Thermochimica Acta 492 (2009) 85–88

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

AC-calorimetry for detecting electronic phase transitions at low temperatures using micro-chip devices

Y. Inoue, Y. Nakazawa*

Department of Chemistry, Graduate School of Science, Osaka University, Machikaneyama 1-1, Toyonaka, Osaka 560-0043, Japan

ARTICLE INFO

Article history:
Available online 4 February 2009

Keywords:
AC-calorimetry
Electronic phase transition
Micro-chip

ABSTRACT

The MEMS device of TCG3880 was used for thermodynamic measurements in order to detect electronic phase transitions occur at low temperature region below 300 K under vacuum atmosphere. Using square wave currents which produce temperature modulation around the sample and the lock-in detection technique, we studied frequency dependence of the thermopile output (V_{ac}) and observed a characteristic feature in a low-frequency region. From the temperature dependence of V_{ac} at a fixed frequency of 3.3 Hz, we investigated a thermodynamic properties of high-T_c superconductor $YBa_2Cu_3O_{7-\delta}$ and organic charge transfer salt of $(DMe\text{-}DCNQI)_2Li$. A thermal anomaly being associated with the superconductive transition of the former compound and the broad heat capacity hump probably in relevant to the spin-Peierls transition of the latter one were observed using this micro-chip device.

1. Introduction

The development of micro-fabrication techniques in these years has brought about new possibilities in fundamental researches of materials, since advanced measurements of small area have become realistic levels. By using precise fabrication methods, one can form micron or submicron size sensors and electric circuits, *etc*. on Si-based membranes. A systematic arrangement of different functional parts on the same membrane gives a kind of small-size devices which are generally called as micro-electron-mechanical systems (MEMSs). They are now extensively used for various purpose including physical property measurements in fundamental researches. For the purpose of studying micro-crystals which are difficult to obtain large crystals, thin films, nano-particles, *etc*. and also for studying the local area of samples, the usage of MEMS devices is effective. The idea of utilizing such MEMS devices for thermodynamic measurements gives great advantages on exploring researches of condensed matters, since the background heat capacity has been much reduced and consequently thermodynamic data for extremely small amount of samples can be obtained with good resolution.

Reflecting on these advantages, thermodynamic researches have already been performed by several groups and reported in several literatures [1–5], where the MEMS devices are used as micro-chip calorimeters or as a kind of scanning probe to perform the local area measurements. However, the design and the manufacture of MEMS devices still require special techniques accessible only by people in special facilities with micro-fabrication apparatus. Recently, Schick et al. has used commercial available micro-chip devices (TCG3880, XEN-3935, *etc*. which is supplied by Xensor Integration Co. Ltd.) for general use and introduced a technique for measuring thermodynamic properties by small amount of samples [6–8]. They succeeded to establish highly sensitive thermal analysis way and reported numerous interesting results for polymeric materials. Details are reported for example in Refs. [6–8] and some of the test data are displayed in the web page of Xensor Co. Ltd. [9]. The interesting idea emphasized by their group is an application of this chip-calorimetry technique for studying non-equilibrium state produced through the rapid scanning measurements ranging to 10^3–10^5 K s^{-1}. Since the sample heat capacity as well as the background heat capacity is quite small in the case of micro-chips, the extremely rapid temperature control is possible.

Using the merits of high sensitivity and easy handling of these commercially available chips with membrane structure, it is fascinating to measure heat capacity of micrometer sized crystals which show some electronic phase transitions such as magnetic, superconductive, charge-order transitions at low temperature region. These transitions are usually observed as a second order one, which has very small ΔC_p as compared with the heat capacity jump owing to the melting and the crystallization. In the case of organic charge transfer salts and metal complexes, the crystals usually grown from solutions are very small in the order of 10^{-2}–10^0 mm, even though their sample quality is recognized as very good. Development of thermodynamic technique using the MEMS apparatus for such micro-crystals is expected for detecting phase transitions and exploring physics of these materials. We, therefore, tried to

* Corresponding author.
E-mail address: nakazawa@chem.sci.osaka-u.ac.jp (Y. Nakazawa).

0040-6031/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2009.01.024

construct an AC-calorimetry apparatus to detect thermodynamic peak related to the electronic phase transition appears at low temperatures.

2. Experimental

For this purpose, we used the chip-type MEMS device of TCG3880 which is the same one adopted by Schick et al, since the fundamental properties of the chip have extensively been studied. This chip is consisting of a SiN membrane part surrounded by the base Si frame which serves as a heat sink. In the center of the membrane, small resistance heater of approximately 600 Ω at room temperature is fabricated. The heater resistance decreases moderately with the decrease of temperatures and reaches to nearly about 480 Ω at liquid helium temperature. Surrounding this heater part of which dimension is 50 μm × 100 μm, six hot junctions of a thermopile is arranged. Since the cold junction is situated very close to the Si-flame, the temperature difference between the Si-flame and center part of the membrane is detected as an output signal of the thermopile. The sensitivity (S) of the thermopile is nearly 0.75 mV/K at room temperature and decreases to about 30 μV/K at 15 K [7]. Although the sensitivity decreases with the decrease of temperatures especially below 100 K, the usage down to the low temperatures of about 10 K seems to be possible if we use the DC amplifier with low-pass filters to enlarge the signal. The chip devices are mounted on a Cu block with a diameter of 25 mm of which temperature is accurately controlled using a calibrated Pt resistance (PT-111 Lake Shore) and a manganine heater of 120 Ω by a temperature controller (Lake Shore 340). The Cu block is fastened to the sample stage of an adiabatic cryostat of which outer diameter is 28 mm. The cryostat is inserted in the variable temperature insert (VTI) system equipped with a superconducting magnet and the experiments under magnetic fields up to 15 T are possible.

The measurement using this chip has been performed by ac-method in vacuum atmosphere. The inside of the adiabatic can was evacuated better than 1.3×10^{-4} Pa using a diffusion pump. The already reported measurements in Refs. [6–8] by this chip are aimed at studying the drastic phase transitions and glass behavior for polymer materials in relatively higher frequencies of about 10^2 Hz. The experiments are mainly performed above room temperature and a small amount of exchange gas to release the heat effectively at relatively high frequency has been used. The example of the measurements of intermetallic compounds in this condition are also reported in Refs. [7,10]. However, our measurement is aimed at detecting small anomaly owing to the electronic phase transition below room temperature. Therefore, to get the large sample signal which directly contains the sample heat capacity information, it is necessary to test the device under good vacuum condition where the heat release should occur only through the SiN membrane to the heat sink.

The signal detection was performed by the standard lock-in technique. The temperature oscillation was produced by the square wave currents produced by the Keithley 220 programmable current source. Using this current source, it is possible to estimate the heater power accurately. The temperature oscillation signals are amplified by DC amplifier (YOKOGAWA 3132) and detected by an analog lock-in amplifier (EG&G 5302). Since we have used a square wave current to make temperature oscillation, the signal should become exactly the same frequency as the excited current which can be detected by normal 1f mode of the lock-in amplifier. Fig. 1 displays the block diagram used for the present measurements. To perform the temperature scan from 13 to 300 K, the temperatures of the Cu block and the vacuum can were swept by the constant rate of 0.1 K min^{-1}. The amplitude of the ac oscillations of the sample temperature are 0.1 K at 200 K and 0.03 K at 20 K which was adjusted

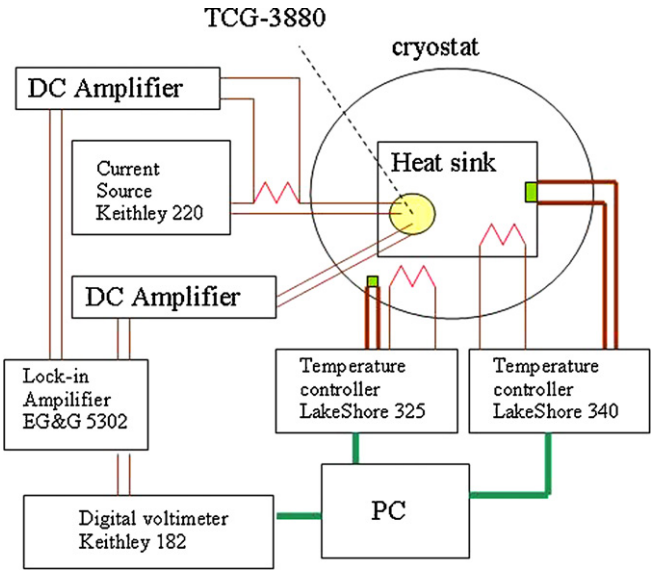

Fig. 1. Block diagram of the AC-calorimetry used for this experiment. The heater current is supplied by a square wave by the current source and detected by the lock-in amplifier. The frequency of the excitation currents are variable from DC to 150 Hz.

by the magnitude of the heater current applied typically from 10 to 500 μA. The small pieces of crystals of which bottom surface is as flat as possible is attached on the heater part of the SiN membrane by a small amount of Apizon N grease.

3. Results and discussion

At first, we have measured frequency (f) dependences of the ac amplitude of the sensor output (V_{ac}) at several selected temperatures between 13 and 240 K in order to know the characteristic feature of this MEMS device in the vacuum environments. For this purpose, we have used a single crystal of organic charge transfer complex of $(DMe\text{-}DCNQI)_2Ag$ salt, where DMe-DCNQI is an abbreviation of dimethyle-dicyanoquinonediimine. The obtained frequency dependence of the ac-amplitude signal (V_{ac}) multiplied by f is shown in Fig. 2. The V_{ac} can be converted to the temperature modulation amplitude T_{ac} using the sensitivity S of the thermopile. In general, T_{ac} depends on the modulation frequency of the heat-flow produced at the sample and characterized using

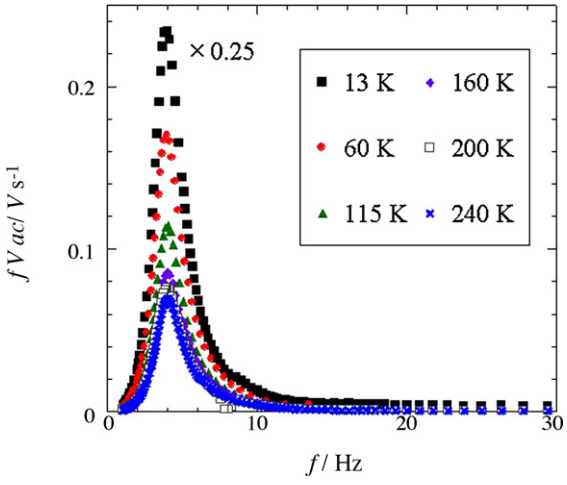

Fig. 2. Frequency dependences of the ac-amplitude signals multiplied by frequency at 13, 60, 115, 160, 200 and 240 K. The data of 13 K are multiplied by a factor of 0.25.

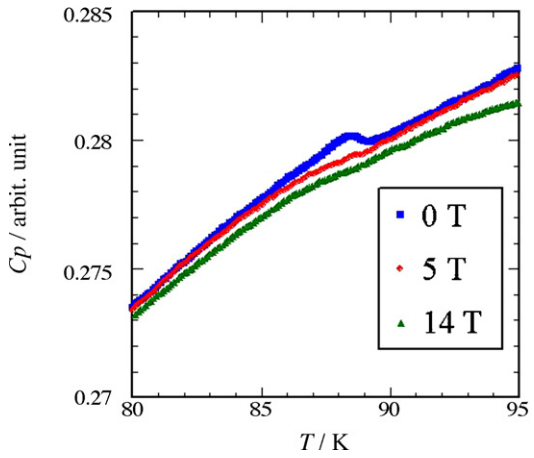

Fig. 3. Temperature dependence of the ac-heat capacity of $YBa_2Cu_3O_{7-\delta}$ obtained under 0 T and with magnetic fields of 5 and 14 T.

two time constants τ_1, τ_2. The τ_1 is the external time constant determined by the heat release through the membrane and the τ_2 is the internal time constant determined by the thermal contact between the sample and the sensor. When the relation of $\tau_1 \gg \tau_2$ is hold and the modulation frequency is within the range of $(2\pi\tau_1)^{-1} < f < (2\pi\tau_2)^{-1}$, the heat capacity of the sample is expressed by a simple formula of $C_s = P_0/2\pi f T_{ac}$ using the heat-flow amplitude P_0. The appropriate region for determining the heat capacity should be given by a plateau appears between two characteristic frequencies f_1 (=$(2\pi\tau_1)^{-1}$) and f_2 (=$(2\pi\tau_2)^{-1}$) in f vs. $f{\cdot}V_{ac}$ plot [11]. In the present experimental condition under high vacuum, the heat release through the membrane dominated by τ_1 might be close to the value of τ_2, since the distribution of the hot junctions is large in TCG3880. In such case, the sample heat capacity should have a complicated f dependence expressed by $C_s = F(f)P_0/2\pi f T_{ac}$, where $F(f)$ is a function including τ_1 and τ_2 as parameters. The results shown in Fig. 2 give peak structures which is different from the plateau appears in the case of $\tau_1 \gg \tau_2$. At present, we do not know why the peak structure at low-frequency region of 3.0–5.0 Hz appears, since the monotonous increase with lowering the frequencies seems to be reasonable if we assume that $F(f) = A/(1 + (2\pi f\tau_1)^{-2} + (2\pi f\tau_2)^2)^{0.5}$ where A is a proportional constant. However, from the data in Fig. 2, we can observe a systematic decrease of fV_{ac} values with the increase of temperature, which probably reflecting the increase of sample heat capacity C_s with increasing temperature. In addition, it is interesting to note that the curvaturs obtained at different temperatures shown in Fig. 2 has a good scaling relation in their profiles. Therefore, we can consider that the fV_{ac} data contain the information related to the sample heat capacities and temperature dependences of this signal at fixed frequency can give thermodynamic information of the sample. We set the frequency at the peak temperature of Fig. 2 hereafter and performed measurements.

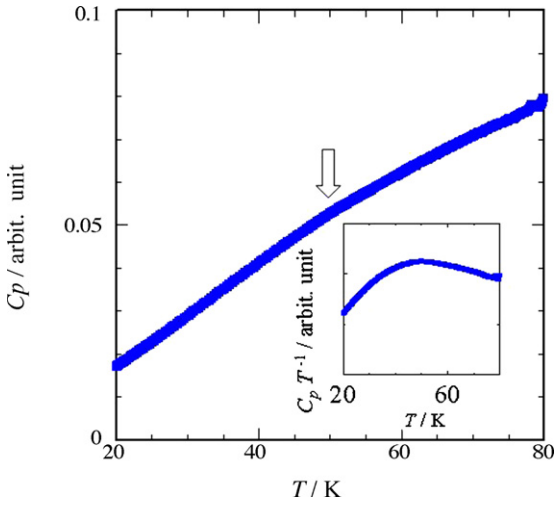

Fig. 4. Temperature dependence of the ac-heat capacity of organic charge transfer salt of $(DMe\text{-}DCNQI)_2Li$ which is known to show spin-Peierls transition at 51 K.

The temperature dependences of the ac heat capacities of two different samples obtained by the frequency of 3.3 Hz are shown in Figs. 3 and 4. The former sample is a sintered polycrystal of $YBa_2Cu_3O_{7-\delta}$, which is one of the high-T_c cuprates with the transition temperature of 91 K. In the figure, we can see a thermal anomaly owing to the superconducting transition and its variation by applying external magnetic fields. The detection of the thermal anomaly of the superconductive transition using only 34 μg sample suggests that the micro-chip devise of this kind are available to detect electronic phase transitions. Since the sample used for this measurement was a small piece cut from a bulk pellet of which bottom surface has been polished, the quality of the sample, especially the superconductivity volume fraction is not so good as compared with single crystal sample. However, the clear detection of the signal in such pellet sample demonstrates that the system is sensitive enough for detecting small superconductive anomalies [12–13]. The application of magnetic fields influences the transition, which seems to be consistent with the early works performed by pellet sample of this material.

In Fig. 4, we also show the temperature dependence of heat capacity of organic charge transfer salt of $(DMe\text{-}DCNQI)_2Li$ sample, which is known to show a spin-Peierls transition at 51 K, according to the previous report in Ref. [14]. The broad hump structure related to the transition is detected in the corresponding temperature as is clearly observed in the C_pT^{-1} vs. T plot in the inset of Fig. 4, but the transition itself is broader than that observed in the previous reported. Since the spin-Peierls transition is very sensitive to the lattice disorder as is reported in Ref. [14], the broadening of the thermal anomaly may be attributed to the inhomogeneous stress due to the adhesion by Apiezon N grease. However, the detection of thermal anomaly at the same temperature demonstrates that this chip device is still available at low temperatures region where various type electronic phase transitions occurs in molecular based compounds.

4. Conclusion

Using the micro-chip MEMS device of TCG3880, we have tried to detect electronic phase transition through the ac-temperature modulation technique. The frequency dependence of the ac amplitude signal produced by the square wave currents were detected by the lock-in amplifier. The observed frequency dependence gives a peak structure different from the plateau, which demonstrates that the τ_1 and τ_2 are comparable order in the vacuum environment. Through the temperature dependence of the ac signal, we have studied the thermodynamic character of high-T_c cuprate of $YBa_2Cu_3O_{7-\delta}$ and organic charge transfer salt of $(DMe\text{-}DCNQI)_2Li$. Thermal anomalies related to the electronic phase transitions have been detected for tiny piece of crystals.

Acknowledgements

This work was supported in part by Grant-in-Aid for Scientific Research (nos. 18340103 and 20654033) by JSPS. The authors thank Prof. C. Schick and Dr. H. Huth for important suggestions on the experiments.

References

[1] M.Yu. Efremov, E.A. Olson, M. Zhang, F. Schiettekatte, Z. Zhang, L.H. Allen, Rev. Sci. Instrum. 75 (2004) 179–191.
[2] O. Nakabeppu, T. Suzuki, J. Therm. Anal. Calorimet. 69 (2002) 727–737.
[3] B.L. Zink, B. Revaz, R. Sappey, F. Hellmann, Rev. Sci. Instrum. 73 (2002) 1841–1844.
[4] D.W. Denlinger, E.N. Abarra, K. Allen, P.W. Rooney, M.T. Messer, S.K. Watson, F. Hellman, Rev. Sci. Instrum. 65 (1994) 946–959.
[5] F. Fominaya, T. Fournier, P. Gandit, J. Chaussy, Rev. Sci. Instrum. 68 (1997) 4191–4195.
[6] A.A. Minakov, S.A. Adamovsky, C. Schick, Thermochim. Acta 432 (2005) 177–185.
[7] A.A. Minakov, S.B. Roy, Y.V. Bugoslavsky, L.F. Cohen, Rev. Sci. Instrum. 76 (2005), 043906 1–9.
[8] H. Huth, A.A. Minakov, C. Schick, J. Polym. Sci. Part B Polym. Phys. 44 (2006) 2996–3005.
[9] Xensor Integration http://www.xensor.nl.
[10] A.A. Minakov, A.W. van Herwaarden, W. Wien, A. Wurm, C. Schick, Thermochim. Acta 461 (2007) 96–106.
[11] M. Sorai (Ed.), Comprehensive Handbook of Calorimetry and Thermal Analysis, Wiley and Sons, 2004, pp. 75–76.
[12] D.M. Ginsberg, (Ed.), Physical Properties of High Temperature Superconductors II, World Scientific, pp. 13–120.
[13] M. Ishikawa, Y. Nakazawa, T. Takabatake, A. Kishi, R. Kato, A. Maesono, Solid State Commun. 66 (1988) 201–204.
[14] Y. Nakazawa, A. Sato, M. Seki, K. Saito, K. Hiraki, T. Takahashi, K. Kanoda, M. Sorai, Phys. Rev. B68 (2003), 085112 1–8.