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High-Magnetic Field X-ray Diffraction Studies on $Gd_5(Ge_{2-x}Fe_x)Si_2$ ($x = 0.05$ and 0.2)

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We performed the powder X-ray diffraction measurements in magnetic fields up to 5 T for $Gd_5(Ge_{1.95}Fe_{0.05})Si_2$ and $Gd_5(Ge_{1.8}Fe_{0.2})Si_2$. With heating from 8 K, the matrix of $Gd_5(Ge_{1.95}Fe_{0.05})Si_2$ clearly shows a structural transition from an orthorhombic to a monoclinic structure at the Curie temperature ($T_C = 276$ K). On the other hand, the matrix of $Gd_5(Ge_{1.8}Fe_{0.2})Si_2$ with the orthorhombic structure in the ferromagnetic state shows two-phases co-existence of the orthorhombic and the monoclinic structures above $T_C = 303$ K, indicating that a small amount of the matrix participates in the transformation. For both samples, the monoclinic structure is suppressed but the orthorhombic structure is enhanced just above T_C by applying a magnetic field, which closely relates to the magnetization process.

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1. Introduction

The pseudobinary $Gd_5(Ge_{1-x}Si_x)_4$ compound exhibits peculiar magnetic and structural properties.[1–4] The magnetic properties and crystal structures of $Gd_5(Ge_{1-x}Si_x)_4$ compound are varied with the Si to Ge ratio. The ground state of $Gd_5(Ge_{1-x}Si_x)_4$ for $0.5 < x \leq 1$ is ferromagnetic (FM) with the orthorhombic Gd_5Si_4-type structure, and the Curie temperature T_C decreases with decreasing x. The compound for $0 \leq x < 0.24$ crystallizes in the orthorhombic Gd_5Ge_4-type structure, and the magnetic state varies as a process of paramagnetic (PM)-antiferromagnetic (AFM)-FM with cooling from room temperature. On the other hand, $Gd_5(Ge_{1-x}Si_x)_4$ for $0.24 < x < 0.5$ exhibits a first-ordered phase transition from a PM state with the monoclinic $Gd_5Si_2Ge_2$-type structure to a FM state with the orthorhombic Gd_5Si_4-type structure.

Recently, it was found that the compound for $x \sim 0.5$ shows a large magnetocaloric effect between 270 K and 300 K, so that it attracts much attention from the point of view of application as a magnetic refrigeration at room temperature.[3,4] However, the compound exhibits a field-induced magnetic transition (metamagnetic transition) with a large hysteresis just above T_C, which makes the magnetic refrigeration less efficient due to the hysteresis losses.[5] Quite recently, Provenzano *et al.* showed that doping iron for Germanium in $Gd_5(Si_2Ge_2)$ effectively reduces the hysteresis losses.[5] According to their report, the iron doped sample $Gd_5(Ge_{1.9}Fe_{0.1})Si_2$ does not clearly show the field-induced magnetic transition around T_C, resulting in the reduction of the hysteresis losses and the increase of the net refrigerant capacity.

The magnetic phase transition in $Gd_5(Ge_{1-x}Si_x)_4$ system closely relates to the structural properties. Therefore, it is important to clarify the relationship between the magnetic and structural properties under magnetic fields, because the magnetic refrigeration materials will be controlled by the magnetic field as well as temperature.

In this study, in order to clarify the structural properties of two iron-doped compounds $Gd_5(Ge_{1.95}Fe_{0.05})Si_2$ and $Gd_5(Ge_{1.8}Fe_{0.2})Si_2$ under magnetic fields, we have performed the powder X-ray diffraction measurements in magnetic fields up to 5 T and in the wide temperature ranging from 8 to 320 K.

2. Experimental

The synthesis and characterization of the polycrystalline powder samples are carried out at the National Institute of Standard and Technology, USA. The as-cast samples $Gd_5(Ge_{2-x}Fe_x)Si_2$ with $x = 0.05$ and 0.2 were homogenized in vacuum at 1573 K. Magnetization was measured using a conventional SQUID magnetometer (Quantum Design[6]). Powder X-ray diffraction measurements with Cu Kα radiation were carried at the temperatures T ranging from 8 to 320 K using a Gifford–McMahon type cryocooler-cryostat and magnetic fields $\mu_0 H$ up to 5 T using a cryocooled split-pair NbTi superconducting magnet.[7] The diffraction data were taken in the angle 2θ ranging from 20° to 40° with a step size of 0.02°. We confirmed that the powder sample was not removed by the magnetic force during the measurements in magnetic fields.

3. Results and Discussion

In Fig. 1, we show the temperature dependence of the magnetic moment M of $Gd_5(Ge_{1.95}Fe_{0.05})Si_2$ and $Gd_5(Ge_{1.8}Fe_{0.2})Si_2$ for heating process in a magnetic field $\mu_0 H$ of 0.1 T. From these M–T curves, the Curie temperatures T_C are determined to be 276 K and 303 K for $Gd_5(Ge_{1.95}Fe_{0.05})Si_2$ and $Gd_5(Ge_{1.8}Fe_{0.2})Si_2$, respectively. An additional hump on the M–T curve of $Gd_5(Ge_{1.8}Fe_{0.2})Si_2$ was clearly seen below 100 K, and a very weak anomaly is also observed in $Gd_5(Ge_{1.95}Fe_{0.05})Si_2$ below 100 K. The pure iron phase is not confirmed in these M–T curves. Provenzano *et al.* reported that the iron-additional alloy $Gd_5(Ge_{1.9}Fe_{0.1})Si_2$

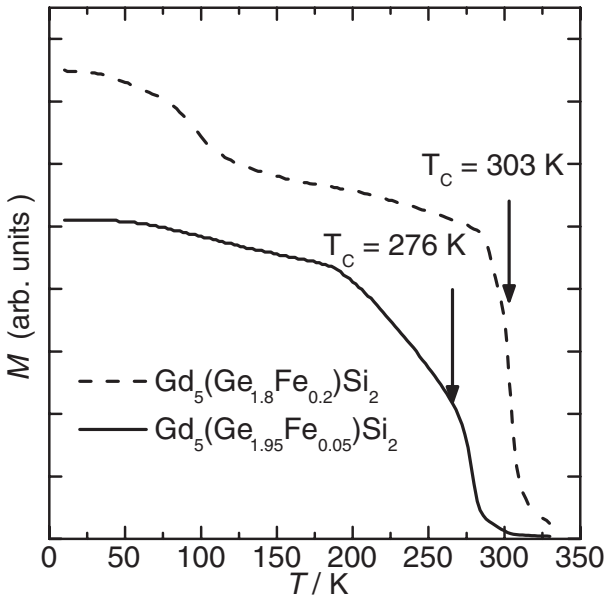

Fig. 1 Temperature dependence of the magnetic moment of $Gd_5(Ge_{2-x}Fe_x)Si_2$ for $x = 0.05$ (solid line) and $x = 0.2$ (dashed line) in magnetic fields of 0.1 T. Arrows indicate the Curie temperatures.

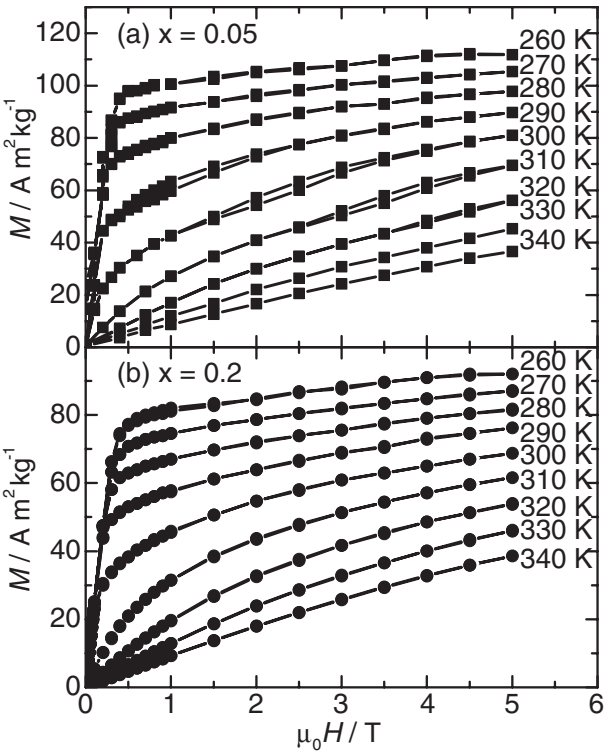

Fig. 2 Magnetic field dependence of the magnetic moment M at various temperatures for (a) $x = 0.05$ and (b) $x = 0.2$ around T_C.

contains the dominant matrix phase (off-stoichiometric matrix) without iron and the minor phases with the high iron content in a grain boundary.[5] In our magnetization data, any impurity phase having higher ordering temperature over room temperature and the pure iron phase is not confirmed in the samples. Therefore, it is considered that the observed magnetic properties around room temperature is mainly due to the magnetic characteristic of the dominant matrix phases having $T_C = 276$ K ($x = 0.05$) and $T_C = 303$ K ($x = 0.2$), respectively. Below 100 K, on the other hand, the magnetic properties are probably affected by the minor phase contribution in addition to the matrix.

Figure 2 shows the magnetic field dependence of the magnetic moment M at various temperatures for (a) $x = 0.05$ and (b) $x = 0.2$ around T_C. As seen in this figure, we cannot see a typical metamagnetic transition from the PM to the field-induced ferromagnetic (FFM) state. Small hysteresis is observed for $Gd_5(Ge_{1.95}Fe_{0.05})Si_2$. However, $Gd_5(Ge_{1.8}Fe_{0.2})Si_2$ does not exhibit any hysteresis on the M–$\mu_0 H$ curves. This behavior is consistent with the previous report for $Gd_5(Ge_{1.9}Fe_{0.1})Si_2$.[5] The results of Ref. 5 and this work indicate that the dominant matrix composition among Gd, Ge and Si is very sensitive to the iron concentration in the alloys, which probably affects the magnetic and structural properties.

In Fig. 3, we show the typical X-ray diffraction patterns of $Gd_5(Ge_{1.95}Fe_{0.05})Si_2$ at several temperatures in a zero magnetic field. The diffraction patterns of both structures are very similar because the monoclinic structure is caused by a small distortion in the orthorhombic one. In this figure, solid squares and circles denote some characteristic peaks of the monoclinic and orthorhombic structures, respectively. At low temperature below $T_C = 276$ K, the dominant structure is orthorhombic, but it transforms to the monoclinic structure above T_C. For example, the characteristic peaks of the

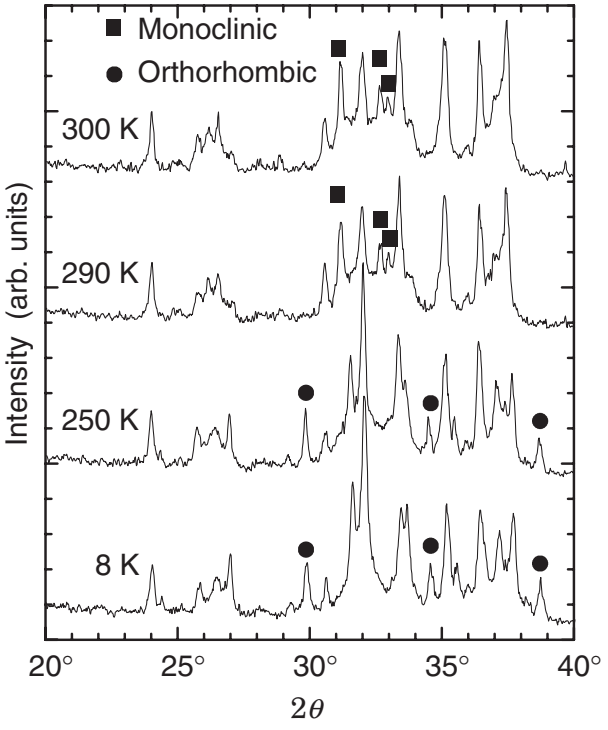

Fig. 3 Powder X-ray diffraction patterns of $Gd_5(Ge_{1.95}Fe_{0.05})Si_2$ at various temperatures. The solid squares and the circles denote the characteristic peaks of the monoclinic and the orthorhombic phases, respectively.

monoclinic phase appear around $2\theta = 30.6°$, 32.8° and 33.1°, and the peaks of the orthorhombic phase around $2\theta = 30.0°$, 34.7°, 35.8° and 38.9° disappear above 290 K ($> T_C$), as shown in Fig. 3. This result shows that the crystallographic

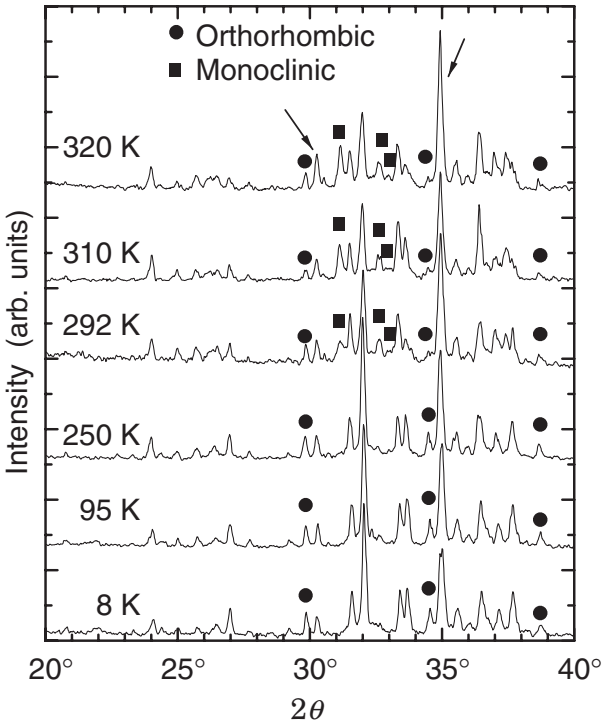

Fig. 4 Powder X-ray diffraction patterns of $Gd_5(Ge_{1.8}Fe_{0.2})Si_2$ at various temperatures. The solid squares and the circles denote the characteristic peaks of the monoclinic and orthorhombic phases, respectively. Arrows indicate the diffraction peaks of the miner phase.

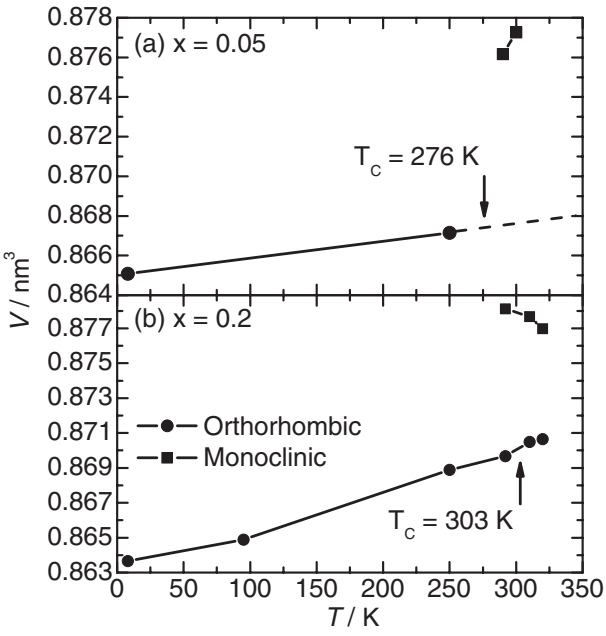

Fig. 5 Temperature dependence of the unit cell volume V of $Gd_5(Ge_{2-x}Fe_x)Si_2$ for (a) $x = 0.05$ and (b) $x = 0.2$. The solid squares and the circles denote the volumes of the monoclinic and orthorhombic phases, respectively.

phase transition occures simultaneously with the magnetic phase transition.

As shown in Fig. 4, the behavior of the X-ray diffraction patterns of $Gd_5(Ge_{1.8}Fe_{0.2})Si_2$ is slightly different from that of $Gd_5(Ge_{1.95}Fe_{0.05})Si_2$. The characteristic peaks of the orthorhombic phase are seen even above $T_C = 303$ K, but the intensity seems to be suppressed. On the other hand, the characteristic peaks of the monoclinic phase appear and are gradually enhanced with increasing temperature above T_C. This indicates that only parts of the matrix undergo a structural transformation from the orthorhombic to the monoclinic structure, accompanied by the magnetic transition from the FM to PM phase. As shown by arrows in Fig. 4, some additional peaks are also observed in the patterns (2θ $\sim$30.3° and $\sim$35°). Provenzano *et al.* observed similar additional peaks for $Gd_5(Ge_{1.9}Fe_{0.1})Si_2$[5] and suggested that these peaks are caused by minor phases. Our results show clearly that the peaks due to the minor phases are induced by the increasing iron doping, indicating that the volume fraction of the minor phases of $Gd_5(Ge_{1.8}Fe_{0.2})Si_2$ is larger than that of $Gd_5(Ge_{1.95}Fe_{0.05})Si_2$.

Figure 5 shows the temperature dependence of the unit cell volume V of the orthorhombic and monoclinic structures. The orthorhombic phase shows the typical thermal expansion for both samples with increasing temperature from 8 K. The volume V of monoclinic phase is larger than that of the orthorhombic phase ($\Delta V/V = 1.2\%$ for $Gd_5(Ge_{1.95}Fe_{0.05})Si_2$). For $Gd_5(Si_2Ge_2)$ compound, it was reported that the cell volume of the monoclinic structure in the PM phase is larger than that of the orthorhombic structure in the FM phase.[8] Our result is consistent with that of $Gd_5(Si_2Ge_2)$. The previous report by Choe *et al.* shows that the structural transition from the orthorhombic to the monoclinic structure is caused by a shear mechanism in which the (Si,Ge)-(Si,Ge) dimmers. This leads the volume expansion in $Gd_5(Si_2Ge_2)$.[9] It is supposed that the same mechanism occurs in the off-stoichiometric matrix of our samples for the structural transformation.

Magnetic field dependences of the X-ray diffraction patterns for $Gd_5(Ge_{1.95}Fe_{0.05})Si_2$ at 290 K and $Gd_5(Ge_{1.8}Fe_{0.2})Si_2$ at 310 K are shown in Figs. 6 and 7, respectively. That is, these patterns are taken just above their T_C. For $x = 0.05$ (Fig. 6), the crystal structure of the matrix is the monoclinic in the PM phase under a zero field. The peaks of the orthorhombic phase appear and then gradually increase with a increasing magnetic field. On the contrary, the peak intensity of the monoclinic phase becomes weaker in a high magnetic field, although the peak remains at 4 T. After removing the field, the X-ray pattern recovers. Similar phenomenon is observed for $x = 0.2$ (Fig. 7), although the peaks of the orthorhombic phase already present in a zero field. That is, this weight variation of the characteristic peaks for magnetic fields suggests that a field-induced structural phase transition occurs from the monoclinic to the orthorhombic structure. Moreover, the two-phases coexistence at higher fields suggests that the transformation does not completely finish even in applying the field of 5 T. These structural properties for a magnetic field are consistent with the results of the M–$\mu_0 H$ curves for $x = 0.05$ [Fig. 2(a)] and $x = 0.2$ [Fig. 2(b)]. In addition, it seems that the peak intensity varies with changing magnetic fields without hysteresis in both phases for $Gd_5(Ge_{1.8}Fe_{0.2})Si_2$.

As mentioned above, the magnetizations do not show a sharp metamagnetic transition just above T_C. The magnetic moment gradually increases with increasing fields, but does not saturate even at 5 T, which is quite different from the

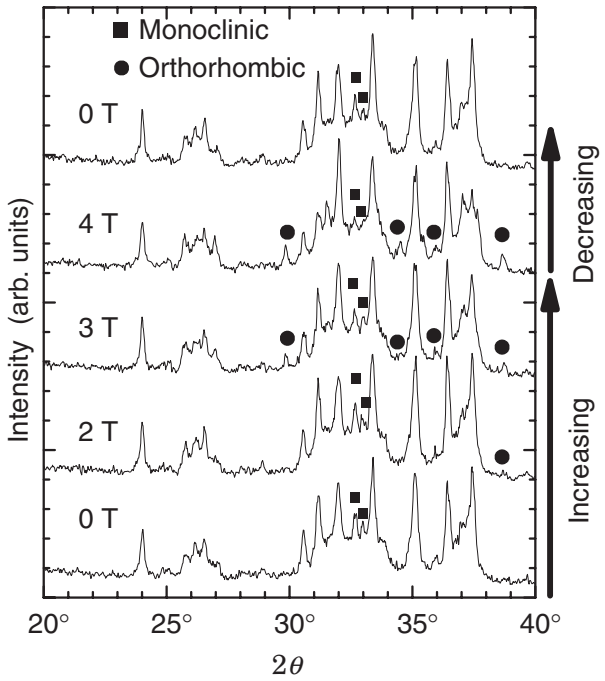

Fig. 6 Field dependence of the powder X-ray diffraction patterns of $Gd_5(Ge_{1.95}Fe_{0.05})Si_2$ at 290 K. The solid circles and the squares denote the characteristic peaks of the orthorhombic and the monoclinic phases, respectively.

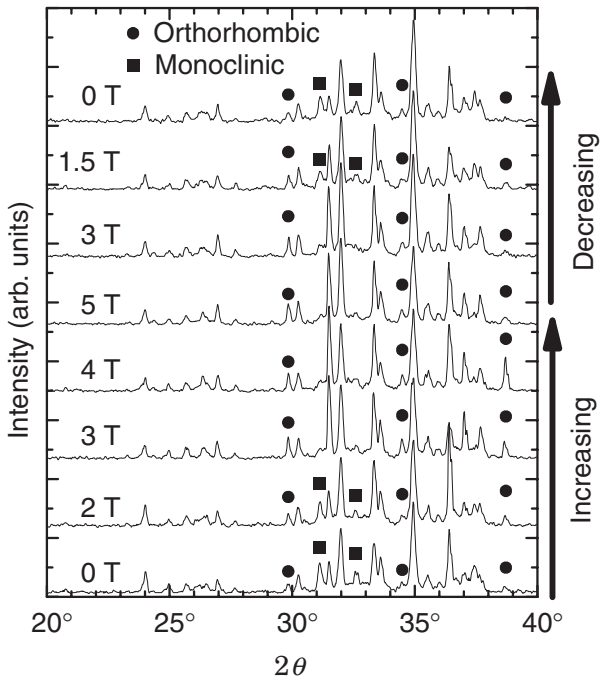

Fig. 7 Field dependence of the powder X-ray diffraction patterns of $Gd_5(Ge_{1.8}Fe_{0.2})Si_2$ at 310 K. The solid circles and the squares denote the characteristic peaks of the orthorhombic and the monoclinic phases, respectively.

metamagnetic transition observed for $Gd_5(Si_2Ge_2)$.[3–5] That is, our results indicate that applying magnetic fields slightly induce the volume fraction of the FFM phase (having the higher magnetic moment and the orthorhombic structure) in the PM matrix with the monoclinic structure above T_C. At present, the driving force of this field-induced structural transformation has been unclear. However, one of the key roles is probably due to further decrease of the Zeeman energy by applying a magnetic field, because the magnetic field induces the transition from the PM phase to the FFM phase having the higher magnetic moment.

4. Summary

We measured the powder X-ray diffraction of $Gd_5(Ge_{1.95}Fe_{0.05})Si_2$ and $Gd_5(Ge_{1.8}Fe_{0.2})Si_2$ in magnetic fields up to 5 T. With heating from 8 K, $Gd_5(Ge_{1.95}Fe_{0.05})Si_2$ clearly shows the structural transition from the orthorhombic to the monoclinic structure at the vicinity of T_C (= 276 K). On the other hand, $Gd_5(Ge_{1.8}Fe_{0.2})Si_2$ with the orthorhombic structure in a ferromagnetic state shows two phases coexistence of the orthorhombic and the monoclinic structures above T_C (= 303 K), indicating that a small amount of the matrix participates in the phase transformation. The volume of the monoclinic structure is larger than that of the orthorhombic structure ($\Delta V/V = 1.2\%$ for $Gd_5(Ge_{1.95}Fe_{0.05})Si_2$). By applying a magnetic field, the monoclinic structure is suppressed but the orthorhombic structure is enhanced for both samples just above T_C, which closely relates to the magnetization process.

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