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Article

High-Pressure AC Calorimetry System Using Pt Chip Thermometer

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A high-pressure ac calorimetry system available between 20-200 K and 0-1.2 GPa was constructed for measuring ac heat capacities of single crystals and pellet samples with 0.5-5 mg. We used a thin film Pt chip sensor in order to cover this temperature region. We report temperature and pressure dependences of the resistance of Pt sensor which ensure the availability in high-pressure measurements. We also introduced a set of DC amplifiers and filters for minimizing noise in the signal line efficiently. Using this apparatus, thermodynamic data of Fe_3O_4 which shows a charge order (CO) transition accompanied by a step like change in temperature dependence of magnetization are presented. The heat capacity peak observed around 124 K was found to be broadened under external pressure of 1.05 GPa.

Keywords: Heat capacity, Pressure, AC calorimetry, Fe_3O_4, Phase trensition.

1. Introduction

To measure heat capacity of small amount of samples under various external pressures has been an important subject to attain in the chemical thermodynamics of condensed matter systems. The application of pressure can decrease inter-atomic or inter-molecular distance in the condensed phases and produces various kind of transformations in structures, molecular or atomic arrangements, dielectric and magnetic properties, and transport properties which are dominated by orbital overlap between neighboring atoms and molecules. In molecule based compounds such as charge transfer complexes of electron donors and electron acceptors, to study physical properties under pressures is widely performed. Electronic structures of these compounds are sensitively affected by molecular stacking in the crystal and various kind of insulator to metal transitions such as Mott transition, density wave (DW) formation *etc*.[1-4] occurs in them. A delicate valance of electron correlation, electron-phonon interaction, and band-width *etc*. can be controlled by pressures. Furthermore, drastic neutral to ionic transitions[5-9] in mixed stacked donor-acceptor compounds are induced by applying pressures. It is also important to point out that in these molecular compounds, drastic changes of electronic properties occurs by relatively weak pressures attained easily by handy cramp type pressure cell made of Cu-Be alloy. In spite of these fascinating possibilities of high pressure researches of molecular compounds, the calorimetry under pressure is not performed so widely up to now. The existence of pressure medium cannot attain adiabatic condition which is essential to perform accurate measurements by usual adiabatic technique and thermal relaxation technique. Well known way to explore absolute calorimetry is high-pressure adiabatic technique in which one can measure heat capacity of sample with pressure cell and subtracted the data of it as addenda heat capacity[10]. This method usually requires large amount of sample in the order of 10^{0-1} grams whose heat capacity should be comparable with that of the cramp cell and the experiments performed by this method is limited to several cases. Due to the difficulties of this adiabatic method, the heat capacity measurements under pressure have been performed mainly by ac calorimetry technique by several groups[11].

In 2008, Kubota *et al*.[12] reported a new high-pressure ac calorimetry apparatus available at low temperature region and under magnetic fields. The important idea in their apparatus is to use tiny ruthenium oxide chip (KOA Co. Ltd.) as a thermometer and sensitive detection by the four probe technique which is reliable for monitoring temperature change around the sample becomes possible. The usage of high-precision ac resistance bridge combined with lock-in amplifier has improved the S/N ratio of the ac signals at low temperature region. Using this technique, they detected qualitative changes of thermodynamic properties of single-molecular magnets behaviors in Mn_4 cluster complexes[12-14]. Subsequently, Tokoro *et al*.[15] succeeded in detecting thermal anomaly related to superconductive transitions of 10 K class organic superconductors consisting of BEDT-TTF molecules and counteranions. Although there still remains serious difficulty in subtracting background heat capacity, the improved sensitivity using the ac bridge is fascinating for detecting phase transitions of compounds.

The ruthenium oxide chip adopted by Kubota *et al*.[12] are useful for experiments at low temperatures below 10 K and under magnetic fields. However, to study more detail physical properties by thermodynamic measurements, the data in a wide temperature range is necessary. To apply this ac technique in higher temperature region, we constructed a high-pressure ac calorimetry system by the usage of chip-type thin film Pt sensor. We tested the performance of the apparatus by measuring heat capacity of Fe_3O_4 with various pressures up to 1.0 GPa to see how the phase transition predicted by Verwey *et al*.[16-17] changes by applying pressures.

2. Experimental

2.1 Construction of the apparatus

The fundamental idea and experimental setup of the present high-pressure calorimeter is similar to that reported by Kubota *et al*. [12] constructed for the purpose of measuring heat capacity of molecular magnets.

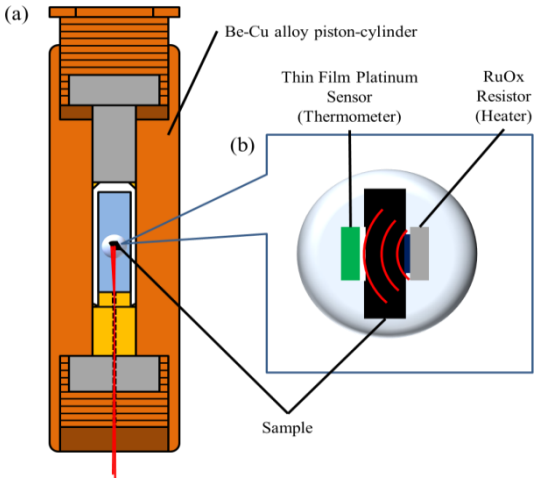

Fig. 1 (a) Cramp type pressure cell made of Cu-Be alloy. (The diameter of the sample space is ϕ6 mm). (b) Sample part of the ac calorimetry. Ruthenium oxide chip is used as a heater and platinum chip is used as a thermometer. The sample part is covered by Stycast 1266 or 2850FT.

We used cramp type pressure cell made of Cu-Be alloy available up to about 1.2 GPa. The diameter of the sample space is ϕ6 mm. A schematic illustration of the pressure cell and sample arrangement is shown in Fig. 1(a). We used Daphne 7373 oil (Idemitsu Co. Ltd.) as a pressure medium to get hydrostatic pressure and sealed them in a Teflon capsule with a sample and a sensor[18]. The pressure cell was covered by the cell holder made of oxygen free copper to attain good thermal equilibrium inside the cell. In order to get good thermal contact between pressure cell and the holder, Apiezon-N grease was glued between the pressure cell and the Cu holder.

The sample part of the ac calorimeter is shown in Fig. 1(b). We used a chip type Pt sensor instead of ruthenium oxide sensor reported by Kubota *et al*.[12] in order to perform measurements above 20 K. The size of the sensor is 1.20 mm× 1.71 mm× 0.9 mm whose volume is about four times larger than that of ruthenium oxide chips. This chip sensor was adhered on a surface of a single crystal or pellet samples (ϕ1.5 mm) with small amount of GE7031 vanish. On the other side of the sample, we also attached a 1 kΩ ruthenium oxide chip which worked as a heater. In order to get good thermal contact between sample and two chips used as a heater and a thermometer, the sample part was coated by small amount of stycast 1266 or 2850FT (Emerson & Cuming, Inc.) as is shown in Fig. 1(b). The Pt chip resistance sensor used as a sample thermometer was supplied by Teijin engineering company of which good reproducibility against thermal cycling was studied already in different experiment. We selected a sensor with room temperature resistance of 100 Ω so as to measure accurate resistance with the high-precision ac resistance bridge usually available between 0-400 Ω (ASL F700). The residual resistance of this Pt chip was 0.80 Ω at the liquid helium temperature. We confirmed that the chip resistance at room temperature shows almost the same values up to 1.05 GPa. The temperature dependence of the chip resistance obtained under several pressures is shown in Fig. 2.

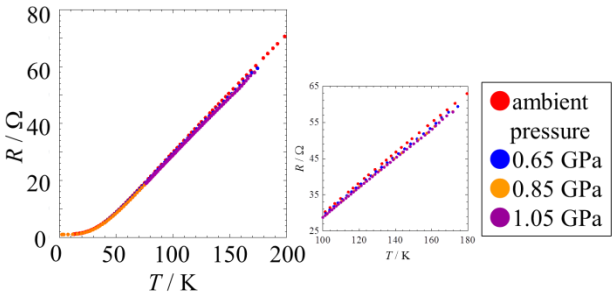

Fig. 2 Temperature dependences of the Pt resistance thermometer obtained under several pressures.

It obeys typical temperature dependence of resistance curvature of metals and the sensitivity of the thermometer determined by the slope of the curvature is almost constant between 40 K and 200 K. The pressure dependence of the resistance was found to be very small up to 1.05 GPa. The sensor recovered its original behavior after releasing the pressure from 1.05 GPa to ambient pressure. Therefore, we concluded that this Pt chip was available even under pressures in the cramp-cell region.

The high-pressure calorimetry system shown in Fig. 1 was mounted on a ^{4}He cryostat. The sample cell was sealed in vacuum can made of brass using wood alloy and the sample space was evacuated down to 10^{-4} Pa by diffusion pump system. The structure of the cryostat system is also shown in Fig. 3.

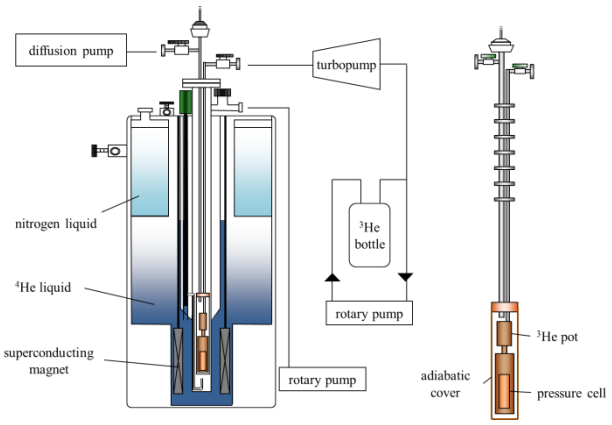

Fig. 3 A schematic view of the cryostat and VTI system.

It was inserted in the sample space of variable temperature insert (VTI) system equipped with 8 T superconductive magnets. The temperature of the VTI system can be controlled from 1.8 K to 300 K.

In this paragraph, we explain the detection system. We show schematic drawing of the block diagram to obtain temperature modulation signal in Fig. 4. An on/off DC current within a frequency range between 0.05 Hz and 30 Hz was supplied by DC current source (Keithley 220) to the chip type resistance heater to induce a temperature oscillation around the sample part. The temperature of the chip was measured by the high-precision ac bridge. By monitoring the analogue output voltage corresponding to the error signal of the measured resistance from the set point value to valance the bridge, we detected the temperature modulation of the sample part. We confirmed the

existence of the modulation signal by an oscilloscope. Large noises in the output signal were deleted by low-pass filters system (Yokogawa 3131 & 3132) and band pass filter (SR-560) and finally oscillation signal was amplified by lock-in amplifier (SR-850). This multi-step filtering system works efficiently to cut the noise level of small ac signal. Since the size of the sample part including chips of the present system was larger than that reported by Kubota *et al.* [12], we selected lower frequency in the present set up. Since the frequency dependence of the ac amplitude had a broad peak around 10^{-1}-10^{0} Hz's, we determined the frequency of 0.5 Hz for this experiment. The temperature of the pressure cell and that of VTI were controlled by different temperature controller (Lake Shore Model 340) using the calibrated cernox thermometers (Lake Shore) so as to avoid temperature gradient inside the sample cell.

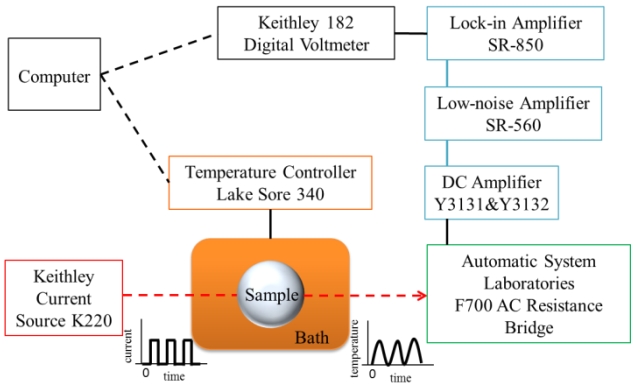

Fig. 4 The block diagram of the signal detection system to obtain temperature modulation signal under pressures.

3. Results and Discussion

3.1 Heat Capacity of Fe_3O_4

In Fig. 5, we show temperature dependence of the ac heat capacity of Fe_3O_4 sample obtained by this high-pressure ac calorimetry system. In this work, the powdered sample of Fe_3O_4 (3N) was pelletized into a disk with a diameter of ϕ 1.5 mm and thickness of about 0.5 mm. The weight of the pellet was 2 mg. The magnetization data of the powder sample from the same batch are shown in Fig. 6. We can confirmed that the temperature dependence of magnetization of this sample shows a step like anomaly around 124 K that is known as the Verwey transition. This fact demonstrates that the electronic states surely changes at this temperature and the sample quality is enough well for studying the phase transition by thermodynamic measurements. The temperature dependence of C_p between 80 K and 200 K is monotonous except for a sharp peak and C_p increased gradually with the increase of temperature as is predicted by simple Debye model. The data shown in Fig. 5 are C_p vs T plot between 110 K and 140 K. We observed a sharp peak around 124 K, corresponding to the thermal anomaly of the Verwey transition. The heat capacity shows a single peak structure as is reported by adiabatic calorimetry by Takai *et al.*[19] and there is no tendency of formation of double transition as is reported by Evans *et al.*[20] in the old data. However, the peak was broadened gradually by applying pressure of 0.45 GPa, 0.65 GPa, 0.85 GPa and 1.05 GPa. The fine structure seems to appear around 0.45 GPa and 0.85 GPa, probably due to inhomogeneous distribution of micro domains of CO phase. The resistivity measurement by Rozenberg *et al.*[21] shows that the resistivity increases drastically below the phase transition temperature. The application of external pressures gradually suppresses this transition.

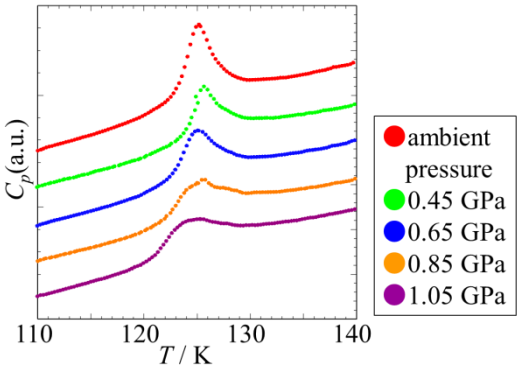

Fig. 5 Temperature dependence of ac heat capacity of Fe_3O_4 between 110 K and 140 K and under pressure up to 1.05 GPa.

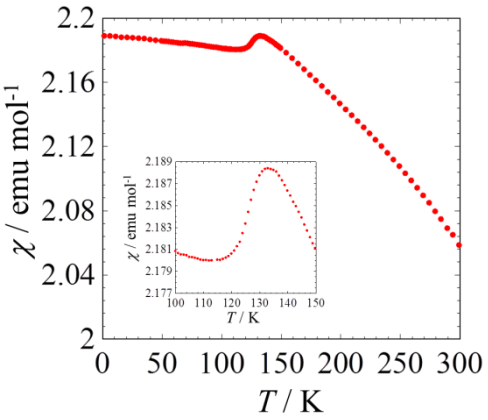

Fig. 6 Temperature dependence of magnetic susceptibility. Inset shows an enlarged area around the transition.

When the external pressure is increased up to 12.5 GPa, the resistivity shows no anomaly and smooth temperature dependence is disclosed. It is interesting to indicate that the peak broadening occurs at much lower pressures than those observed by resistivity. The change of the peak was reproducible and it recovered its original sharp peak after releasing the pressure, which seems to be intrinsic for this compound.

In order to perform thermodynamic investigation of molecular compounds accompanied by various type of electronic phase transitions, high accuracy detection of the electronic phase transitions and separation from the large lattice heat capacity is important. For this purpose background subtraction including sensor and heater by differential method or subtraction by blank measurements should be necessary at the next step. It is also emphasized that experiments in a wide temperature range above 200 K is possible, if we select suitable pressure medium and avoid glass like behaviors of grease and pressure medium. We are now trying to detect various kinds of phase transitions such as glass transitions and CO transitions in BEDT-TTF based molecular compounds using single crystal samples.

4. Conclusion

We have developed an apparatus to obtain thermodynamic information using a tiny single crystal or a small pellet samples under pressure. The small chip type Pt sensor was used as a sensor to detect small temperature modulation around the sample with high accuracy. The high pressure calorimeter was used in a variable temperature insert (VTI) of superconducting magnet. We observed a sharp thermal anomaly around 124 K for pellet sample of Fe_3O_4 which broadens with the increase of pressure up to 1.05 GPa.

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