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# Thermal expansion studies on the unusual first order transition of $Gd_5Si_{2.09}Ge_{1.91}$: effects of purity of Gd

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Two polycrystalline samples were made by using high purity Gd and commercial Gd, respectively, but with Si and Ge starting materials of the same purity in both cases. Thermal expansion results showed that both samples exhibited a first order phase transformation, with a discontinuity in thermally-induced strain and with hysteresis in the Curie temperature. Magnetic force microscopy has been used to demonstrate the magnetic phase transformation process from paramagnetic to ferromagnetic upon cooling. It was found that the Curie temperature was lower and the thermally-induced strain higher, in the sample made from lower purity level Gd starting materials compared with the sample made from high purity Gd metal. These results indicate that the impurities (mainly C, O, N, and F) in the Gd starting material can significantly alter the strain and Curie temperature of $Gd_5(Si_xGe_{1-x})_4$ alloys. © *2003 American Institute of Physics.*
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## INTRODUCTION

The properties of $Gd_5(Si_xGe_{1-x})_4$ were first studied in 1967.[1] In recent years, this material has attracted much attention due to its unusual giant magnetocaloric effect (MCE),[2] giant magnetoresistance (GMR), and colossal magnetostriction (CMS).[3] It is very unusual for a single material to possess these three effects together. The magnetocaloric effect is a phenomenon on which the alignment of randomly oriented magnetic moments caused by application of an external magnetic field results in heating, while randomizing the magnetic moments by removing the magnetic field results in cooling. Previous results indicated that the impurities in starting Gd material play a critical role in determining the magnitude of the giant MCE in the final material.[4] In this study, the effect of impurities on the magnetoelastic properties of $Gd_5(Si_xGe_{1-x})_4$ system is also reported through the measurement of thermal expansion. The results show that the strain amplitude is higher in the material made from lower purity Gd.

## EXPERIMENTAL DETAILS

Two polycrystalline $Gd_5(Si_{2.09}Ge_{1.91})$ samples were prepared by arc-melting a stoichiometric mixture of pure components in an argon atmosphere under normal pressure. The two samples used the same purity Si and Ge starting materials (both >99.99 at.%). One of the samples was prepared using Ames Laboratory (AL) Gd(99.8% pure), the major impurities (in atomic ppm) of which were: 440-O, 200-C, 160-H. Sample 2 was fabricated by using commercial purity Gd (96.9 at.% pure) which contained 18300-O, 4300-C, 4300-N, and 3700-F (in atomic ppm). Mass losses after arc-melting were less than 0.5 wt.%, so the alloy chemical compositions were assumed to be, to a first approximation, unchanged in the final product. The thermal expansion

 

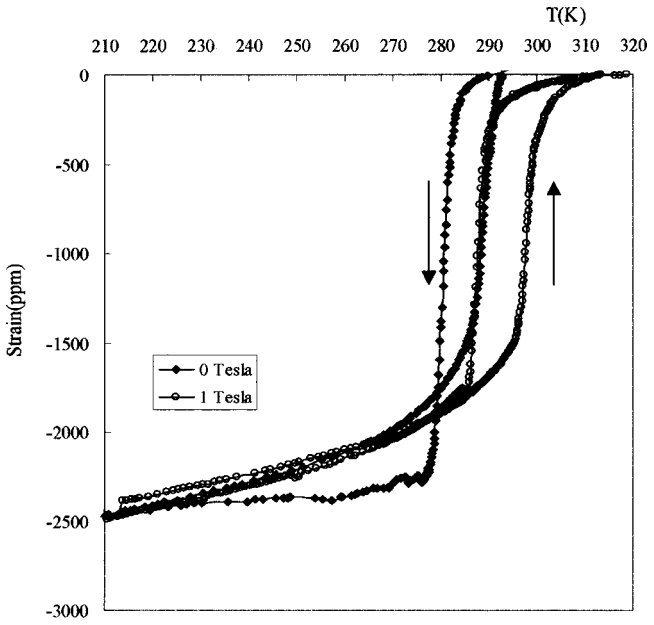


FIG. 1. Linear thermal strain (under fields of 0 and 1 T) of polycrystalline $Gd_5Si_{2.09}Ge_{1.91}$ made from Ames Laboratory high purity gadolinium.

measurements were conducted using the strain-gauge method in a Janis Research 2-stage closed cycle helium refrigeration. The sample was cooled down from room temperature through the Curie point transition, and then later was heated up through the Curie point transition. The linear thermal expansion was measured during both cooling and heating. The Curie temperatures was determined by differentiating the cooling and heating curves and finding the maximum derivative of the strain with respect to temperature. In addition, a magnetic field $B=1$ T was applied along the measurement direction to study the effect of magnetic field on the magnetoelastic properties. *In situ* magnetic force microscopy (MFM) was used to observe the phase transformation. This was carried out by using an MFM equipped with a heating-cooling stage.

## RESULTS AND DISCUSSION

Thermal expansion measurement results are shown in Fig. 1 for the sample $Gd_5(Si_{2.09}Ge_{1.91})$ made from AL Gd at $B=0$ and 1 T. An abrupt change in strain was observed at 283 K on cooling and 288 K on heating for $B=0$ T; and at 287.5 K on cooling and 298 K on heating for $B=1$ T. A discontinuity in thermal strain and thermal hysteresis are signatures of a first-order phase transition. Above the transition temperature, the sample is paramagnetic and monoclinic. Below the transition temperature, it is ferromagnetic and orthorhombic. Previous references have indicated that this first order coupled magnetic-crystallographic transition only occurs within the composition range[5] $0.24 \leqslant x \leqslant 0.5$. Recently, a more complete magnetic and crystallographic phase diagram has been established for the $Gd_5(Si_xGe_{1-x})_4$ system,[6] where a two-phase region $0.503 < x < 0.575$ is added between two regions that show a single phase around room temperature.

The composition of the present samples ($x=0.5225$) falls into this so-called two-phase region. For this composition the two crystallographic structures that can exist around room temperature are: monoclinic $Gd_5Si_2Ge_2$-type paramagnetic state (the $\beta$ phase) which is formed above 1200 K and can be retained at room temperature, and orthorhombic $Gd_5Si_4$-type paramagnetic state (the $\gamma$ phase) which is formed on heat treating the $\beta$ phase above 690 K but below 1200 K and which appears to be stable at room temperature. When the paramagnetic $\beta$ phase is cooled down below its Curie temperature, a coupled first-order magnetic-crystallographic phase transition occurs, and the ferromagnetically ordered $Gd_5Si_4$-type structure ($\alpha$ phase) is formed. This transformation is reversible. When the paramagnetic orthorhombic $Gd_5Si_4$-type $\gamma$-phase is cooled, it undergoes only an ordinary second-order transition from paramagnetic to ferromagnetic with no associated crystallographic change. This transition is also reversible. In the two-phase region, one can get either or both of $\beta$ or $\gamma$ phase to exist at room temperature, depending on heat treatment.

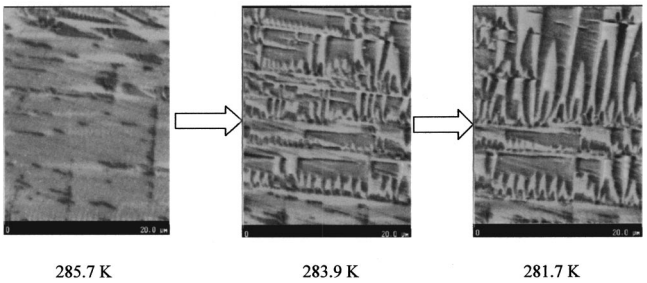


FIG. 2. MFM images showing the magnetic phase transformation process for the sample made with high purity Ames Laboratory gadolinium. The leftmost image shows the sample in the paramagnetic state; the middle and the rightmost images show the ferromagnetic state with increasing domain size.

The present samples were heat treated to ensure single phase before they were used for thermal expansion measure-

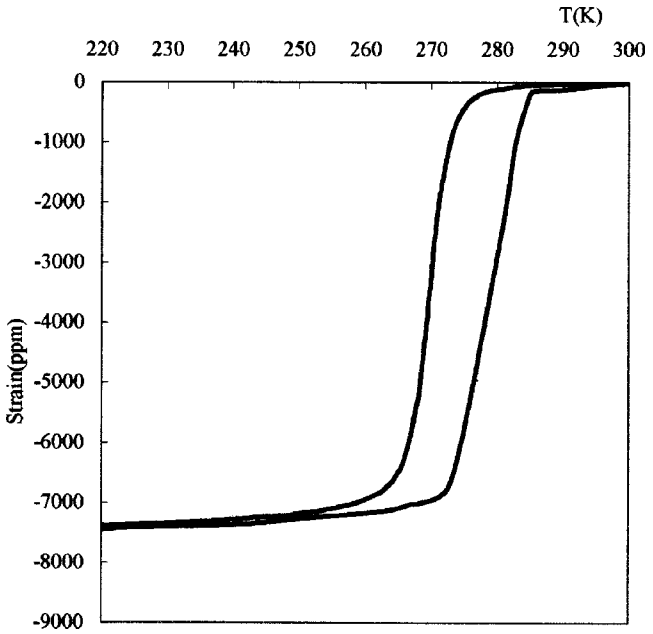


FIG. 3. Linear thermal strain in zero applied field of polycrystalline $Gd_5Si_{2.09}Ge_{1.91}$ made from commercial quality gadolinium.

ment. In Fig. 2, the MFM images show the transition from paramagnetic state to ferromagnetic state upon cooling. Fig. 1 shows a discontinuity in thermal strain at transition temperature of 283 K on cooling and at 288 K on heating, and hysteresis in the Curie temperature. These are both indicative of a first order phase transition. Thus taken together, they appear to indicate a first-order simultaneous magnetic-crystallographic phase transition. The $\gamma$ phase of $Gd_5Si_4$ is expected to be ferromagnetic at room temperature and therefore not subject to a phase transformation upon cooling. Therefore on the basis of these results, it is believed that at room temperature, these samples adopted the crystal structure of the $\beta$ phase. In addition, as shown in Fig. 1, the magnetic field can shift the Curie point to higher temperatures which also demonstrates that this first order transformation can be triggered by either temperature or applied magnetic field. In Fig. 1, the linear thermal expansion $(\Delta l/l)$ of 0.26%, corresponds to a volume expansion of $(\Delta V/V = 3\Delta l/l)$ about 0.78%, assuming minimal texturing. The thermal expansion results for sample 2 made from commercial Gd are shown in Fig. 3. On cooling $T_c = 270$ K, on heating $T_c = 275$ K. Thus the higher levels of impurities in the commercial Gd appear to have the effect of decreasing the transition temperature by $\Delta T_c = 13$ K (on either cooling or heating). The linear thermal expansion was 0.85%, corresponding to volume expansion of 2.55%, assuming minimal texturing. These values are considerably higher than those obtained in the sample made with high-purity Gd.

## ACKNOWLEDGMENTS

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