Pressure tuning of the magnetic transition in $Gd_5(Si_{0.375}Ge_{0.625})_4$ giant magnetocaloric effect material

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The effect of hydrostatic pressure on the ferromagnetic ordering transition of the monoclinic $Gd_5(Si_{0.375}Ge_{0.625})_4$ giant magnetocaloric effect compound was investigated using x-ray magnetic circular dichroism measurements in a diamond anvil cell. The Curie temperature T_C increases linearly with applied pressure up to ~7.2 GPa, at which point a discontinuity in dT_C/dP occurs. This discontinuity, which appears when T_C reaches ~277 K, is also observed when the unit cell volume is reduced by Si doping and is associated with the volume-driven monoclinic (M) to orthorhombic $[O(I)]$ structural transition. © *2008 American Institute of Physics*.
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I. INTRODUCTION

The $Gd_5(Si_xGe_{1-x})_4$ family of magnetocaloric materials has attracted attention due to its potential in environmentally friendly magnetic refrigeration applications that do not rely on harmful hydrofluorocarbons found in traditional vapor-compressed refrigerators.[1–3] Unlike the common magnetic refrigerant materials, which exhibit a simple adiabatic demagnetization process, the $Gd_5(Si_xGe_{1-x})_4$ compounds absorb/expel heat by harnessing changes in both magnetic and structural entropies that occur at the first-order magnetostructural transition responsible for their giant magnetocaloric effect.[4,5] This transition is characterized by the breaking/reforming of Si/Ge covalentlike bonds connecting Gd-containing slabs with the simultaneous disappearance/appearance of ferromagnetic ordering. To date, this martensiticlike transition has been demonstrated to be handily altered by temperature,[1–6] magnetic field,[7,8] composition,[1–5] and pressure.[9–11] Our previous x-ray magnetic circular dichroism (XMCD) experiments in a diamond anvil cell provided strong evidence for a close correspondence between Si doping and pressure.[12] However, due to the limited pressure range attained in these experiments (≤15 GPa),[12] two different compounds, namely, $Gd_5(Si_{0.125}Ge_{0.875})_4$ and $Gd_5(Si_{0.5}Ge_{0.5})_4$, needed to be measured in order to fully explore the correspondence of pressure and chemical Si doping over the entire $0<x\leq 1.0$ range. In particular, we were not able to directly demonstrate that the observed discontinuity in $T_C(x)$ at $x\sim 0.5$ (Ref. 13) is volume driven. In this paper, we report results on a $Gd_5(Si_{0.375}Ge_{0.625})_4$ sample, whose Si content is between those of the two previously studied samples (x=0.125 and x=0.5). This allowed us to directly prove that the discontinuity in $T_C(x)$ at $x\sim 0.5$ is volume driven and also to further establish the correspondence between Si doping (chemical pressure) and physical pressure in this class of the giant magnetocaloric effect compounds.

II. EXPERIMENT

Polycrystalline samples of $Gd_5(Si_{0.375}Ge_{0.625})_4$ were prepared as described in Ref. 2. The x-ray measurements were carried out at beamline 4-ID-D of the Advanced Photon Source, Argonne National Laboratory. XMCD (Ref. 14) measurements at the Gd L_3 edge ($2p_{3/2}\rightarrow 5d$ transition at 7.243 keV) were performed to probe the magnetic polarization of Gd $5d$ states at various applied pressures. X-ray absorption fine structure measurements[15] at the Cu K edge (8.979 keV) of copper powders loaded with the sample were used for *in situ* pressure calibration. Further details on the high-pressure XMCD setup can be found in Ref. 16. Ambient pressure measurements were done with the sample outside the cell.

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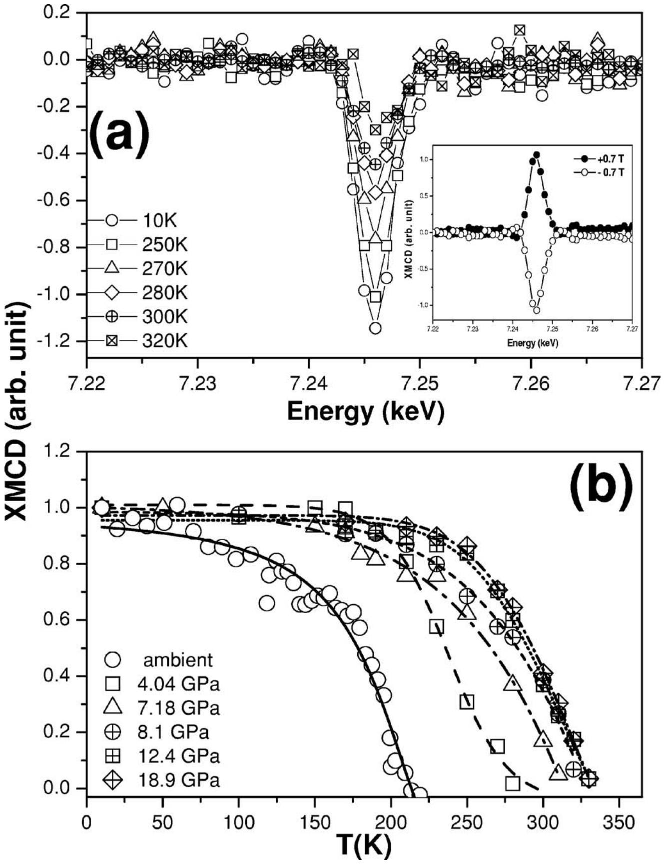

FIG. 1. (a)Temperature-dependent Gd L_3-edge XMCD signal measured at $P=12.4$ GPa. The inset shows the reversal of XMCD upon reversal of applied magnetic field. (b) Integrated area under XMCD curve as a function of temperature for selected pressures. The XMCD is normalized to its saturation value at 10 K.

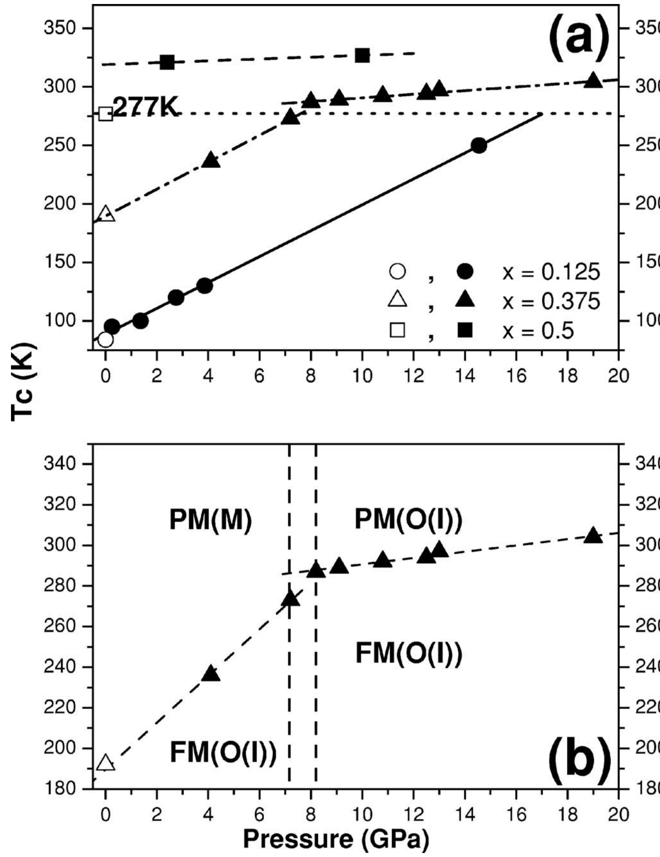

FIG. 2. (a) The transition temperature as a function of pressure of $x=0.125$, 0.375, and 0.5 samples, respectively. Open symbols represent the data measured at ambient conditions. The horizontal dashed line marks slope discontinuity observed for the $x=0.375$ sample and also the T_C (277 K) of $Gd_5(Si_{0.5}Ge_{0.5})_4$ under ambient conditions. (b) The pressure-temperature (P-T) phase diagram of $Gd_5(Si_{0.375}Ge_{0.625})_4$. The data points indicate the transition temperatures under different pressures. The transition regime is marked by dashed lines located in between 7.18 and 8.1 GPa.

III. RESULTS AND DISCUSSION

The pressure-dependent measurements were carried out in the pressure range from ambient up to 18.9 GPa. Figure 1(a) shows the temperature-dependent Gd L_3-edge XMCD data for the $Gd_5(Si_{0.375}Ge_{0.625})_4$ sample under an applied pressure of 12.4 GPa. The inset shows the full reversal of the XMCD signal upon reversal of the 0.7 T applied field. Data at other pressures are of comparable quality.

Figure 1(b) shows the effect of pressure on the magnetic transition. The T_C of $Gd_5(Si_{0.375}Ge_{0.625})_4$ increases with pressure, as was also observed for both $Gd_5(Si_{0.125}Ge_{0.875})_4$ and $Gd_5(Si_{0.5}Ge_{0.5})_4$ samples[12] (T_C is determined by the highest absolute value of the derivative of the fitted lines). Unlike $Gd_5(Si_{0.125}Ge_{0.875})_4$, which displays an intermediate ferromagnetic (FM)-antiferromagnetic transition before becoming paramagnetic on warming leading to a nonzero XMCD signal above T_C at low pressures,[12] $Gd_5(Si_{0.375}Ge_{0.625})_4$ does not show any remanent XMCD signal above T_C for all pressure points, indicating a direct FM-paramagnetic transition. In addition, as shown in Fig. 1(b) the rate of increase in the ferromagnetic transition temperature for $Gd_5(Si_{0.375}Ge_{0.625})_4$ is reduced for pressures beyond 8.1 GPa. A similar result was shown in Fig. 1 of Ref. 17 for a $Gd_5(Si_{0.5}Ge_{0.5})_4$ sample.

The magnetic transition temperatures as a function of pressure for $x=0.125$, $x=0.375$, and $x=0.5$ samples are presented in Fig. 2(a). The data sets for $x=0.125$ and $x=0.5$ samples are taken from Ref. 11. It is easy to see that the sample with $x=0.125$ yields a linear dT_C/dP up to $\sim$15 GPa, while that with $x=0.375$ exhibits a discontinuity in dT_C/dP at $\sim$7.2 GPa. A similar discontinuity induced by pressure was also observed for $x=0.5$.[10,12,17] It is known that a β $(M)\rightarrow\alpha$ $[O(I)]$ phase transition is responsible for this discontinuity in T_C for $x=0.5$ as a result of the different compressibilities of M and $O(I)$ structures.[10] Since the discontinuity in dT_C/dP occurs at $\sim$277 K on both $x=0.375$ and $x=0.5$ samples, it is reasonable to assume that the $M\rightarrow O(I)$ structural transition for $x=0.375$ occurs at $\sim$7.2 GPa at T_C $\sim$277 K [see the dashed line in Fig. 2(a)]. In addition, the dT_C/dP for $x=0.375$ at pressures below 7.2 GPa in Fig. 2(a) is 1.5 K kbar^{-1}, which is comparable to 1.2 K kbar^{-1} obtained in $x=0.125$. Furthermore, dT_C/dP measured at higher pressures reduces to 0.15 K kbar^{-1}, comparable to 0.2 K kbar^{-1} obtained for the $x=0.5$ sample. The good quantitative similarities reveal that $x=0.375$ behaves analogously to $x=0.125$ at low pressures and to $x=0.5$ at high pressures. This behavior is dictated by the change in compressibility introduced by the $M\rightarrow O(I)$ structural transition.

A P-T diagram is plotted in Fig. 2(b) for the $x=0.375$ sample. The discontinuity in dT_C/dP at 277 K is also observed at this temperature in the x-T phase diagram, where the $M \rightarrow O(I)$ structural transition occurs for $x \sim 0.5$.[13] Hence, our results indicate that this transition is volume driven. When the volume reduction causes T_C to reach 277 K, a low-Si/low-pressure phase (monoclinic) will be converted into a high-Si/high-pressure phase [orthorhombic(I)].

IV. CONCLUSION

A high-pressure XMCD study on $Gd_5(Si_{0.375}Ge_{0.625})_4$ shows that the monoclinic $\rightarrow$ orthorhombic(I) structural transition in this class of materials is volume driven. This transition can be triggered by Si doping or applied pressure and occurs when the volume reduction causes T_C to reach $\sim$277 K. The results further highlight the correspondence between Si doping and applied pressure in determining the magnetic behavior of this important class of materials.

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