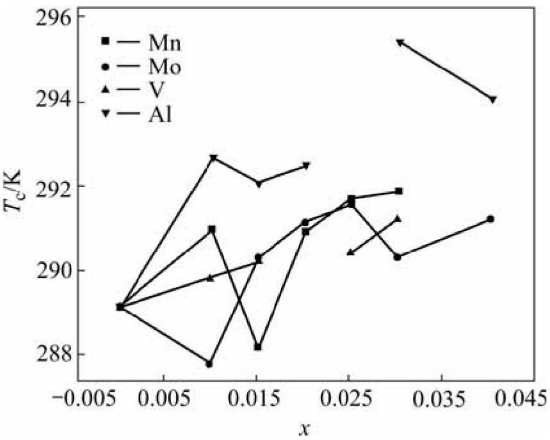

Fig.2 Relation curve of content x of M and Curie temperature T_c before annealing

Fig.3 presents the corresponding relation between the content x of M and Curie temperature T_c after annealing. It can be found that the Curie temperature of $Gd_5Si_{2-x}Ge_{2-x}M_{2x}$ compound decreases when the contents of Mn and V are added, when the content of M is 0.01<x<0.015 and the content of V is 0.015<x< 0.02, the Curie temperature of the sample increases when the content of Mn and V rises in other range of content, the Curie temperature of $Gd_5Si_2Ge_2$ compound increases when elements Mn and V are added.

Compared with those before annealing, the changes of Curie temperature T_c of $Gd_5Si_{2-x}Ge_{2-x}M_{2x}$ after annealing are more obvious. When x=0.03, the Curie temperature of $Gd_5Si_{2-x}Ge_{2-x}M_{2x}$ (M=Mn and V) is about 20 K higher than that of the parent phase. On the other

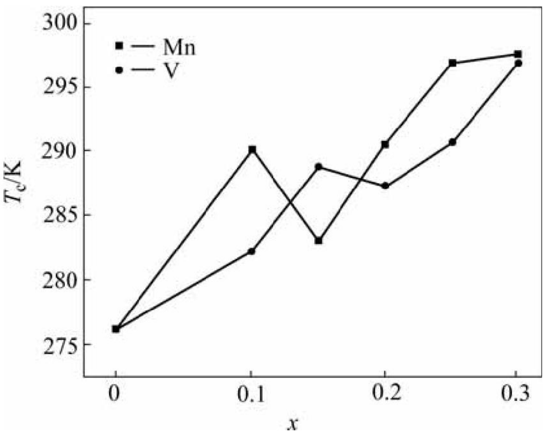

Fig.3 Relation curve of content x of M and Curie temperature T_c after annealing

hand, the Curie temperature of $Gd_5Si_2Ge_2$ is 289.15 K before annealing and 276.21 K after annealing. LIU et al[3] reported that there are two transition points of $Gd_5Si_2Ge_2$. The first is 276 K, the other is 298.6 K. That is to say, the Curie temperature of $Gd_5Si_2Ge_2$ after annealing is consistent with the transition temperature of the first-order magnetic transition in Ref.[12].

From the study of meltalloscope and scanning electron microscope of the microcosmic tissue of $Gd_5(Si_{2-x}Ge_{2-x}M_{2x})$ (M=Mo, Mn, Al and V) before and after annealing, it can be found that the tissue and crystal grain after annealing are more uniform than those before annealing, the single-phase of the sample after annealing is better, the surface is more compact, the crack is more tiny and the pit is slighter, but the crystal grain is larger.

Derived from molecular field theory[14], the equation of Curie temperature T_c is

$$T_c = \frac{ng^2 J\mu_B^2 J(J+1)\lambda}{3k} \quad (1)$$

From Eqn.(1) it can be found that Curie temperature T_c rises when the molecular field coefficient quantum number λ and the total angular momentum J rise, which is in relation to the content and crystal structure of the materials, but has no relation with the preparation of the materials[14]. The substitution of a small amount of elements Mn, Mo, Al and V for (Si+Ge) hypo-lattice can result in the change of the atoms exchange in the crystal structure. The indirect exchange in $Gd_2Si_2Ge_2$ existed in Gd and Gd atoms in $Gd_2Si_2Ge_2$ compound can mainly affect Curie temperature. But the amount added is small, and the defect is produced when the crystal forms, which adds the distance of magnetic atoms, reduces the exchange energy among them, so as to decrease Curie temperature of the compound[15]. Thus, the Curie temperature of parent phases is not affected so obviously when substituting a small amount of stable elements Mn.

Mo, and V for non-magnetic Si and Ge before annealing. The Curie temperature decreases when the added elements increase in some range, which is mainly because of the defect of compound and the lattice distance distortion due to the added elements. After annealing, the Curie temperature increases when the content of added elements changes, because the defect is removed by melting. From the experimental result, it can be found that the Curie temperature is improved to room temperature and keeps crystal structure unchanged in $Gd_5Si_2Ge_2$ compound when non-magnetic Si and Ge are replaced by a small mount of stable elements Mn, Mo, Al and V. Thus $Gd_5Si_{2-x}Ge_{2-x}M_{2x}$ (M=Mn, Mo, Al and V) compound is the perfect magnetic refrigeration material near room temperature.

4 Conclusions

1) The Curie temperature of $Gd_5Si_2Ge_2$ increases by the substitution of a small amount of alloying elements for Si+Ge.

2) The replacing effect of Curie temperature is more obvious under annealing.

3) There is no change in the crystal structure of parent phase $Gd_5Si_2Ge_2$ when being substituted by stable elements.

4) Annealing can affect the crystalline micro-structure and surface microstructure in the alloy after substitution.

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