Thermal expansion and magnetostriction measurements using a Quantum Design Physical Property Measurement System

Oshi Iwakami, Naoaki Kawata, Misato Takeshita, Yusuke Yao, Satoshi Abe and Koichi Matsumoto
Department of Physics, Kanazawa University, Kanazawa, Ishikawa 920-1192, Japan
E-mail: ou4.e-66@stu.kanazawa-u.ac.jp

Abstract. Capacitive dilatometers that could be installed in a Quantum Design Physical Properties Measurements System (PPMS) were developed. Two types of dilatometers were constructed. One dilatometer was compact enough to be installed in small magnet bore of various cryostats and had a reference capacitor so that high sensitivity and stability were achieved. The other dilatometer with a movable capacitor supported by a flat spring enabled to measure large strain and exchange samples easily. We measured the thermal expansion and magnetostriction of single crystalline clathrate compound Pr$_3$Pd$_{20}$Ge$_6$ and polycrystalline hydrogenated La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$ in the temperature range between 2 and 340 K and magnetic field up to 8 T. The dilatometers allowed to detect the strain responses with a sensitivity of 10 ppb. We could measure strain from $10^{-8}$ to $10^{-3}$ using two dilatometers.

1. Introduction
Thermal expansion and magnetostriction, the strain responses of a material to temperature and a magnetic field, are thermodynamic quantities closely related to specific heat and magnetization. These quantities are very useful to study electronic and phononic properties, phase transitions, quantum criticality, and other interesting phenomena [1]. Quantum Design Physical Properties Measurements System (PPMS [2]) has been widely used for measurements of thermodynamic quantities, such as specific heat, magnetization, electrical resistance, and thermal conductivity.

In this report, we present the thermal expansion and magnetostriction measurements using homemade capacitive dilatometers installed in a PPMS in the temperature range of 2 to 340 K and magnetic fields up to 8 T. Capacitive dilatometers have been used in various thermal expansion and magnetostriction measurements because capacitive methods give very high sensitivity in detecting small length changes [3]. We developed a compact capacitive dilatometer that was installed in a dilution refrigerator [4], and quantum criticality was studied for CeRu$_2$Si$_2$ [5]. Similar dilatometer was made in order to measure thermal expansion and magnetostriction using a PPMS in higher temperature and magnetic field. Using this system, we observed temperature and magnetic field dependence of the linear thermal expansion of single crystalline Pr$_3$Pd$_{20}$Ge$_6$. This compound has attracted attention because of the electric quadrupole order of 4$f$-electrons and a rattling motion of a guest rare-earth ion in an oversize cage [6]. There are lots of magnetic materials that have large thermal expansion and magnetostriction around magnetic phase transition. For example, La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$ has been
Figure 1. Schematics of the capacitive dilatometers. (1) brass screws, (2) upper holder, (3) fixed capacitor plate, (4) movable capacitor plate, (5) lower holder, (6) cigarette paper and Stycast, (7) gap \( D \), (8) sample (length \( L \)), (9) silver paste, (10) flexible coaxial cables, (11) copper foil spacers, (12) stainless screws, (13) BeCu flat spring, (14) locknut, (15) sample platform. (16) Stycast studied as a magnetic refrigerant for magnetic refrigeration because of the giant magnetocaloric effect around the ferromagnetic phase transition at the Curie temperature \( T_c = 195 \) K. The working temperature range having large magnetocaloric effects is around \( T_c \). \( T_c \) of La(Fe\(_{0.88}\)Si\(_{0.12}\))\(_{13}\) is shown to be increased up to about 330 K by hydrogen absorption \[7\]. Therefore, this material is expected as magnetic refrigerant for room temperature magnetic refrigerator. Volumetric change around transition is thought to contribute significantly to the giant magnetocaloric effects in this material \[8, 9\]. In order to measure large strain, we developed new capacitive dilatometer that had a movable capacitor supported by a flat spring. This dilatometer was used to measure linear thermal expansion of hydrogenated La(Fe\(_{0.88}\)Si\(_{0.12}\))\(_{13}\). It was confirmed that these dilatometers worked with enough sensitivity and stability.

2. Dilatometers

When a capacitive dilatometer with a pair of capacitor plates is used, the dilation \( \Delta L \) due to longitudinal thermal expansion and magnetostriction of a sample with length \( L \) is measured as a change in the gap \( D \) between capacitor plates. Many types of capacitive dilatometers have been developed for various experiments, such as absolute-expansion dilatometers \[1\], dilatometers with an open-architecture sample mounting arrangement \[10\], and small dilatometers for magnet systems \[3\]. Figure 1 schematically illustrates two different types of capacitance dilatometers used in the present study. Most of the parts were made of oxygen-free high-conductivity (OFHC) copper. Our dilatometers were small enough to be installed in a PPMS. The dilatometer of type A which has a composite structure with a reference capacitor was constructed similarly to the one used in our previous studies \[4, 5\]. The dilatometer of type B has a movable capacitor supported by a flat spring made of 0.1 mm thick BeCu that was annealed at 315 °C for about 3 hours. Movable capacitor plate supported by a spring is used by other researchers such as Schmiedeshoff et al. \[10\]. The spring is insulated from the movable capacitor plate using kapton films. The sample was glued to the sample platform with Arzerite VL-10 silver paste. The platform was adjusted by screw thread so that the sample was touched softly to the movable capacitor plate, then the platform was fixed with locknut. Sample and capacitor plate were
insulated with thin layer of Stycast 2850GT. The fixed capacitor plate is attached to the upper holder with Stycast 2850FT using cigarette paper for insulation. The flexible, silver-coated copper coaxial cables as electrical leads were glued to the side of the capacitor plate using silver epoxy Eccobond 56C. The surfaces of the capacitor plate and holder were sandpapered to be flat, smooth, and coplanar. The gap \( D \) was adjusted by the thickness of the copper foil spacers and monitored by capacitance bridge. The parallelism and the edge effect of two capacitor plates in the dilatometer of type A has been discussed in our previous study [4]. The dilatometer of type B was checked and calibrated in the same way as Ref. [10], and was used within the range of linear response to the gap.

3. Experimental procedures

We have measured the thermal expansion and magnetostriction of \( \text{Pr}_3\text{Pd}_{20}\text{Ge}_6 \) using the dilatometer of type A. The single crystal of \( \text{Pr}_3\text{Pd}_{20}\text{Ge}_6 \) used in our investigation was from the same batch of high-quality samples, grown by a floating zone method, for ultrasound and ac-susceptibility experiments [6, 11]. The sample size of \( \text{Pr}_3\text{Pd}_{20}\text{Ge}_6 \) was about \( 4 \times 4 \times 6 \) mm\(^3\). The polycrystalline hydrogenated \( \text{La(Fe}_{0.88}\text{Si}_{0.12})_{13} \) was measured using the dilatometer of type B. \( T_c \) of the present sample was determined as 313 K by magnetization and specific heat measurements. The sample size of \( \text{La(Fe}_{0.88}\text{Si}_{0.12})_{13} \) was about \( 5 \times 5 \times 5 \) mm\(^3\).

The capacitive dilatometers were installed in a PPMS using the homemade insert that had two coaxial cables for capacitance bridge and a cernox resistance thermometer (Lake Shore) that was thermally anchored near the dilatometer. Capacitance was determined by a digital capacitance bridge (Andeen-Hagerling, 2500A [12]).

For an ideal parallel-plate capacitor with area \( A \) and gap \( D \), the capacitance is given as \( C = \epsilon_r\epsilon_0A/D \), where \( \epsilon_0 = 8.854 \times 10^{-12} \) Fm\(^{-1} \) and \( \epsilon_r \) is the dielectric constant of the medium between pair of capacitor plates. In our experiments, the medium is gaseous helium for heat transfer in a sample chamber of the PPMS, and the chamber pressure varied from about 1.3 to 0.03 kPa in the temperature from 300 to 2 K. Though the dielectric constant of the gas depends on the gas density, we can assume \( \epsilon_r = 1 \) since even at atmospheric pressure helium has \( \epsilon_r \) very close to unity (\( \epsilon_r = 1.00007 \) at 273 K [13]). The relative capacitance change \( \Delta C/C \) due to change in \( \epsilon_r \) was estimated on the order of \( 10^{-6} \) (\( \Delta L/L \sim 10^{-8} \)) and was sufficiently smaller than that due to the dilation of the sample.

The observed gap change \( \Delta D \) is caused by difference between sample dilation \( (\Delta L)_{\text{Sample}} \) and dilation of a copper cell body \( (\Delta L)_{\text{Cu}} \) as \( -\Delta D = (\Delta L)_{\text{Sample}} - (\Delta L)_{\text{Cu}} \). In this study, the thermal expansion of \( (\Delta L)_{\text{Cu}} \) was calculated using that of copper from the Ref. [14, 15, 16], and the magnetostriction of the one was negligible. As discussed by Pott and Schefzyk [17], \( \Delta D \) also contains unspecified gap change that is known as “cell effect”. It is thought that the cell effect is originated from epoxy, silver paste, and so on. The cell effect can be determined by measuring a copper standard sample. The cell effects of our two dilatometers were almost the same. The temperature dependence of the cell effect was confirmed to be small compared to the dilation of our sample as shown in Fig. 2. The field dependence of the cell effect was negligibly small compared to the dilation of the sample. In this paper, we show the thermal expansion and the magnetostriction including the cell effect.

4. Results and discussion

We can measure strain \( \Delta L/L \) from \( 10^{-8} \) to \( 10^{-3} \) using two dilatometers. Figure 2 shows the temperature dependence of linear thermal expansion of \( \text{Pr}_3\text{Pd}_{20}\text{Ge}_6 \) along the [001] axis in zero magnetic field and 8 T. No hysteresis was observed in the temperature sweeps. In zero magnetic field, the thermal expansion decreases monotonically with decreasing temperature down to 2 K. The magnitude of \( \Delta L/L \) from 300 to 2 K is about \( 2.5 \times 10^{-3} \). In 8 T, the thermal expansion was almost the same as that in zero magnetic field.
Figure 2. Temperature dependence of linear thermal expansion of Pr$_3$Pd$_{20}$Ge$_6$ along the [001] axis. Open circles ◦ and open triangles △ represent the $\Delta L/L$ in zero magnetic field and 8 T, respectively. The solid line shows the cell effect.

Figure 3 shows the temperature dependence of linear thermal expansion of polycrystalline hydrogenated La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$. As shown in Fig. 3, large negative thermal expansion was observed in the temperature range of 300 to 320 K. Small hysteresis was also observed in the temperature sweep. In this temperature range, the cell effect of the dilatometer of type B was negligibly small compared to the sample dilation. Figure 4 shows the field-dependence of the isothermal linear magnetostriction as a function of $H^2$ at several temperatures. In paramagnetic phase, the magnetostriction increased approximately in proportion to the squared magnetic field. Large magnetostriction was observed near the transition temperature. In ferromagnetic phase, the magnetostriction showed saturation.

We checked a magnetic torque effect. In a magnetic field, the magnetic anisotropy and the ferromagnetic domain may lead to a torque on the sample. Pr$_3$Pd$_{20}$Ge$_6$ has magnetic anisotropy, and [001] axis is the axis of hard magnetization. The hydrogenated La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$ shows ferromagnetic phase transition at 313 K. By measuring magnetostriction in positive and negative directions, it is possible to distinguish the torque effect from magnetostriction. The magnetostriction of Pr$_3$Pd$_{20}$Ge$_6$ at 2 K and La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$ at 310 K were measured in both directions up to 8 T and 5 T, respectively. In each sample, the measured magnetostriction for both directions was identical. This result indicates that the torque effect was small for these samples. We thought that it was hard to detect of magnetic torque effect in our measurements since the magnetization of Pr$_3$Pd$_{20}$Ge$_6$ was small in paramagnetic phase and our La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$ sample was polycrystal and hysteresis was small.

5. Summary
We constructed two different dilatometers that could be used with a PPMS. We measured thermal expansion and magnetostriction of Pr$_3$Pd$_{20}$Ge$_6$ and hydrogenated La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$. Our dilatometers allow to detect the strain responses with a sensitivity of 10 ppb. We can measure strain from $10^{-8}$ to $10^{-5}$ using two dilatometers.

Acknowledgments
This work was supported in part by Grants-in-Aid for Scientific Research from MEXT and JSPS of Japan. We thank T. Goto and H. Kitazawa for providing the sample, and K. Nunomura for technical assistance.
Figure 3. Temperature dependence of linear thermal expansion of hydrogenated La(Fe_{0.88}Si_{0.12})_{13}. Open circles $\bigcirc$ and open triangles $\triangle$ represent the $\Delta L/L$ in warming and cooling, respectively. Broken line represents the ferromagnetic phase transition temperature.

Figure 4. Field-dependence of the isothermal linear magnetostriction of polycrystalline hydrogenated La(Fe_{0.88}Si_{0.12})_{13}. Open circles $\bigcirc$, open triangles $\triangle$, open diamonds $\diamond$, and open squares $\square$ represent the $\Delta L/L$ at 340, 315, 310, and 280 K, respectively.

References
[1] Barron T H K and White G K 1999 Heat Capacity and Thermal Expansion at Low Temperatures International Cryogenics Monograph Series (New York, NY : Plenum) and references therein
[2] Quantum Design, 11578 Sorrento Valley Rd., San Diego, CA 92121.
[3] Rotter M, Müller H, Gratz E, Doerr M and Loewenhaupt M 1998 Rev. Sci. Instrum. 69 2742–6 and references therein
[4] Abe S, Sasaki F, Oonishi T, Inoue D, Yoshida J, Takahashi D, Tsuji H, Suzuki H and Matsumoto K 2012 Cryogenics 52 452–6
[5] Yoshida J, Abe S, Takahashi D, Segawa Y, Komai Y, Tsuji H, Matsumoto K, Suzuki H and Ônuki Y 2008 Phys. Rev. Lett. 101(25) 256402
[6] Ane G et al. 2012 J. Phys. Soc. Jpn. 81 034710
[7] Fujita A, Fujieda S, Hasegawa Y and Fukamichi K 2003 Phys. Rev. B 67(10) 104416
[8] Fujita A, Fujieda S, Fukamichi K, Matamura H and Goto T 2001 Phys. Rev. B 65(1) 014410
[9] Fujieda S, Fujita A, Fukamichi K, Yamazaki Y and Iijima Y 2001 Appl. Phys. Lett. 79 653
[10] Schmiedeshoff G M et al. 2006 Rev. Sci. Instrum. 77 123907 and references therein
[11] Iwakami O et al. 2014 Phys. Rev. B 90(10) 100402
[12] Model 2500A digital capacitance bridge manufactured by Andeen-Hagerling, Inc., 31200 Bainbrigde Road, Cleveland, Ohio, USA.
[13] Kessom W H 1942 Helium (Amsterdam: Elsevier)
[14] Nix F C and MacNair D 1941 Phys. Rev. 60(8) 597–605
[15] Rubin T, Altman H W and Johnston H L 1954 J. Am. Chem. Soc. 76 5289–93
[16] Kroeger F and Swenson C 1977 J. Appl. Phys. 48 853–64
[17] Pott R and Schefzyk R 1983 J. Phys. E: Sci. Instrum. 16 444