Journal of Alloys and Compounds 408–412 (2006) 301–306

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Anomalous thermal expansion and magnetostriction of rare earth compounds under high pressure

G. Oomi[a,*], T. Kagayama[b]

[a] Department of Physics, Kyushu University, 4-2-1 Ropponmatsu, Fukuoka 810-8560, Japan

[b] KYOKUGEN, Research Center for Materials Science at Extreme Conditions, Osaka University, Osaka 560-8531, Japan

Available online 15 July 2005

Abstract

The thermal expansion coefficients of Kondo compounds, $CeBe_{13}$ and $CeRh_2Si_2$, and the magnetostriction of $Tb_{0.3}Dy_{0.7}Fe_2$(Terfenol-D) have been measured at high pressure. By simple analysis using thermodynamical relation, it is found that the density of state at the Fermi level and the Grüneisen parameters Γ of the Kondo compounds decrease rapidly with increasing pressure corresponding to the large pressure-induced enhancement of Kondo temperatures. An anomalous behaviour in the thermal expansion coefficients of $CeRh_2Si_2$ is observed at high pressure above T_N. This anomaly is suggested as an origin of pressure-induced superconductivity. The giant magnetostriction (GMS) of Terfenol-D is found to be enhanced by applying hydrostatic pressure below 0.5 GPa but GMS decreases above it. These results are discussed briefly by comparing with the previous ones.

Keywords: High pressure; Thermal expansion; Giant magenetostriction; Kondo effect; Grüneisen parameter

PACS: 74.62.Fj; 65.40.−b; 75.80.+q

1. Introduction

The intermetallic compounds having unstable 4f electrons show a lot of anomalous lattice properties, which are affected strongly by applying pressure or magnetic fields [1,2]. The thermal expansion and magnetostriction of these compounds have attracted a lot of interest because of the wide range of application and new aspects in the fundamental physics about the relation between the lattice and the magnetism.

In the present work, the thermal expansion, magnetostriction and their response to high pressure are described in detail for the compounds containing Ce, $CeBe_{13}$ and $CeRh_2Si_2$ and $Tb_{0.3}Dy_{0.7}Fe_2$(Terfenol-D), which shows the giant magnetostriction (GMS) [3]. $CeBe_{13}$ is considered as an intermediate valence compound showing no magnetic ordering [4]. $CeRh_2Si_2$ shows a magnetic order at $T_N = 36$ K and a superconductivity at high pressure around 1 GPa [5,6]. In such materials, we expect that the thermal expansion coefficients show some anomalies at high pressure [7]. The GMS of Terfenol-D is also expected to be influenced significantly by applying pressure. A brief analysis of the data using thermodynamical relation will be discussed. The large pressure effect on the thermal expansion coefficients and magnetostriction will be reported in the following sections. The details of experimental procedure have been published previously [8,9].

2. Thermodynamical relation of the thermal expansion coefficients

The volume thermal expansion coefficient β is related to the specific heat at constant volume C_V by the Grüneisen relation:

$$\beta = \frac{\Gamma C_V}{B_T V} \quad (1)$$

where Γ, B_T, and V are the Grüneisen parameter, isothermal bulk modulus and the volume, respectively. In the isotropic materials, β is written as $\beta = 3\alpha$ (α: linear thermal expansion coefficient). Γ is written as, $\Gamma = -\partial \ln T_0 / \partial \ln V$, where T_0

* Corresponding author.
E-mail address: oomi@rc.kyushu-u.ac.jp (G. Oomi).

0925-8388/$ – see front matter © 2005 Published by Elsevier B.V.
doi:10.1016/j.jallcom.2005.04.043

is a characteristic temperature such as ordering temperature or Kondo temperature, which is related to the entropy of the system. Considering the usual relation:

$$C_V = \gamma T + \theta T^3 \quad (2)$$

where γ and θ are the constants. Then we obtain the following equation [8]:

$$\alpha = A'T + B'T^3 \quad (3)$$

where A' is $\gamma\Gamma_e/3B_T V$ and $B = \theta\Gamma_{ph}/3B_T V$. Electron and phonon terms have respective Grüneisen parameters. For the discussion in the following section we may write Eq. (3) as

$$\alpha/T = A' + B'T^2. \quad (4)$$

From these equations and $\gamma \propto N(0)$, α/T at low temperature is roughly proportional to the values $\Gamma N(0)$, where $N(0)$ is the density of state at the Fermi level. We will use these results in the analysis of the present data.

3. Results and discussion

3.1. Thermal expansion of the intermediate valence state (IVS) compound $CeBe_{13}$

The thermal expansion coefficient $\alpha(T)$ is shown in Fig. 1 at various pressures as a function of T. α increases with increasing T without any discontinuities. There is a small difference in $\alpha(T)$ curves depending on pressure. At ambient pressure, α increases rapidly with increasing T up to about 150 K, the change becomes sluggish and then α becomes almost constant above 250 K. But in the $\alpha(T)$ curve at 2 GPa, such behaviour is less prominent, i.e., $\alpha(T)$ at 2 GPa shows a smooth increase against T. For the heavy Fermion material, there is a large enhancement of the value of α/T at low temperature in the plot of α/T versus T^2, which indicates a large mass enhancement of f-electron [8,10]. But we found that there is no such enhancement of α/T at low temperature. This fact indicates that there is no mass enhancement at low temperature and $CeBe_{13}$ should be in the category of IVS compound [4].

Fig. 2 shows the values of α/T at 10 K as a function of pressure. α/T (10 K) is found to decrease rapidly with increasing pressure but above 1 GPa, the change becomes small. As mentioned in Section 2, the magnitude of α/T (10 K) is roughly proportional to $\Gamma N(0)$ ($\Gamma_e = \Gamma$). Considering the relation $N(0) \propto \sqrt{A}$, where A is the coefficient of T^2 term in $\rho(T)$, the following relation is derived:

$$\Gamma \propto \alpha/T(10\,\mathrm{K})/\sqrt{A} \quad (5)$$

The values of $\alpha/T(10\,\mathrm{K})/\sqrt{A}$ are plotted in Fig. 3 as a function of pressure. From this result, the value of Γ is found to decrease with increasing P. This is in agreement with the results reported previously for Kondo compounds [11,12].

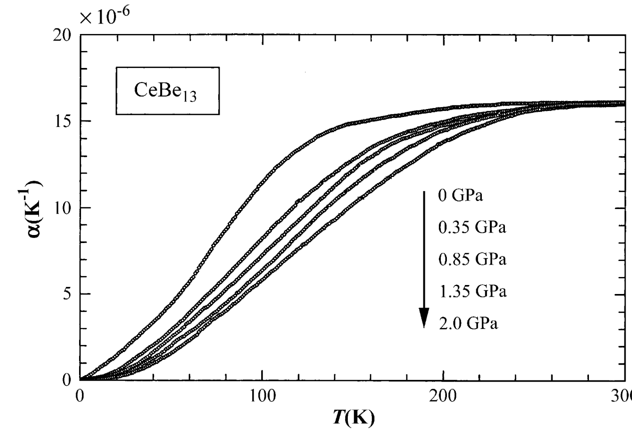

Fig. 1. Thermal expansion coefficients $\alpha(T)$ of $CeBe_{13}$ at high pressure.

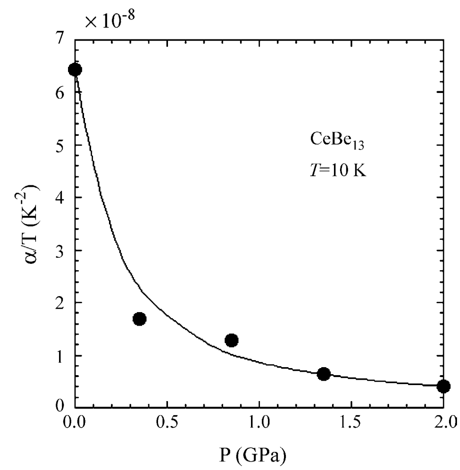

Fig. 2. α/T at 10 K as a function of pressure.

From the result in Fig. 3, Γ at 2 GPa is estimated to be 5–10 because Γ is 39 at ambient pressure [13]. The large decrease in Γ below 0.5 GPa reflects the instability of electronic state against pressure.

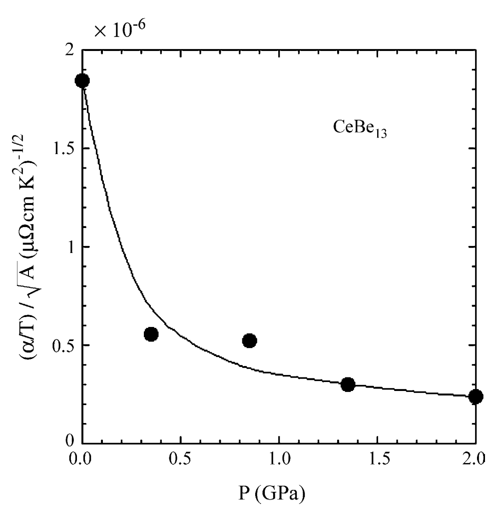

Fig. 3. $(\alpha/T)/\sqrt{A}$ at 10 K against pressure.

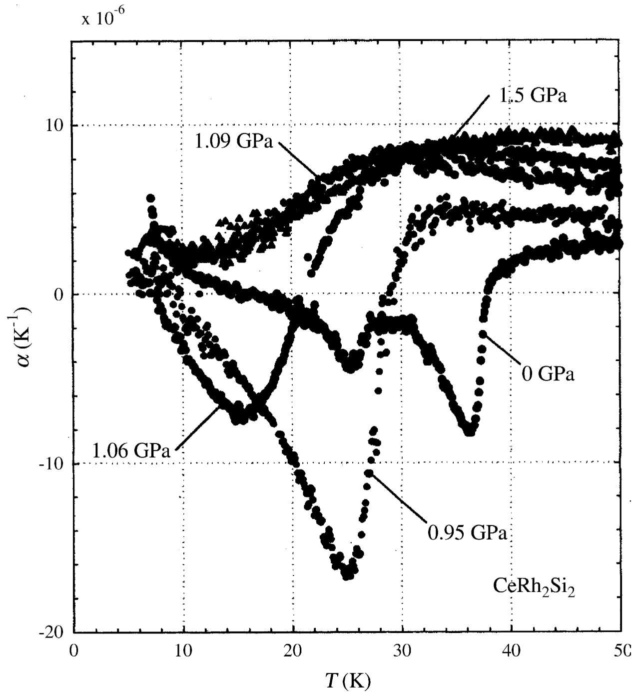

Fig. 4. Thermal expansion coefficients $\alpha(T)$ of $CeRh_2Si_2$ at high pressure.

3.2. Anomalous thermal expansion coefficient of $CeRh_2Si_2$—precursor phenomena to the occurrence of pressure-induced superconductivity

$CeRh_2Si_2$ is well known as a pressure-induced superconductor around 1 GPa having antiferromagnetic order near 35 K (=T_N) at ambient pressure. T_N is largely decreased by applying pressure, which is extrapolated to 0 around 1 GPa [14]. $\alpha(T)$ curves are shown in Fig. 4. Large change in the $\alpha(T)$ is easily seen as pressure is increased.

Two anomalies are found at ambient pressure at $T_{N1} =$ 37 K and $T_{N2} = 25$ K, but at 0.95 GPa, one large dip in $\alpha(T)$ is observed around 25 K, i.e., T_{N2} disappears below this pressure. Above 1.09 GPa, no anomalies are found in $\alpha(T)$. In other words, the antiferromagnetism disappears completely above 1.09 GPa (=P_C).

This result is compatible with that of the specific heat at high pressure [15]. The values of $(\alpha/T)/\sqrt{A}$ are plotted in Fig. 5 as a function of pressure above P_C. From this result, the magnitude of Γ decreases with increasing pressure but tends to saturate above 1.5 GPa. This result is also in qualitative agreement with the previous reports [16]. Γ-value was obtained by using the pressure dependence of A to be $\Gamma = 42$ above 1.5 GPa. Considering this fact and the result in Fig. 5, it is suggested that Γ is enhanced largely near the phase boundary of $T_N = 0$, or the quantum critical point, where the values of Γ may be larger than 50.

In order to examine the pressure dependence of α, the values are shown as a function of pressure in Fig. 6. At 10 K, α shows a discontinuous change around 1.1 GPa, which corresponds to the disappearance of antiferromagnetic order or

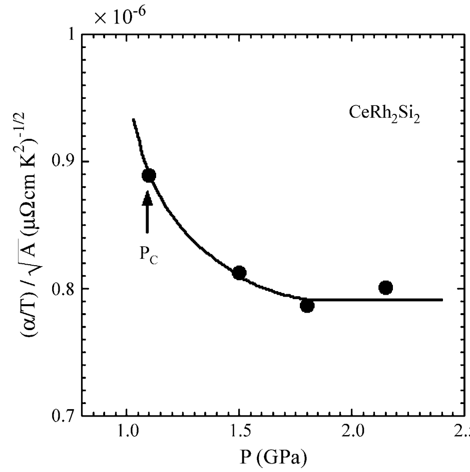

Fig. 5. $(\alpha/T)/\sqrt{A}$ at 10 K against pressure.

quantum critical point. α at 30 K also show an anomaly near 1 GPa, in which the change in the magnitude of α seems to be larger than that at 10 K. It should be very surprising that there are discontinuous changes near 1 GPa in $\alpha(P)$ curve both at 50 and 60 K, which are higher than the magnetic transition temperature 35 K. This fact indicates that there are anomalies in the pressure dependence in α near 1 GPa even in the paramagnetic region.

This result is reminiscent of the case of UGe_2, which is a typical example of pressure-induced superconductivity [17]. For this material, we have reported the anomalous pressure dependence in the thermal expansion coefficients and electrical resistance in the temperature range above the ferromagnetic ordering temperature [18]. In this case, we suggested the existence of some kind of short range order having crystalline or magnetic origins. According to this consideration, we suggest that there are some kind of disorder or magnetic short range order in $CeRh_2Si_2$ specimen in the region above T_N, which gives rise to an anomaly in the pressure depen-

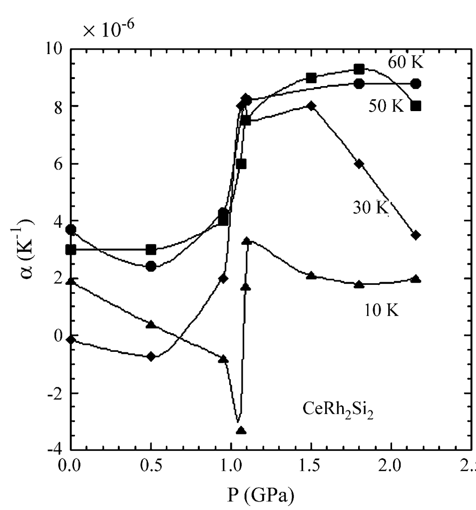

Fig. 6. Thermal expansion coefficients α of $CeRh_2Si_2$ as a function of pressure at various temperatures.

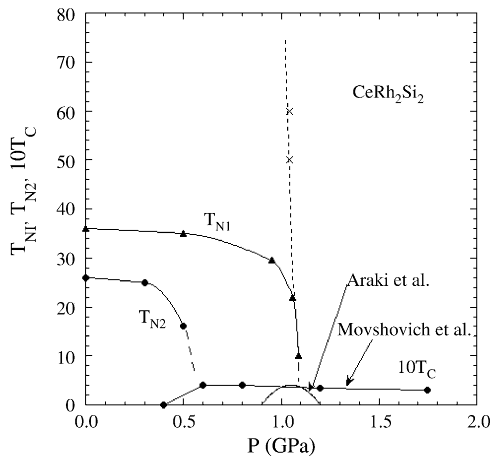

Fig. 7. *P–T* phase diagram of $CeRh_2Si_2$. T_C was obtained from refs. [6,20].

dence of α. In such sense, the large pressure effect on the magnitude of α at 30 K above 1.1 GPa may be due to a large quantum fluctuation effect, which may exist in the wide range of *P–T* phase diagram [19].

Fig. 7 summarizes the present status of the pressure experiment of $CeRh_2Si_2$ including superconducting phase. Some discrepancies exist about the pressure range of superconductivity [6,20]. But it should be emphasized that there is another phase boundary (dotted line in Fig. 7) in the paramagnetic region, which is extrapolated to the maximum of the T_C versus P curve. This is also similar to the phase diagram of UGe_2 [18,21]. This result means that there is a phase boundary or crossover, which is closely related to the occurrence of superconductivity. In the region, $T > T_{N1}$ and $P \geq P_C$, precursor phenomena for the pressure induced superconductivity may be observed.

3.3. Pressure-enhanced giant magnetostriction of $Tb_{0.3}Dy_{0.7}Fe_2$

It is well known that the intermetallic compound $Tb_{0.3}Dy_{0.7}Fe_2$ shows GMS of the order of 10^{-3}, which has attracted a lot of attention of many investigators from the points of application as an actuator of micromachines [22]. In the present work we examined the effect of hydrostatic pressure on the magnitude of GMS. Fig. 8 shows the magnetostriction (MS) at ambient pressure as a function of magnetic fields H (kOe) for the directions of parallel ($\lambda_\parallel$) and perpendicular ($\lambda_\perp$) to H in the range $-4.3\,\text{kOe} \leqq H \leqq +4.3\,\text{kOe}$. The values of $\lambda_\parallel$ and $\lambda_\perp$ at ambient pressure are $+1.0 \times 10^{-3}$ and -0.6×10^{-3} at 4.3 kOe, respectively.

Fig. 9 shows $\lambda_\parallel$ and $\lambda_\perp$ at 0.45 GPa as a function of H. It is easily seen that $\lambda_\parallel$ increases with applying magnetic field more rapidly than that at ambient pressure: the magnitude of $\lambda_\parallel$ at 4.3 kOe is 1.3×10^{-3}, which is about 1.3 times larger than that at ambient pressure. But $\lambda_\perp$ is almost the same as that at ambient pressure. Fig. 10 shows $\lambda_\parallel$ and $\lambda_\perp$ at 4.3 kOe as a function of pressure. It is found that $\lambda_\parallel$ increases with pressure having a peak near 0.5 GPa and decreases above that but the magnitude of $\lambda_\perp$ is almost independent of pressure.

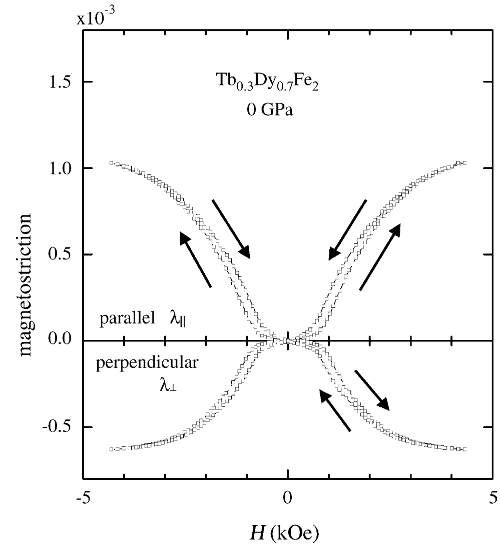

Fig. 8. Magnetostriction parallel to H ($\lambda_\parallel$) and perpendicular to H ($\lambda_\perp$) at ambient pressure.

Effect of uniaxial pressure on MS has been investigated by several authors [23,24]. It has been reported that a jump in the magnetization is induced by applying uniaxial pressure of the order of several tens of MPa, which gives rise to a jump or a sudden increase in the magnitude of MS. In the present work, this type of jump is observed at hydrostatic pressure above 0.45 GPa (=450 MPa) as shown in Fig. 9, which is about one order of magnitude larger than that of uniaxial case. This phenomena is also found in the pressure dependence of strain coefficient $d\lambda/dH(= d_{33})$. Fig. 11 shows the strain coefficient $d\lambda_\parallel/dH(\propto d_{33})$ as a function of

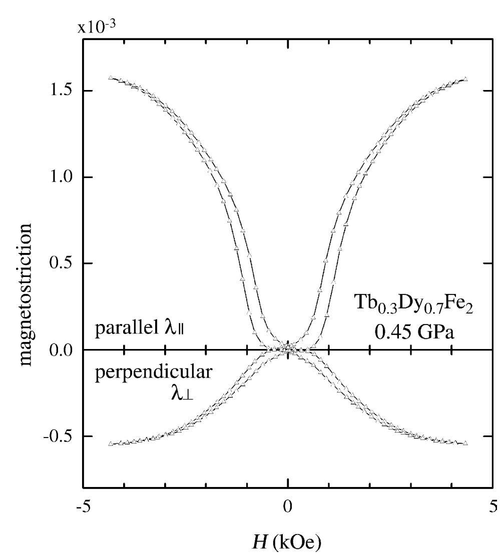

Fig. 9. Magnetostriction parallel to H ($\lambda_\parallel$) and perpendicular to H ($\lambda_\perp$) at 0.45 GPa.

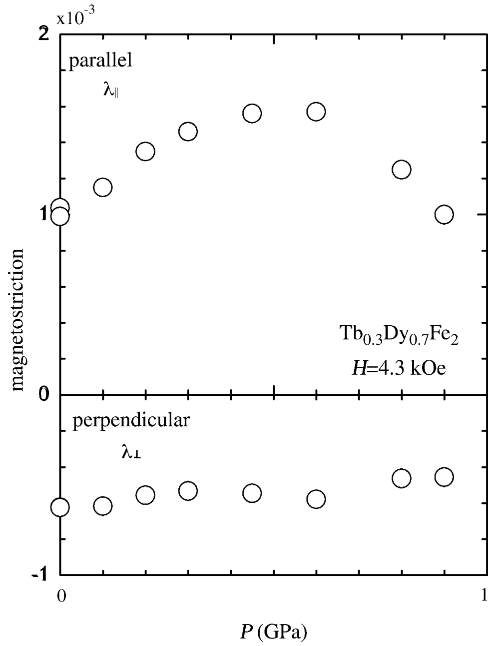

Fig. 10. $\lambda_{\parallel}$ and $\lambda_{\perp}$ at 4.3 kOe as a function of pressure.

hydrostatic pressure, in which a maximum appears around 0.45 GPa. In the case of uniaxial pressure, the maximum in d_{33} is observed around 3 MPa, which is about two orders of magnitude smaller than that at hydrostatic pressure [25]. Such difference is also found in the uniaxial pressure dependence of MS at 2 kOe [25], in which the maximum appears near 10 MPa but around 450 MPa in the hydrostatic case. These facts indicate that the effect of hydrostatic pressure is qualitatively the same as that of uniaxial pressure but different in the quantitative sense.

Clark et al. [23], presented a model to explain the field-induced jump in MS of $[1\,1\,\bar{2}]$ twinned Terfenol-D single crystal by considering Zeeman energy, the anisotropic energy barrier and the work required against the compressive load. They also assumed the direction of magnetic moment is parallel to [1 1 1] direction at $H = 0$ and by increasing H, the moment in one of the twins changes suddenly the direction by about 70° from [1 1 1] direction when Zeeman energy overcomes the anisotropic energy.

When the hydrostatic pressure is applied, the effect on the anisotropic energy is relatively smaller than that in the uniaxial case and then the jump in MS takes place at higher pressure than uniaxial pressure of several tens of Pa. But by applying hydrostatic pressure more than 0.45 GPa, it suppresses the anisotropic energy and the magnitude of MS decreases with increasing hydrostatic pressure. This consideration explains the results obtained in the present work.

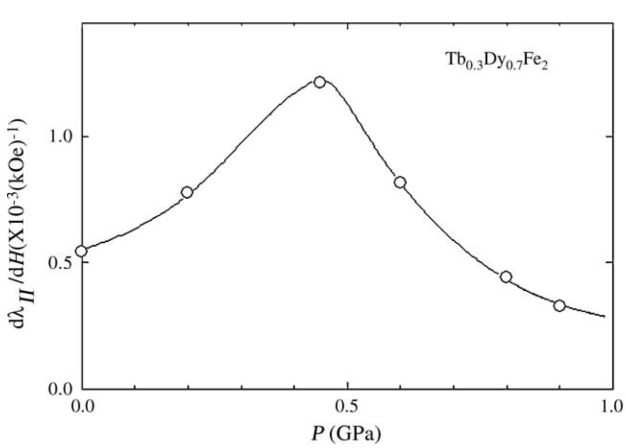

Fig. 11. Strain coefficient $d\lambda_{\parallel}/dH$ as a function of pressure.

4. Conclusion

The main results obtained in the present work are summarized as follows:

(1) The thermal expansion coefficients of $CeBe_{13}$ are affected strongly by applying pressure. This result indicates the density of states at the Fermi level decreases largely at high pressure and Grüneisen parameters decrease significantly with increasing pressure.
(2) The thermal expansion coefficients of $CeRh_2Si_2$ show two clear anomalies at the antiferromagnetic ordering temperatures but by applying pressure, these anomalies disappear above 1 GPa. By analyzing the data carefully, it is suggested that the thermal expansion coefficient anomalies still exist above the antiferromagnetic ordering temperature. We suggest a new phase in the P–T phase diagram.
(3) The magnetostriction of Terfenol-D increases with pressure below 0.4 GPa but it decreases above it. The comparison with uniaxial pressure was examined to show that the effect of hydrostatic pressure on GMS is extremely smaller than that of unaxial one.

References

[1] J. Zieglowski, et al., Phys. Rev. Lett. 68 (2003) 114428.
[2] T. Kagayama, et al., Physica B 199–200 (1994) 23.
[3] J.P. Teter, et al., J. Appl. Phys. 61 (1987) 3787.
[4] J. Röhler, et al., Nucl. Instr. Mech. 208 (1983) 647.
[5] B.H. Grier, et al., Phys. Rev. B 29 (1984) 2664.
[6] R. Movshovich, et al., Phys. Rev. B 53 (1996) 8241.
[7] F. Honda, et al., Magn. Soc. Jpn. 23 (1999) 474.
[8] G. Oomi, et al., J. Phys. Soc. Jpn. 59 (1990) 803.
[9] G. Oomi, T. Kagayama, Physica B 239 (1997) 191.
[10] T. Kagayama, G. Oomi, J. Magn. Magn. Mater. 90–91 (1990) 449.
[11] T. Kagayama, et al., J. Alloys Compd. 213–214 (1994) 387.
[12] T. Kagayama, G. Oomi, J. Phys. Soc. Jpn. 65 (Suppl. B) (1996) 42.
[13] T. Kagayama, et al., Physica B 230–232 (1997) 204.
[14] G. Oomi, et al., Physica B 281–282 (2000) 393.
[15] T. Graf, et al., Phys. Rev. Lett. 78 (1997) 3769.
[16] M. Ohashi, et al., Phys. Rev. B 68 (2003) 114428.

[17] S.S. Saxena, et al., Nature 426 (2001) 587.
[18] G. Oomi, et al., J. Phys.: Condens. Matter 15 (2003) S2039.
[19] See for example, S. Sachdev, Phys. World 12 (1999) 33.
[20] S. Araki, et al., Acta Phys. Polt. B 34 (2003) 439.
[21] G. Oomi, et al., J. Nucl. Sci. Technol. 3 (Suppl.) (2002) 90.
[22] K. Prajapati, et al., J. Appl. Phys. 73 (1993) 6171.
[23] A.E. Clark, et al., J. Appl. Phys. 63 (1988) 3910.
[24] J. Wang, et al., J. Appl. Phys. 79 (1996) 4668.
[25] J.P. Teter, et al., J. Appl. Phys. 67 (1990) 5004.