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Effect of pressure on the spontaneous volume magnetostriction of $GdAl_2$

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Abstract

The thermal expansion and lattice constants of polycrystalline $GdAl_2$ have been measured under high pressure. It is found that as pressure increases, the Curie temperature T_C increases with a ratio of $\partial T_C/\partial P = 8.56$ K/GPa and the spontaneous volume magnetostriction ω_s decreases rapidly. C15 structure is stable up to 12.4 GPa and the bulk modulus is 75.3 GPa at room temperature. Grüneisen parameter of T_C is estimated to be 3.84. Using these experimental results, the pressure dependence of T_C is discussed on the basis of the itinerant electron model of ferromagnetism.

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Keywords: Thermal expansion; The spontaneous magnetostriction; X-ray diffraction; High pressure

1. Introduction

RAl_2 (R: rare earth element) compounds with Laves phase have been extensively studied because these compounds show a wide variety of magnetic and electronic properties by changing R. The compound of R = Tb or Dy shows ferromagnetism having $T_C = 111$ K or 54 K [1,2], but in the case of R = Ce, it is antiferromagnetic with $T_N = 3.8$ K [3]. $GdAl_2$ has the highest Curie temperature ($T_C \sim 168$ K) among these ferromagnetic compounds. The previous reports have revealed that $GdAl_2$ has 5d-like electrons [4] and its spontaneous magnetic moment lies between 6.83 and 7.20μ_B [5]. The elastic properties are also anomalous because the longitudinal elastic constant C_L increases below T_C, i.e., the lattice becomes hard accompanied by the magnetic ordering [6]. This is in sharp contrast with the elastic properties of ferromagnetic materials such as Invar alloys [7]. Since the magnetic and elastic properties of $GdAl_2$ are anomalous as mentioned above, it is interesting to study the relation between magnetism and volume of $GdAl_2$ not only at ambient but also at high pressure. In the present work, we have measured the thermal expansion and lattice constants of $GdAl_2$ under high pressure in order to make clear the stability of ferromagnetism under high pressure.

2. Experimental procedures

Polycrystalline $GdAl_2$ was prepared by an arc-melting of constituent metals, Gd (99.9%) and Al (99.992%). To obtain homogeneity, the ingot was turned over and remelted five times. The sample was annealed in an evacuated ($\sim 10^{-6}$ Torr) silica tube at 800 °C for 2 weeks. The susceptibility was measured by the ac method. The linear thermal expansion was measured by means of strain gauge method using molybdenum as a reference in the range 77.4 K $\leq T \leq$ 300 K. The hydrostatic pressure was generated by a piston-cylinder apparatus up to 2.0 GPa. Lattice parameters were measured at room temperature by X-ray diffraction method under high pressure, in which we used a WC Bridgman type

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anvil with Be gasket and a 4:1 mixture of methanol and ethanol as a pressure transmitting medium.

3. Results

Fig. 1 shows the temperature dependence of the ac susceptibility χ_{ac} (a.u.) at ambient pressure. From this data, T_C was determined as the temperature where χ_{ac} shows a sudden change by the ferromagnetic phase transition with decreasing temperature. T_C of $GdAl_2$ was determined as 170 K, which is in good agreement with the previous one [8].

Fig. 2 shows the temperature dependence of the linear thermal expansion $\Delta L/L$ at various pressures. $\Delta L/L$ decreases almost linearly with decreasing temperature. But the decrease below T_C becomes steeper than that above T_C. This fact indicates that the magnitude of the thermal expansion coefficient below T_C is larger than that above T_C. In other words, this shows a negative magnetostriction, i.e., the length (or volume) shrinks with the magnetic ordering. By applying pressure, the decrease in $\Delta L/L$ is found to be less prominent.

The linear thermal expansion coefficient $\alpha(T)$ is defined as

$$\alpha(T) = \frac{\mathrm{d}}{\mathrm{d}T}\left(\frac{\Delta L}{L}\right). \tag{1}$$

The results at ambient pressure and 2.0 GPa are shown as a function of temperature in Fig. 3. T_C was determined as the temperature where $\alpha(T)$ curve begins to increase suddenly with decreasing temperature (see the two lines in Fig. 3). T_C (=168 K) at ambient pressure agrees well with that of the susceptibility. The magnitude of discontinuous change in $\alpha(T)$ below T_C decreases with increasing pressure. The pressure dependence of T_C is shown in Fig. 4. T_C increases with pressure almost linearly below 2.0 GPa with the rate, $\partial T_C/\partial P = 8.56$ K/GPa, which is a little bit larger than the previous one, 7.1 K/GPa [1]. This may be due to the difference in the determination of T_C and in some sample dependence.

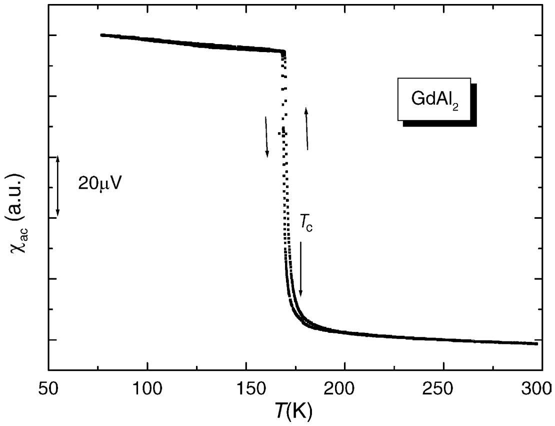

Fig. 1. Temperature dependence of the ac susceptibility of $GdAl_2$ in arbitrary unit at ambient pressure.

The pressure derivative of T_C is expressed by the following Ehrenfest relation:

$$\frac{\mathrm{d}T_C}{\mathrm{d}P} = \frac{VT_C\Delta\beta}{\Delta C_P}, \tag{2}$$

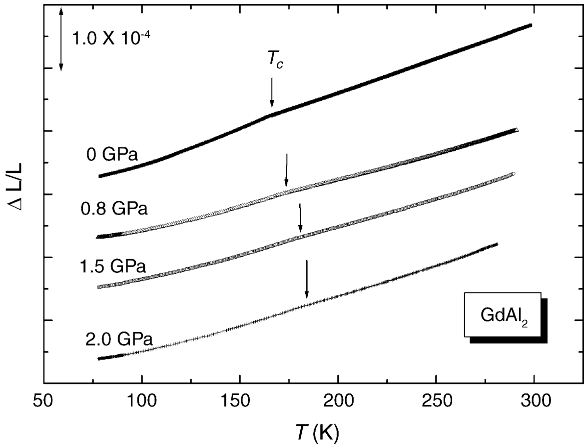

Fig. 2. Thermal expansion of $GdAl_2$ as a function of temperature T (K) at high pressure. T_C is determined by the linear thermal expansion coefficient (see Fig. 3).

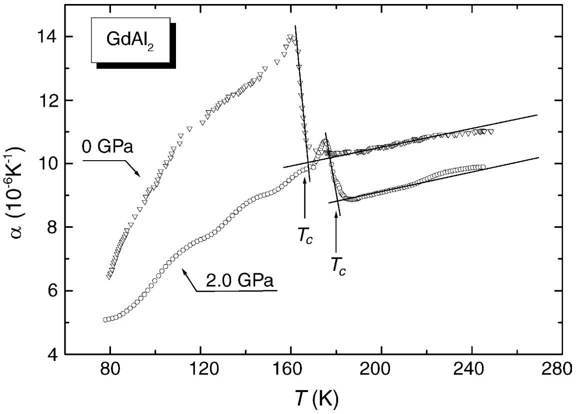

Fig. 3. Temperature dependence of the linear thermal expansion coefficients of $GdAl_2$ at 0 and 2.0 GPa.

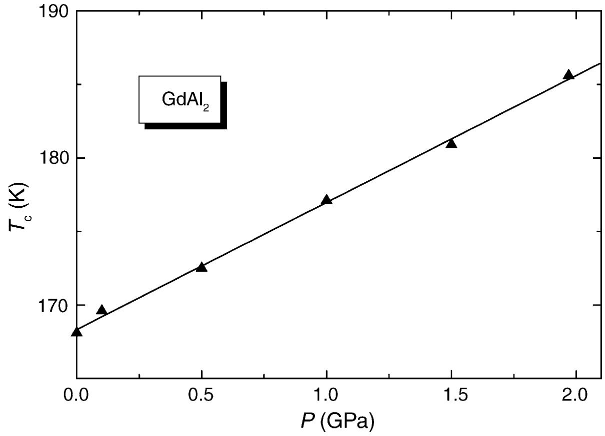

Fig. 4. The Curie temperature T_C (K) of $GdAl_2$ as a function of the pressure.

where V is the volume, $\Delta\beta$ and ΔC_P are the changes at the phase transition in the volume thermal expansion coefficient ($\beta(T) = 3\alpha(T)$) and the specific heat at the constant pressure. $\partial T_C/\partial P$ is estimated to be 10 K/GPa using our experimental data of $\beta(T)$ and the previous data of $C_P(T)$ [9], which is in agreement with the present result, considering the roughness of the estimation.

To extract the spontaneous volume magnetostriction $\omega_s(T)$, we approximate the volume thermal expansion $\omega(T)(= \Delta V/V = 3\Delta L/L)$ into two contributions, one is from the phonon (lattice vibration) $\omega_{ph}(T)$ and the other from the spontaneous volume magnetostriction $\omega_s(T)$:

$$\omega(T) = \omega_{ph}(T) + \omega_s(T). \tag{3}$$

$\omega_{ph}(T)$ is calculated on the basis of the Debye model and the Grüneisen relation [10]:

$$\omega_{ph}(T) = \frac{\kappa\Gamma}{V}\int C_V(T)\,dT, \tag{4}$$

where Γ is the Grüneisen parameter and $C_V(T)$ the specific heat at constant volume. We obtained the value of $(\kappa\Gamma)/V$ by fitting the experimental data $\omega(T)$ well above T_C to Eq. (4) using $\Theta_D = 380$ K [8] assuming its negligible pressure dependence and then obtained $\omega_{ph}(T)$. The solid line in Fig. 5 shows an example of the fitting. We estimated the values of $\omega_s(T)$ at ambient pressure to be about -0.9×10^{-3} at 77.4 K and -1.5×10^{-3} at 0 K, which are negative and the magnitude is smaller than that of typical Invar alloy ($\omega_s \sim 20 \times 10^{-3}$) by an order of magnitude. Fig. 6 shows $-\omega_s(T)$ at high pressure. The absolute value of $\omega_s(T)$ at 77.4 K is shown in the inset of Fig. 6, which decreases rapidly below 1 GPa and tends to saturate above that.

Fig. 7 shows the relative volume V/V_0 at room temperature as a function of pressure up to 12.4 GPa, where V and V_0 are the volumes at high and ambient pressure, respectively. The volume shows a smooth decrease with increasing pressure without any discontinuities. This fact indicates that there is no structural phase transition, i.e., the C15 structure is stable up to 12.4 GPa at room temperature. To obtain the bulk modulus, we attempted a least-square fit of the data to the first-order Murnaghan's equation of state:

$$P = \left(\frac{B_0}{B_0'}\right)\left[\left(\frac{V}{V_0}\right)^{-B_0'} - 1\right], \tag{5}$$

where B_0 is the bulk modulus at ambient pressure at room temperature, and B_0' is its pressure derivative. The result is shown by the solid curve in Fig. 7. We obtained $B_0 = 75.3$ GPa, which agrees with the previous one, $B_0 = 69.0$ GPa [11].

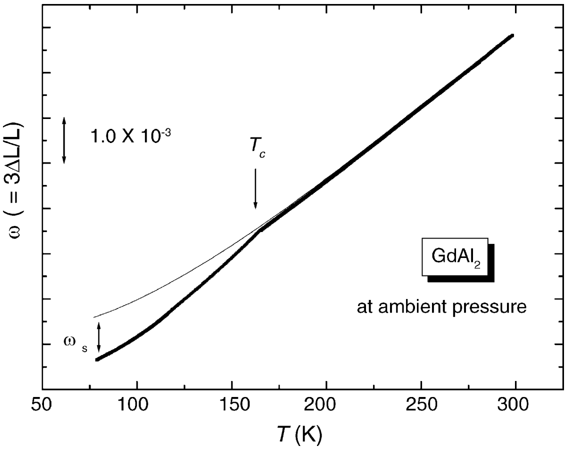

Fig. 5. Fractional volume change $\omega = \Delta V/V$ of GdAl$_2$ as a function of temperature at ambient pressure.

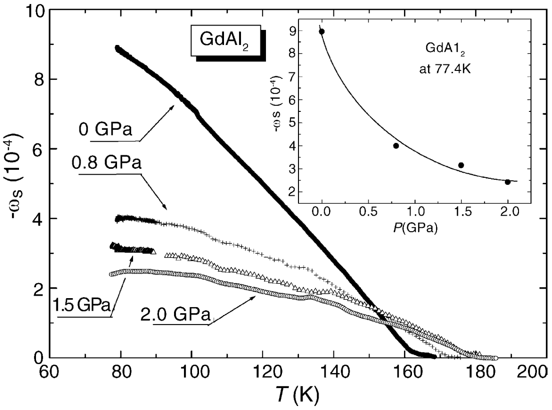

Fig. 6. Temperature dependence of the spontaneous volume magnetostriction ω_s of GdAl$_2$ at high pressure. The inset shows ω_s at 77.4 K at high pressure.

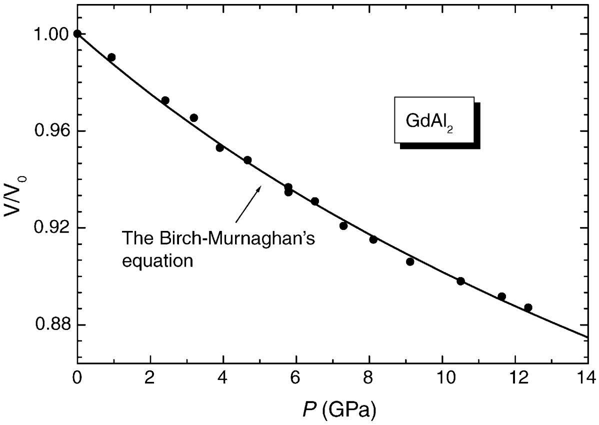

Fig. 7. Relative volume change of GdAl$_2$ as a function of pressure up to 12.4 GPa at room temperature.

4. Discussion

In order to examine the volume dependence of T_C, we discuss our data using the Grüneisen parameter. In Eq. (4), the Grüneisen parameter Γ of T_C is defined as

$$\Gamma \equiv -\frac{\partial \ln T_C}{\partial \ln V} = \frac{B_0}{T_C}\frac{\partial T_C}{\partial P}. \tag{6}$$

Using the bulk modulus $B_0 = 75.3\,\mathrm{GPa}$, Γ is estimated to be 3.84, which is larger than that of Ni ($\Gamma = 1$), but the same as that of $\mathrm{TbAl_2}$ ($\Gamma = 3.8$). For $\mathrm{CeAl_2}$, Γ of the Kondo temperature T_K is 64, which is much larger than $\Gamma(T_C)$ of $\mathrm{RAl_2}$ (R = Gd, Tb).

It is well known that $\omega_s(T)$ is proportional to the square of the spontaneous magnetization $M_s(T)$:

$$\omega_s(T) = \kappa C M_s^2(T), \tag{7}$$

where κ, C and $M_s(T)$ are the compressibility, the magnetoelastic coupling constant and the spontaneous magnetization, respectively. From the present result, C should be negative. Furthermore, using the spontaneous magnetization $M_s(T)$ at 77.4 K [5], κ and $\omega_s(T)$ at 77.4 K at ambient pressure, κC is estimated to be $-8.0 \times 10^{-4}\,\mathrm{m^4/Wb^2}$. κC of typical Invar alloys is of the order of $10^{-2}\,\mathrm{m^4/Wb^2}$ [12], which is about 10 times larger than that of $\mathrm{GdAl_2}$.

$\omega_s(T)$ is rewritten by [13]:

$$\omega_s(T) = -A\left(\frac{\partial T_C}{\partial P}\right), \tag{8}$$

where A is the positive constant. This equation is derived by using molecular field theory and Eq. (7). Eq. (8) indicates that the material having a large pressure derivative of T_C shows a large $\omega_s(T)$. Since $\omega_s(T)$ of $\mathrm{GdAl_2}$ is negative, the sign of $\partial T_C/\partial P$ should be positive, which is in agreement with our experimental result.

The conduction electrons of ordered $\mathrm{GdAl_2}$ have been revealed to have 5d-like character [4], which may play an important role in determining the value of $\partial T_C/\partial P$. Considering this fact, we estimate the pressure derivative of T_C on the basis of the itinerant electron model of ferromagnetism. In this model, it is expressed by

$$\frac{\partial T_C}{\partial P} = \frac{5}{3}\kappa T_C - \frac{\lambda}{T_C}, \tag{9}$$

where λ is the constant which is proportional to κC [14]. The first term in Eq. (9) reflects the strong or localized ferromagnetic character, while the second term weak ferromagnetic one. All ferromagnetic materials have both characters. In the case of Ni ($T_C = 633\,\mathrm{K}$, $\partial T_C/\partial P = 3.5\,\mathrm{K/GPa}$), the contribution from first term is lager than that of second term. But in the case of Invar alloys which are considered as a weak ferromagnet, the second term is main. For $\mathrm{GdAl_2}$, the value of first term is estimated to be 3.7 K/GPa. Since the sign of λ is negative for $\mathrm{GdAl_2}$ as pointed out in the foregoing section, the second term gives a positive contribution to $\partial T_C/\partial P$. Using this fact we estimated the value of λ to be $-0.84 \times 10^3\,\mathrm{K^2/GPa}$.

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