Development of a pressure cell using a beta-titanium alloy for a Differential Scanning Calorimeter

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Abstract. We have developed downsizing a piston-cylinder clamp-cell to measure a specific heat under pressure using a commercial Differential Scanning Calorimeter (Shimadzu DSC-60 plus). The downsized cell with a diameter of 6.0 mm and a height of 5.0 mm has been achieved by a simplification of the cell design and using a high-yield-strength alloy of β-titanium (KOBELCO, KS15-5-3). The cell allows us to achieve pressures of 0.7 GPa at room temperature as our designed value. As a demonstration of the cell, we have measured the specific heat anomaly due to the first-order transition at around 357 K in Ca2RuO4. The pressure variation of the transition temperature indicates that our cell allows us to achieve pressure of ~0.3 GPa. Moreover, we have estimated that a heat capacity of ~0.6 mJ/K is fully possible to measure within β-Titanium cell as absolute accuracy.

1. Introduction

As well known, pressure is a key tool to tune the electronic states indirectly via the change of lattice parameters. In particular, a phase transition can be controlled by applying pressure. Measurements of electrical transport, magnetization and x-ray diffraction have been progressed by pressure techniques. In contrast, a specific heat, C, is the most suitable tool to understand the phase transitions thermodynamically. A specific heat at ambient pressure has generally been measured by using adiabatic [1], thermal relaxation [2], alternating current [3] and Differential Scanning Calorimetry; however, it is quite difficult to measure C at around a first-order transition under pressure and in the wide temperature range.

Our attention has been paid to the metal-insulator (M-I) transition accompanied by structural change in the Mott insulator Ca2RuO4 (CRO) [4]. The M-I transition can be induced by heating above ~360 K, pressurising over 0.5 GPa and applying electric field over 40 V/cm. Moreover, CRO shows a variety of novel quantum phenomena, such as an antiferromagnetic (AFM) Mott insulator, a ferromagnetic quasi-two-dimensional metal and an unconventional superconductivity under pressure. In particular, there has recently been growing interest in the negative thermal expansion observed in the wide temperature range below ~360 K [5]. Thus, we have strong concern to understand the thermodynamics in CRO. However, there has been a lack of the thermodynamic data at around TM-I. This is because the transition accompanied by a latent heat is difficult to detect by using a thermal relaxation calorimetry, which has been the most popular method for researchers in low temperature physics to measure a specific heat as the recent trend.

In contrast, thermodynamics information related to a transition accompanied by a latent heat can be
obtained by using a Differential Scanning Calorimetry, which is popular method for chemists. However, the smallness of the sample space prevents us to equip a typical piston-cylinder clamp-cell. We report here a development of downsizing a piston-cylinder clamp-cell to measure a specific heat under pressure using a commercial Differential Scanning Calorimeter (DSC).

2. Design of the pressure cell

In order to measure \( C(T) \) in the vicinity of the first-order transition in CRO, we have used a heat flux type DSC system (Shimadzu DSC-60 plus). The measurement was performed in the temperature range between 130 and 873 K. The sample space of our DSC system is \( \phi 6.0 \times 5.0 \) mm; however, it is too small to equip a typical size of a piston-cylinder clamp-cell (i.e., \( \phi 22 \times 40 \) mm for our PPMS). Thus, drastically downsizing the pressure cell is required. Moreover, our goal of pressurisation is above 0.5 GPa, and it might be achieved by using a high-yield-strength alloy and a simplification of the cell design. In the Differential Scanning Calorimetry, absolute value of \( C(T) \) can precisely be obtained by a heat flux differential between a sample and a reference cells. For this, it is necessary to conform the cell's geometry and weight precisely.

The details of the sample chamber of our DSC-60plus instrument is illustrated by figure 1(a). Reference and sample cells are equipped with the left and the right sides of the chamber, respectively. Circle line indicates the maximum diameter of the reference cell is \( \phi 6.0 \). In contrast, figure 1(b) shows a cross-sectional view of our piston-cylinder clamp-cell. The diameter and the height are \( \phi 6.0 \) and 5.0 mm, respectively. A simplification of the cell design and using a high-yield-strength alloy is key of the downsizing. In concrete, a number of the parts was reduced from eleven to four. The downsized cell consists of an outer cylinder, a piston, a Teflon sheet and a Teflon tube. We took out a pressurisation system outside of the cell as mentioned next section, and the sample was pressurised by tightening an end screw used as the piston.

To establish both downsizing of the piston-cylinder clamp-cell and attain high sensitivity of the measurement, we must take into consideration both powerful tensile strength of materials and a small heat capacity. In table 1, some alloys CuBe, NiCrAl, WC, MP35N and \( \beta \)-Ti are compared as a candidate for the cell. We use the \( \beta \)-Titanium alloy (KOBELCO, KS15-5-3) [6] is the most suitable material for

![Figure 1](image-url). (a) Top view of the sample chamber of the DSC-60 plus. There are reference and furnaces of Circle indicates the maximum size of \( \phi 6.0 \) diameter. (b) Cross-sectional view of our pressure cell.
Table 1. Mechanical and thermodynamic properties of the materials at room temperature (RT). The bulk densities and specific heats have been measured in the present study.

|                         | CuBe | NiCrAl | WC   | MP35N | β-Titanium |
|-------------------------|------|--------|------|-------|------------|
| Tensile Strength (GPa)  | > 1.00 GPa\(^7\) | 2.00 GPa\(^8\) | 1.77 GPa\(^9\) | 2.0 GPa\(^{10}\) | 1.76 GPa\(^6\) |
| Bulk density (g/cm\(^3\)) | 8.3  | 7.9    | 15.1 | 8.4   | 4.7        |
| Specific heat (J/K·g)   | 0.36 | 0.32   | 0.17 | 0.39  | 0.45       |
| Heat capacity (J/K·cm\(^3\)) | 3.0  | 2.5    | 2.6  | 3.3   | 2.1        |

Table 2. Mass and thermodynamic properties of the materials used in the pressure cell at RT.

|                      | Daphne oil 7373 | Teflon tube & sheet | β-Titanium |
|----------------------|-----------------|---------------------|------------|
| Mass in a cell (mg)  | ~5              | ~15                 | ~400       |
| \(C_p\) (J/K·g)     | 2.0             | 0.78                | 0.45       |
| Heat capacity (mJ/K) | ~10             | ~12                 | ~180       |

our cell because of good tensile strength and the smallest heat capacity per unit volume. By using this alloy, we can obtain the expected maximum pressure \(P_{\text{max}} \approx 0.7\) GPa from the following equation:

\[
P_{\text{max}} = \frac{\sigma_y(b^2 - a^2)}{2b^2}
\]

where we use the tensile strength \(\sigma_y = 1760\) MPa, the inner diameter \(a = 4.0\) mm and the outer diameter \(b = 6.0\) mm.

3. Measurements

Two of pressure cells are equipped with each of the sample and the reference furnaces. In order to improve the accuracy of the measurement, differences in the weight of the each cells were balanced within 5%. In figure 1(b), we illustrate a schematic view of our pressure cell. A Teflon tube with an inner space of φ3.0 diameter and 2 mm height was put into the cylindrical β-Titanium cell. The several pieces of crystal were put into the cell with Daphne oil 7373 (Idemitsu Kosan Co., Ltd.) as a pressure-transmitting medium [10]. Our pressurising procedures are shown in figure 2. The force from hydraulic press system was loaded to the screw cap via a hard metal sphere and a ratchet wrench. The sample was pressurised, and then it finally sealed by applying a torque to the Teflon-coated screw cap. Table 2 shows mass and thermodynamic properties of the materials used in a pressure cell at RT. The ratio of the oil and the Teflon components to the pressure cell was within ~10%.

To demonstrate the performance of this cell, we used single crystals of CRO grown by a floating-zone method with RuO\(_2\) self-flux. Several pieces of crystal with total masses of 3-5 mg were put into the pressure cell. Figure 3 shows specific heat \(C\) in the vicinity of the M-I transition at several pressures as a function of temperature. The peak temperature is reduced with pressurising. Such reductions have been observed in the M-I transition as same as with temperature, electric field, and substitution of Sr for Ca[4,12,13]. The generated pressure \(P\) can be estimated by determining the M-I transition temperature \(T_{M1}\) of CRO[14], the pressure dependence \(dT_{M1}/dP\) is well described as \(dT_{M1}/dP = -114\) K/GPa. In this measurement, hydrostaticity most likely be kept since there is little broadening of the peak in \(C(T)\)
We can obtain the maximum pressure in this measurement to be 0.3 GPa from the shift of $\Delta T_{M-I} \sim 35$ K, so far. The further high-pressure can fully expected from our designed cell.

Let us next evaluate the accuracy of $C$ measurement by utilizing the $\beta$-Titanium cylinder. In principle, the DSC should not detect signals of the cell, the Teflon tube, the pressure medium and so forth by subtracting the heat flow of the reference cell from that of the sample one by a measurement. However, mechanical inhomogeneity of the cell and variations in the weights of loading materials in the cell, might influence on the background of $C$. In the DSC measurement under pressure, signals within $\sim 0.2$ J/g·K was occasionally obtained in background level. From the background we evaluate the minimum measurable value of the heat capacity within the $\beta$-Titanium cell to be $\sim 0.6$ mJ/K. That is, $T_{M-I}$ can be detected by using CRO samples over than $\sim 3$ mg, as absolute accuracy.

In conclusion, a pressure cell for a DSC has been developed by utilizing $\beta$-Titanium alloy; this cell allows us to pressurise up to 0.3 GPa. The minimum heat capacity measurable within the cell is $\sim 0.6$ mJ/K.

**Figure 2.** Our pressurising system of the pressure cell.

**Figure 3.** DSC profiles at various pressures. The curves normalized at $T_{M-I}$ correspond to $C(T)/C(T_{M-I})$. Red, Green and Blue colors indicate those of ambient pressure, pressurised and more pressurised, respectively. The figures on the profiles denote temperatures of peak positions.
mJ/K at \(\sim\)RT. The maximum pressure that we can generate is now limited not by the cylinder but by the piston with poor toughness. Moreover, downsizing of pressure cell allows us to reduce the heat capacity of the cell and enables a wide variety of measurement at low temperature by using commercial instruments such as MPMS, PPMS (Quantum Design Inc.) and dilution refrigerator.

Acknowledgment
A part of this work was supported by JSPS KAKENHI Grant Numbers JP26247060 and JP17H06136.

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