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STUDY OF A STRUCTURAL PHASE TRANSITION IN $Gd_5(Si_{1-x}Ge_x)_4$ BY MEANS OF TEMPERATURE DEPENDENT X-RAY POWDER DIFFRACTION

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Recently, a giant magnetocaloric effect (MCE) in $Gd_5(Si_{1-x}Ge_x)_4$ alloys had been reported and considered as a milestone in developing an efficient and environment friendly magnetic refrigeration technology. The crystal structure and magnetic properties of $Gd_5(Si_{1-x}Ge_x)_4$ compound are systematically investigated by means of temperature dependent X-ray powder diffraction and magnetic measurements. There exists a first-order structural and magnetic transition when Ge substitution for Si or warming the samples through Curie temperature. A crystallographic and magnetic phase diagram of the pseudobinary system Gd_5Si_5-Gd_5Ge_5 was constructed. An intriguing observations is that $Gd_5(Si_{1-x}Ge_x)_4$ alloy forms a completely miscible solid-solution at low temperature (below Curie temperature) and decomposes into three partially miscible solid-solutions above Curie temperature.

1. Introduction

A milestone in developing an efficient and environment friendly magnetic refrigeration technology is the recent discovery of a giant magnetocaloric effect (MCE) in $Gd_5(Si_{1-x}Ge_x)_4$ compounds (x$0.5). They exhibit a MCE of 2-10 times larger than that of the best known magnetic refrigeration materials (e.g. Gd) [1, 2]. Of particular interest for potential application of the materials is that the temperature, at which the giant MCE occurs, can be tuned conveniently from -20 to -290 K by adjusting the Si:Ge ratio in $Gd_5(Si_{1-x}Ge_x)_4$. The crystal structure and magnetic properties of the pseudobinary system $Gd_5(Si_{1-x}Ge_x)_4$ were studied 30 years ago [3, 4]. The phase relation, crystallography and magnetic properties of this pseudobinary system were reinvesti-gated recently by Pecharsky and Gschneidner [5, 6]. Although both the end compounds, Gd_5Si_4 and Gd_5Ge_4 crystallize in the Sm_5Ge_4-type orthorhombic structure (Pnma) and have the same crystallographic positions occupied by atoms, the significant difference in the axial ratio a/c (and a/b) and atomic parameters indicates that the germanide and silicide are not isostructural. Such a structural difference results in limited solubilities of Ge in Gd_5Si_4 (x$0.5, O(I) phase or Gd_5Si_4 based solid solution) and Si in Gd_5Ge_4 (x$0.8, O(II) phase or Gd_5Ge_4 based solid solution) in $Gd_5(Si_{1-x}Ge_x)_4$ alloys on the one hand, and a monoclinic distortion ($Gd_5Si_2Ge_2$-type structure, $P112_1/a$,M phase or $Gd_5Si_2Ge_2$ based solid-solution) of the orthorhombic Sm_5Ge_4-type structure in the intermediate composition range (0.5#x<0.8) on the other hand [5]. For 0.5#x<0.8, it was proved that the magnetic transition is accompanied by a first-order structural transition from a monoclinic to an orthorhombic symmetry as the temperature decreases [7, 8]. For x=0.9, a first-order structural transition from an orthorhombic (Gd_5Ge_4-type) to another orthorhombic structure (Gd_5Si_4-type) was reported recently [9]. The occurrence of the giant MCE in $Gd_5(Si_{1-x}Ge_x)_4$ is believed to associate with a simultaneous first-order magnetic and structural transition. Therefore, further systematic studies may be of great significance and future impact.

The aim of this contribution is to systematically study the structural and magnetic transition in $Gd_5(Si_{1-x}Ge_x)_4$ system by means of temperature dependent x-ray diffraction (XRD) and magnetic measurement.

2. Experimental Procedure

$Gd_5(Si_{1-x}Ge_x)_4$ alloys (around 4g) with x ranging from 0 to 1 were prepared by arc melting of 99.9 wt% pure Gd and 99.9999wt% pure Si and Ge in an argon

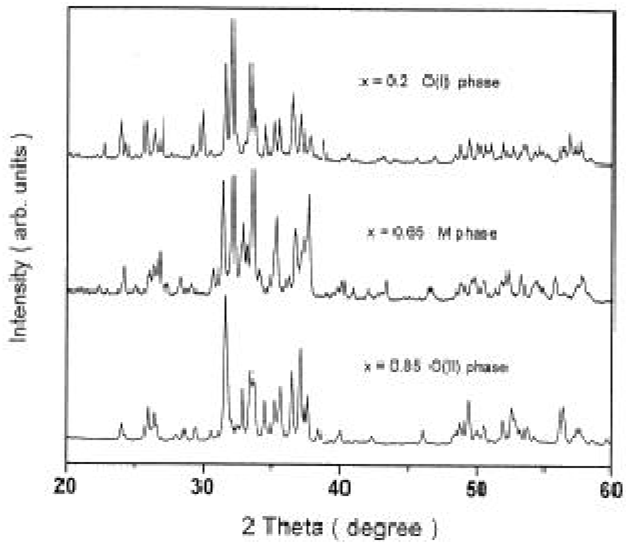

Fig. 1 The XRD patterns of three different structures in $Gd_5(Si_{1-x}Ge_x)_4$ depending on composition at 298 K

atmosphere under ambient pressure. The alloys were arc-melted four times with the button being turned over after each re-melting to improve homogeneity of the alloys. Weight loss during melting was less than 2wt% and therefore the initial composition was assumed unchanged.

X-ray diffraction data were collected at different temperature ranging from 80 K to 550 K with appropriate temperature interval in order to investigate the structural transition temperature, using a Rigaku Rint D/max 2500 type diffractometer with a medium & low temperature attachment. The diffractometer use a rotating Cu target (Cu Kα radiation) with voltage of 40 kV and current of 300 mA and a graphite monochromator. The X-ray diffraction data used to refine the crystal structure parameters were collected by a step-scan mode with a scanning step of $2\theta = 0.02°$ and a sampling time of 2s. The powder diffraction Rietveld profile fitting technique [10] was adopted to refine the crystal structures using the program DBW-9411 [11]. The Curie temperature was determined on the temperature dependence of magnetization curve measured by a SQUID magnetometer with increasing temperature.

3. Results and Analysis

At 298 K $Gd_5(Si_{1-x}Ge_x)_4$ compounds crystallize in three different structures depending on composition as shown in Fig. 1, i.e. Gd_5Si_4-based phase (O(I) phase or Gd_5Si_4 based solid solution), Gd_5Ge_4-base phase (O(II) phase or Gd_5Ge_4 based solid solution) and $Gd_5Si_2Ge_2$-based phase (M phase or $Gd_5Si_2Ge_2$ based

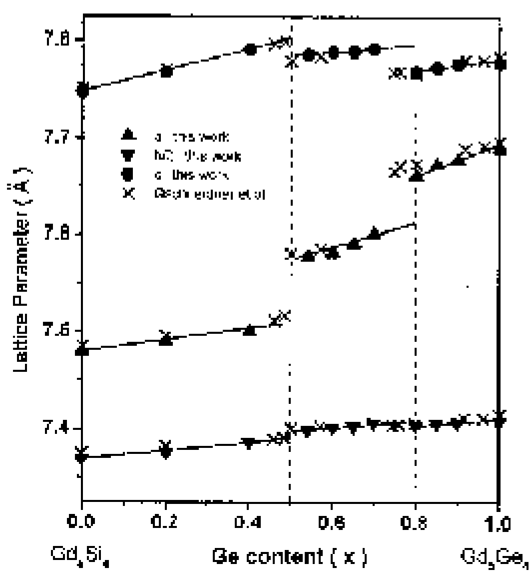

Fig. 2 Dependence of lattice parameters on Ge content in the $Gd_5(Si_{1-x}Ge_x)_4$ system at 298 K. The lines are guides for eye.

solid-solution). Figure 2 shows the concentration dependence of the lattice parameters (a, b, and c) of the $Gd_5(Si_{1-x}Ge_x)_4$ compounds at 298 K. The lattice parameters in present investigation agree well with the reports of Gschneidner et al. [5] except that in our work the lattice parameter c in the range of 0.5#x<0.8 increases slightly with Ge content x. This should be more acceptable due to the fact that the atomic radius of Ge is larger than that of Si. Figure 2 also indicates the homogenous range of the three phases: x< 0.5 for

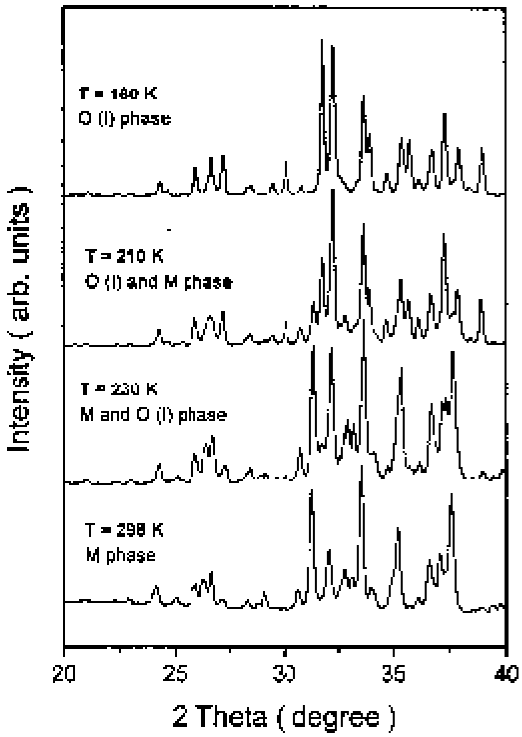

Fig. 3 Temperature dependence of XRD patterns of $Gd_5(Si_{0.4}Ge_{0.6})_4$ alloy.

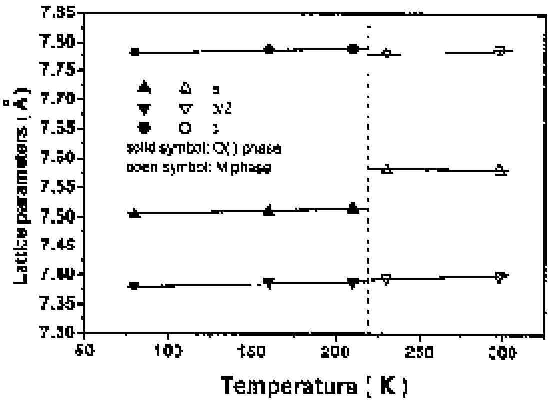

Fig. 4 Temperature dependence of the lattice parameters of $Gd_5(Si_{0.4}Ge_{0.6})_4$ as obtained from the Rietveld analysis of the XRD patterns. The lines are a guide to the eye. The dash line indicate the magnetic and crystallographic phase boundary.

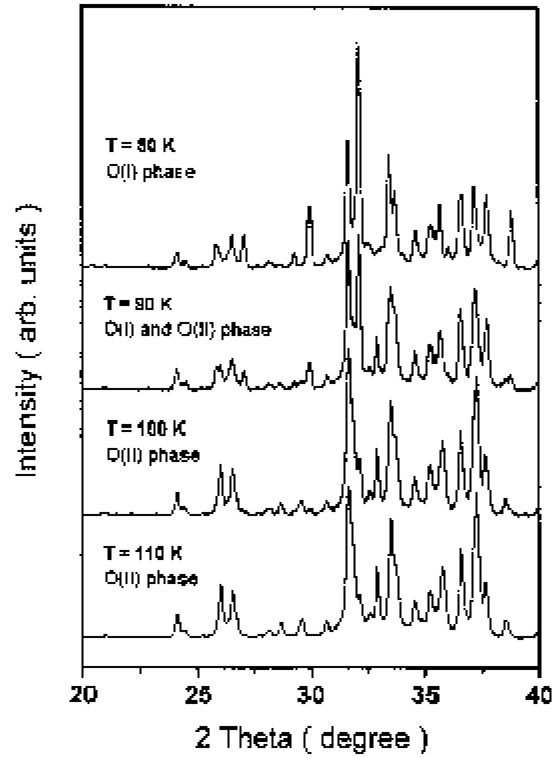

Fig. 5 Temperature dependence of XRD patterns of $Gd_5(Si_{0.15}Ge_{0.85})_4$ alloy.

Gd_5Si_4-based phase, 0.5-x<0.8 for $Gd_5Si_2Ge_2$-based phase and x-0.8 for Gd_5Ge_4-base phase. There are abrupt changes of lattice parameters around phase boundaries: Δa/a . 0.7%, Δb/b . 0.1%, and Δc/c . -0.2% when x=0.5, and Δa/a . 0.5%, Δb/b . -0.05% and Δc/c . -0.3% when x=0.8.

There exists a structural and magnetic transition between $Gd_5Si_2Ge_2$-based phase and Gd_5Si_4-based phase when warming or cooling the samples through the Curie temperature T_c. Figure 3 shows the XRD patterns of $Gd_5(Si_{0.4}Ge_{0.6})_4$ compound at various temperature. The structural transition occurs around 220K as indicated in Fig. 3. The temperature dependence of lattice parameters of $Gd_5(Si_{0.4}Ge_{0.6})_4$ compound is shown in Fig. 4. The sharply changes of lattice constants around 220K are: Δa/a . 0.9%, Δb/b . 0.05% and Δc/c . -0.2%.

Figure 5 shows the XRD patterns of $Gd_5(Si_{0.15}Ge_{0.85})_4$ alloy at various temperature, indicating that a structural transformation occurs around 90 K. The temperature dependence of lattice parameters of $Gd_5(Si_{0.15}Ge_{0.85})_4$ is depicted in Fig. 6. There also exist abrupt changes of lattice parameters around 90K: Δa/a . 1.8%, Δb/b . -0.1% and Δc/c . -0.6%.

The abrupt changes of lattice parameters of $Gd_5(Si_{1-x}Ge_x)_4$ compounds resulting from Ge substitution have a remarkable resemblance to those of the compounds with x=0.65 and x =0.85 when warming samples through T_c. This is not a

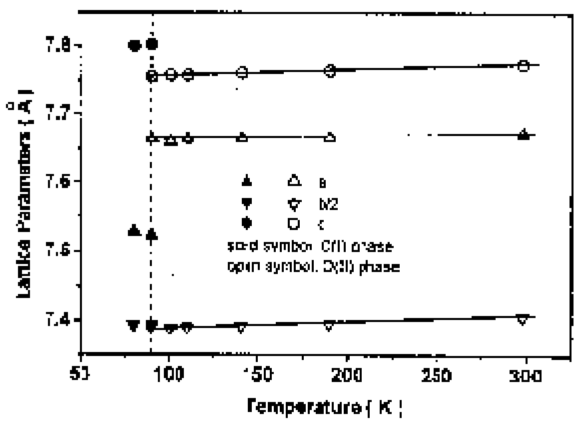

Fig. 6 Temperature dependence of the lattice parameters of $Gd_5(Si_{0.15}Ge_{0.85})_4$ as obtained from the Rietveld analysis of the XRD patterns. The lines are a guide to the eye. The dash line indicates the magnetic and crystallographic phase boundary.

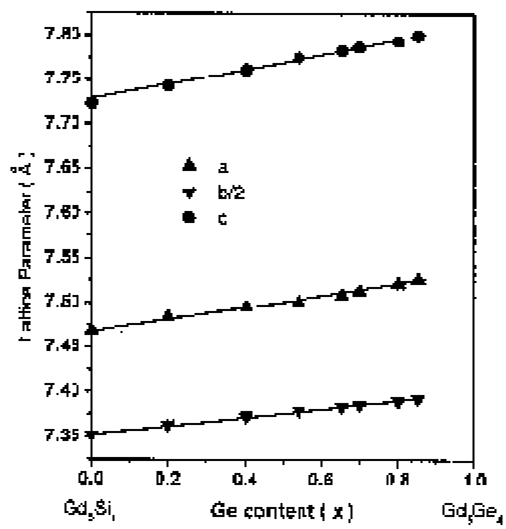

Fig. 7 Dependence of lattice parameters on Ga content in the $Gd_5(Si_{1-x}Ge_x)_4$ system at 80 K. The lines are guides for eye.

coincidence. As shown in Table 2 in Ref. [5] and Table II in Ref. [8], The difference of atomic positions between the three structures is large along **a** axis, and small along **b** and **c** axes. According to Choe et al. [8], the main structure changes result from making and breaking covalent bonds of pairs of Si(Ge)-Si(Ge), and a large shear movement of pairs of (3^2434) atom slabs along the **a** direction. The atomic position movements lead to the large expansion of the unit cell along **a** axis, correspondingly slightly reduction along **c** axis, and a slightly change along **b** axis.

$Gd_5(Si_{1-x}Ge_x)_4$ compounds crystallize in the Gd_5Si_4-type structure below T_c regardless of the composition based on the temperature dependent XRD. The powder diffraction Rietveld profile fitting technique was used to refine the XRD patterns of $Gd_5(Si_{1-x}Ge_x)_4$ at 80 K using the program DBW-9411. The concentration dependence of lattice parameters (a, b, and c) of these compounds at 80 K are shown in Fig 7. A linear increase of a, b, and c with x, the Ge content, in the investigated range of 0.0#x#0.85 is observed. This indicates that $Gd_5(Si_{1-x}Ge_x)_4$ compounds form a completely miscible solid-solution crystallized in Gd_5Si_4-type structure at low temperature.

Based on the temperature dependent XRD and magnetic measurements, a crystallographic and magnetic phase diagram of the pseudobinary system Gd_5Si_4-Gd_5Ge_4 was constructed as shown in Fig. 8 [12]. It shows that the temperature of structural phase transition always coincides with Curie temperature

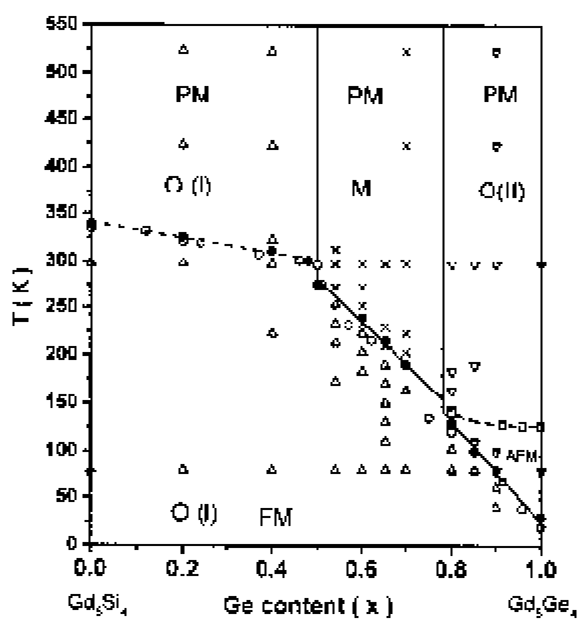

Fig. 8 Crystallographic and magnetic phase dia-gram of $Gd_5(Si_{1-x}Ge_x)_4$ alloys.

M stands for T_c from Ref. [12], **F** T_c from Ref. [5], **G** T_N from Ref. [5], Δ Gd_5Si_4-based phase, ∇ Gd_5Ge_4-based phase, × monoclinic phase M. PM, FM, and AFM label paramagnetic, ferromagnetic and antiferromag-netic (or ferromagnetic) phases, respectively. The solid lines depict crystallographic phase boundaries. The dash lines depict magnetic phase boundaries.

Tc, and that the ferromagnetic state of the compounds occurs exclusively in the Gd_5Si_4-type structure (Pnma). These indicate that there exists a close correlation between the structural transition and the magnetic transition. An intriguing observation is the formation of a completely miscible solid-solution $Gd_5(Si_{1-x}Ge_x)_4$ with Gd_5Si_4-type structure at low temperature. It is contrary to the common sense that a completely miscible solid-solution usually forms at high temperature and decomposes into partially miscible solid-solutions at low temperature. This unusual feature can be understood by considering the competing effects of lattice strain and ferromagnetic exchange interaction [12].

Acknowledgments

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