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UNIVERSITY OF ALBERTA

SPECIFIC HEAT MEASUREMENTS OF HIGH TEMPERATURE SUPERCONDUCTORS

BY

MINGKANG YU

A THESIS
SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE
OF DOCTOR OF PHILOSOPHY

IN
SOLID STATE PHYSICS

DEPARTMENT OF PHYSICS

EDMONTON, ALBERTA
FALL, 1991

ISBN 0-315-70056-4

UNIVERSITY OF ALBERTA

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NAME OF AUTHOR: MINGKANG YU
TITLE OF THESIS: SPECIFIC HEAT MEASUREMENTS OF HIGH TEMPERATURE SUPERCONDUCTORS
DEGREE: DOCTOR OF PHILOSOPHY
YEAR THIS DEGREE GRANTED: 1991

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ABSTRACT

Specific heat measurements have been performed on a YBCO superconducting sample in the vicinity of T_c, and on several Bi-compound superconducting samples from about 2.6 to 120 K. The YBCO sample shows that the ratio $\Delta C(T_c)/\gamma T_c$ larger than 3.0, and thus appears to be in the strong coupling limit. For some Bi-compound samples, specific heat jumps at two transition temperature have been observed. However, the sizes of anomalies are different from sample to sample. For the Bi-compound sample whose Meissner fraction and Debye temperature are small, the anomaly at transition temperature cannot be detected. The low-temperature specific heat data of Bi-compound superconductors can be fitted with the equation $C(T)=A/T^2+\gamma_0 T+\beta T^3+mC_E(T)$, where $C_E(T)$ is an Einstein term, and the least-squares fits tell us that there is no temperature-linear term in the low-temperature specific heat within the experimental uncertainty. There are big differences among Debye temperatures which are obtained from low temperatures and from high temperatures for Bi-samples. This means that the Debye theory is not a good theory for these complicated compounds. However, perhaps the lattice specific heat of these compounds can be understood with the assumption of several sets of lattice vibrations, every of which has its own individual Debye temperature θ_{Di}, and $\theta_{Di}/\theta_{Dj} = (M_j/M_i)^\delta$, where M_i represents atomic mass, δ is considered as the coupling coefficient among different lattice vibrations.

ACKNOWLEDGEMENTS

I wish to express my deep gratitude to my supervisor, Professor J. P. Franck, for his generous support and direction.

A special thanks goes to my wife Linjiao for her continual support and encouragement.

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CHAPTER 1

INTRODUCTION

Before 1986, if the word 'superconductivity' was mentioned, it referred to a remarkable combination of electric and magnetic properties which appeared in certain metals when they are cooled to **very low temperatures**. However, this concept has changed since mid 1986 when Bednorz and Muller reported a sharp drop in the electrical resistivity of Ba-La-Cu oxide near 30 K, and suggested that it was a possible superconducting transition. Their revolutionary discovery was soon confirmed by Meissner effect measurements (Bednorz et al. 1987, Uchida et al. 1987, Takagi et al. 1987). In March 1987, superconductivity above liquid nitrogen temperature was reported by Wu and colleagues in the Y-Ba-Cu-O system. However, it should also be mentioned that the earliest discovery of a superconducting oxide was made by Schooley et al. in 1964. The first known example was $SrTiO_3$, but its transition temperature was low.

Bednorz and Muller's discovery has posed a new challenge to solid-state physics, induced the intense interest in these remarkable materials, and led to the creation of a new terminology **"high temperature superconductor (HTSC)"**. In the past four years, a tremendous amount of research on high temperature oxide superconductors has been done, and progress has been steadily made, however, the mechanism responsible for the high transition temperature still remains unclear.

The knowledge of specific heats is of fundamental significance for understanding of physical systems, because it is one of the most powerful tools to study lattice vibrations, electronic distributions, transition properties, and so on. Especially, in the history of the development of conventional superconductors, the specific heat measurements played a very important role in understanding the mechanism, and helping to shape the development of the BCS theory (Bardeen, Cooper and Schrieffer 1957, Bardeen and Schrieffer 1961). Recall, as just one fact, that the first quantitative experimental evidence for the energy gap in the conventional superconductivity came from the accurate measurements of the specific heat of superconducting electrons in Vanadium made by Corak et al. in 1954.

Those measurements revealed that at very low temperatures the specific heat of superconducting electrons varied as

$$C_{es} \approx a \exp(-\frac{b}{T}), \qquad (1.1\text{-}1)$$

where a and b are constants. Such an exponential variation is the form to be expected if there is a gap in the range of energies available to an electron. When the temperature rises, electrons are excited across the energy gap above their ground state, and each of these electrons absorbs an amount of energy equal to the energy gap E_g in this process. The number of electrons excited across such a gap is proportional to $\exp(-E_g/ 2k_BT)$ according to statistical mechanics, where k_B is the Boltzmann's constant. The specific heat associated with the process is proportional to the derivative of the energy absorbed in exciting these electrons, therefore its variation with temperature is very nearly exponential.

The BCS theory shows that the energy gap $E_g=2\Delta$ almost is constant at very low temperatures, but decreases as the temperature is raised towards to the transition temperature, falling to zero at T_c. Because of the rapid decrease in the energy gap just below T_c, the specific heat of a superconductor quickly increases as the temperature approaches T_c.

Besides the electronic specific heat, another main contribution to C comes from the lattice. In the superconducting transition, no structural changes are observed in the lattice. Therefore, it is reasonable to suppose that the lattice specific heat is the same in the normal and superconducting states. According to the Debye theory, at very low temperatures, the lattice specific heat can be expressed as

$$C_L = BT^3/\theta_0^3, \qquad (1.1\text{-}2)$$

where θ_0 is the Debye temperature near T=0, an important parameter, and B is a constant. Hence, if a material is in the superconducting state after a complete superconducting transition, and if there is no other contribution to C except the electronic and the lattice specific heat, at very low temperatures (in the limit T→0), we should have

$$C \approx a\exp(-\frac{b}{T}) + BT^3/\theta_0^3. \qquad (1.1\text{-}3)$$

It is obvious from the above equation that there is no term with a linear temperature dependence (T-linear term) in the low-temperature specific heat of a conventional superconductor after a complete superconducting transition.

In contrast with Eq. (1.1-1), the normal-state electronic specific heat is

$$C_{en}=\gamma T, \qquad (1.1\text{-}4)$$

where γ is the Sommerfeld coefficient which is a measure of $N(E_F)$, the electronic density of states at the Fermi surface, and

$$\gamma = (1/3)\pi^2 k_B^2 N(E_F). \qquad (1.1\text{-}5)$$

Therefore, if a material remains in the normal state at very low temperatures, the specific heat is

$$C = BT^3/\theta_0^3 + \gamma T. \qquad (1.1\text{-}6)$$

There is a temperature-linear term in C, and a plot of the experimental data of C/T against T^2 should give a straight line whose slope is B/θ_0^3 and whose intercept is γ. Hence, if the superconductivity is quenched by applying a sufficiently strong magnetic field, which is available in a modern laboratory for the conventional superconductors, the very important parameter γ can be determined from the measurements on the superconductor in the normal state, and then people will be able to separate the electronic and the lattice specific heat from the total specific heat of the sample.

As mentioned above, the electronic specific heat in the normal and superconducting states are different, but the lattice specific heat is usually assumed to be the same, therefore

$$\Delta C(T) = C_n - C_s = C_{en} - C_{es}. \qquad (1.1\text{-}7)$$

From ordinary thermodynamic considerations, it can be obtained that the difference in free energy between the normal and superconducting states without applied magnetic field is

$$G_n - G_s = \frac{H_c^2}{8\pi} V, \qquad (1.1\text{-}8)$$

where H_c is the critical magnetic field, and V denotes the volume of specimen. Since the entropy $S = -\partial G / \partial T$, it can be derived that

$$C_n - C_s = T\frac{\partial}{\partial T}(S_n - S_s) = \frac{TV}{4\pi}\left[H_c \frac{\partial^2 H_c}{\partial T^2} + \left(\frac{\partial H_c}{\partial T}\right)^2\right]. \qquad (1.1\text{-}9)$$

At the transition temperature, $H_c = 0$, therefore, the jump in the specific heat is

$$(C_n-C_s)_{T_c} = \frac{T_cV}{4\pi}\left(\frac{\partial H_c}{\partial T}\right)^2_{T_c}, \qquad (1.1\text{-}10)$$

This equation is called Rutger's formula. Equation (1.1-9) and (1.1-10) are strictly valid only when H_c is obtained from the experiments in which the magnetic field suppressing the superconductivity is along the axis of a long cylindrical specimen. For other orientation and shapes, an intermediate state must be considered.

For type-II superconductors, H_c in Equation (1.1-10) should be considered as the thermodynamic critical field, the relation between H_c and the upper critical field H_{c2}, and between H_c and lower critical field H_{c1} are

$$H_{c2} = \sqrt{2}\kappa H_c, \qquad (1.1\text{-}11)$$

and

$$H_{c1} = H_c(\ln \kappa + 0.08)/\sqrt{2}\kappa, \qquad (1.1\text{-}12)$$

where κ is the Ginzburg-Landau parameter, and $\kappa=\lambda/\xi$ while λ and ξ denote the penetration depth and the the coherence length respectively. κ for type-II superconductors is larger than $\sqrt{2}/2$, which corresponds to a negative surface energy associated with the boundary between a normal and a superconducting region.

For many conventional superconductors, the dependence of H_c on temperature is approximately of the parabolic form

$$H_c = H_0[1 - (\frac{T}{T_c})^2], \tag{1.1-13}$$

where H_0 represents the critical field at 0 K. From (1.1-10) and (1.1-13), it is easy to get

$$\Delta C(T) = C_n - C_s = C_{en} - C_{es} = \frac{H_0^2}{2\pi T_c^2} VT[1-3(\frac{T}{T_c})^2]. \tag{1.1-14}$$

Therefore, we have

$$\gamma = \frac{H_0^2}{2\pi T_c^2} V, \tag{1.1-15}$$

and

$$(C_s - C_n)_{T_c} = 2\gamma T_c. \tag{1.1-16}$$

Equation (1.1-15) can be used to find γ once H_0 is known. However, as we know, Equation (1.1-15) and (1.1-16) are based on assuming the parabolic temperature dependence of H_c, and there are some deviations of the H_c-T curve from the parabolic law. Therefore, the accurate determination of γ depends on the accurate determination of H_c-T curve if we do not use calorimetric method to find the value of γ.

The BCS theory yielded an exponential variation of C_{es} for the conventional superconductors which agreed well with experiments, and indicated that, for the weak coupling limit, the discontinuity in the specific heat at transition temperature, $\Delta C(T_C)$, should be $1.43\gamma T_c$ (not $2\gamma T_c$, which deviated from experimental data considerably), or, the relation is written as

$$\frac{\Delta C(T_c)}{\gamma T_c} = 1.43. \tag{1.1-17}$$

In cases where the coupling is strong, the ratio $\frac{\Delta C(T_c)}{\gamma T_c}$ increases. For example, it is 2.4 for Hg, and 2.7 for Pb (Mersevey and Schwartz 1969). The strong coupling effects also increase the ratio $\frac{2\Delta}{k_b T_c}$ to a value greater than 3.53 which comes from another BCS-relation in the weak coupling limit.

Finally, the specific heat measurements can be regarded as a reliable test to distinguish between bulk superconductivity and superconducting filaments which might occupy only a small fraction of the material. Such information can not be provided by the resistivity measurements, but may be obtained from $\Delta C(T_C)$ and γT in zero magnetic field, because, for the conventional superconductors, an incomplete transition to the superconducting state means that there would be a T-linear term in the zero-field specific heat, and a reduction in $\Delta C(T_C)$, and both parameters are proportional to the non-superconducting volume of a sample. However, it should be mentioned that in principle γ can be derived from $\Delta C(T_C)$ according to Equation (1.1-17), but in practice, the computation of γ from $\Delta C(T_C)$ is associated with a large uncertainty since the BCS-ratio in Eq. (1.1-17) can vary considerably. Therefore, if one wants to determine f_n, the fraction of the sample which remains normal, and $f_s=(1-f_n)$ accurately, one should get γ from T-linear term in the superconducting state and in the normal state which are denoted by γ_s and γ_n respectively here, then obtain $f_n=\gamma_s/\gamma_n$.

For the high temperature superconductors, although several hundreds of papers on specific heat measurements have been published since 1987, the explanation of the data still remains ambiguous, and the final picture is not yet available. Major problems which have caused this situation are the sample quality and inadequate characterization. They have led to experimental results with sample-to-sample differences and contradictory conclusions. It also should be mentioned that, so far, there is no mature theory for HTSC which can provide quantitative predictions, therefore, comparisons of experiment with theory are mainly based on the theory, both microscopic and phenomenological, of conventional superconductors though there are some obvious differences between high-T_c and conventional superconductors such as the very short coherence length, ξ, of HTSC. Furthermore, there are several other problems which make the specific heat measurements and the analysis of data on HTSC much more complicated and difficult, they are:

1. The superconducting transitions are rather broad in most cases, and the transition temperature is in the temperature

region in which the lattice specific heat, C_L, makes by far the largest contribution in comparison to the electronic part, C_e, and does not have a simple temperature dependence.

2. There is no directly calorimetrical method for determining the extremely important parameter γ and the lattice specific heat, because the upper critical fields of HTSC are very high, and it is impossible to suppress superconductivity (except very near the transition temperature) with the magnetic fields which are available in the laboratory.

3. With few exceptions, there is an upturn in C/T at low temperatures, and it makes the interpretation of the data difficult and uncertain.

We started the specific heat measurements on HTSC in 1988, after the installation of an adiabatic calorimeter. In that year, the Bi-Sr-Ca-Cu-O superconductors were discovered by Maeda, H. et al. (1988). About one year before the Maeda's discovery, a very striking property that there was a T-linear term, $\gamma_0 T$, in the low-temperature specific heat of La-M-Cu oxide (M=Ba and Sr) superconductors was first reported by Ginsberg et al. (1987), Dunlap et al. (1987) and Wenger et al. (1987). Further investigation revealed that, for the Y-Ba-Cu-O superconducting samples, there was also a T-linear term in the low-temperature specific heat (Ayache et al. 1987, Phillips et al. 1987, Fisher et al. 1988c, Eckert et al. 1988, Von Molnar et al. 1988).

Is this striking property a general feature for all high-T_c superconductors? Is it intrinsic or extrinsic? In order to answer these questions which have gotten the most attention, investigation of the specific heat of Bi-compound superconductors is necessary after they are discovered.

It should be pointed out that the origin of the T-linear term has, so far, not been clearly known yet. Therefore, the notation $\gamma_0 T$ which is used here is different from γT (C_{en}), and does not have any implication that it comes from the electronic part of the specific heat in origin.

Investigation of the specific heat of the Bi-compound superconductors is more complicated than that of Y-Ba-Cu-O superconductors. This is because control of the sample quality for Bi-compound superconductors is more difficult. So far, most of the experiments concerning the specific heat of the HTSC's describe the measurements of C of Y-Ba-Cu-O.

In the present work, with one exception, we focus our attention on the specific heat of the Bi-compound superconductors. The details of our investigation on the specific heat will be given in Chapter 4, while Chapter 2 concerns our experimental apparatus.

All high-T_c superconducting samples on which we performed specific heat measurements were made by ourselves except one. Therefore, we will describe the sample-preparation, and give some discussion about it in Chapter 3.

Preliminary results of this work have already been published elsewhere.

CHAPTER 2

APPARATUS FOR THE ADIABATIC SPECIFIC HEAT MEASUREMENTS

The specific heat of a substance is defined as the quantity of heat required to raise the temperature of a unit mass of the substance by a unit degree of temperature.

$$C_X = \lim_{dT \to 0} \left(\frac{dQ}{dT}\right)_X \qquad (2.0\text{-}1)$$

where X is the property which is held constant when a heat input raises the temperature of the substance. Therefore, either P or V can be kept constant during the change of temperature, and correspondingly there are two principal specific heats, C_P and C_V. Heating the substance at constant pressure causes an increase in the internal energy and also forces the substance to do external work in expanding against the pressure of the system. In contrast with this, in heating at constant volume there is no work done against the pressure, and all the heat goes to raise the internal energy. Therefore, C_P is larger than C_V. The difference between C_P and C_V is

$$C_P - C_V = \frac{TV\beta^2}{\kappa_T}, \qquad (2.0\text{-}2)$$

where V is the volume, β denotes the coefficient of cubical expansion, and κ_T represents the isothermal compressibility. The difference is about 5 % in most solids at room temperature, but it decreases rapidly as the temperature drops. Mainly, it is because the coefficient of cubical expansion decreases quickly when the temperature is lowered. For copper, the difference is only 0.6% at 100 K , and can hardly be detected at 4 K. The behavior of other solids is very similar (Gopal 1966).

In the present work, C_P is measured in an adiabatic calorimeter.

2.1 Adiabatic Calorimeter

The adiabatic calorimeter which we designed and installed to measure the specific heats is shown in Figure 2.1.

The copper can C surrounded by liquid helium or nitrogen is connected, through the thin-walled stainless steel tube A , with a high vacuum system which can maintain a pressure of less than 10^{-7} mm Hg in the can.

The copper chamber M, which is supported by the stainless steel tube D from the top of the can C, is used as the radiation shield. It has its own heater F. There are two heat sinks E on the top of the radiation shield. All wires have to pass through the heat sink, and obtain the same temperature as that of the radiation shield, before they get to the calorimeter K.

The calorimeter to which two thermometers and a heater are attached is suspended from four copper bars N by nylon threads. I is the thermometer holder and another heat sink. The wires from E have to go through this sink, then connect with the thermometers. Therefore, it is assured that the temperature measured by the thermometers is the temperature of the calorimeter.

The heat switch L which is used to speed the drop in the temperature of the calorimeter is attached to two copper bars, and controlled by a string of steel. In order to improve the thermal contact between the calorimeter and the switch, both of them are coated by gold. After the temperature of the calorimeter is dropped to the same as that of the radiation shield, the switch will be opened.

A thermocouple (Au+0.07% Fe vs. Chromel) is used to indicate the temperature difference between the radiation shield and the calorimeter. According to the indication, the current of the shield heater is carefully adjusted so that a difference of less than 20 mK can be maintained when the measurements are being performed.

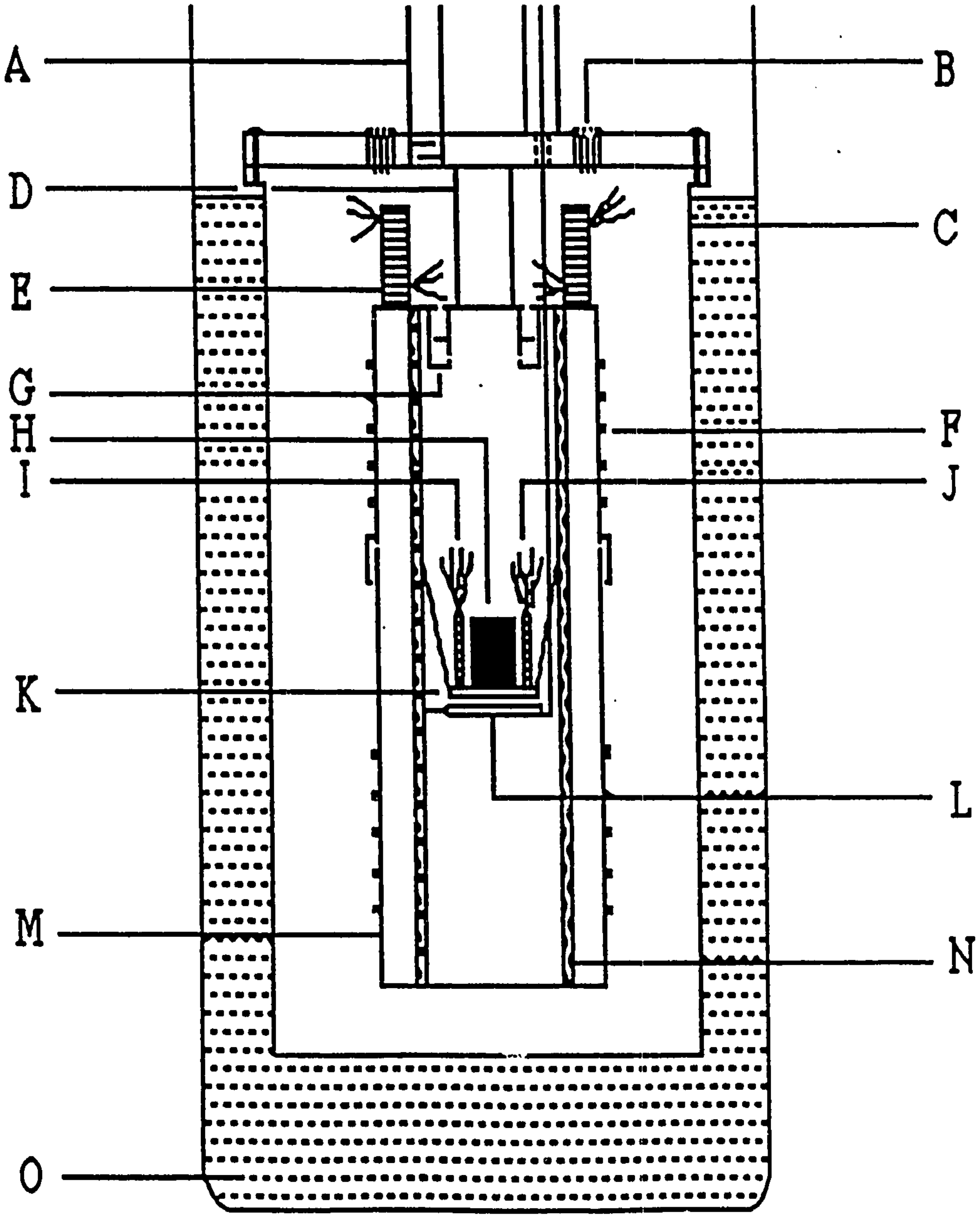
The sample H is placed on the calorimeter. There is a very thin layer of high vacuum grease between the sample and the calorimeter which improves the thermal contact between them very much.

Cooling to about 2.4 K can be obtained by pumping liquid helium. In this case, the liquid helium would last for about 24 hours without a refill.

FIGURE 2.1

THE APPARATUS FOR ADIABATIC SPECIFIC HEAT MEASUREMENTS

A.	Thin-walled stainless steel tube
B.	Feedthrough connector
C.	Vacuum can
D.	Stainless steel tube
E	Heat sinks
F.	Heater for radiation shield
G	Radiation baffle
H	Sample
I.	Thermometer holder and heat sink
J.	Heater for calorimeter
K.	Calorimeter
L.	Heat switch
M.	Radiation shield
N.	Copper bars
Q.	Liquid helium or nitrogen


A
B
D
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O

2.2 Calculation of the Heat Leak

In a measurement of the specific heat by the adiabatic method, the calorimeter and the sample must be thermally isolated from its immediate environment, the cooling medium. In other words, the amount of heat leaking between the calorimeter and its surroundings must be controlled to be sufficiently small, otherwise there will be a large error in a measurement, especially in the measurement at the low temperature range, because the specific heats of substances are very small at this range.

In general, heat may be transferred by conduction, radiation and convection. In most low-temperature apparatuses, convection is eliminated by evacuation of gas. Then effective heat transfer takes place by conduction through the residual low pressure gas, conduction through the solids that interconnect the various parts in the cryostat, and by radiation.

In our design of the adiabatic calorimeter, the amount of heat leaking was targeted for less than one per cent of the heat input dQ in equation (2.1-1).

2.2-1 Conduction of heat by the residual gas

As mentioned above, a pressure of 10^{-7} mm Hg in the vessel B is maintained. In this case, the mean free path of the gas molecule is much large than the dimensions of the system, therefore, for approximately parallel surfaces at temperature T_1 and T_2, the heat transferred to the unit area of a surface per unit time by conduction through the residual gas is (White 1968) :

$$q_1 = K\alpha_0 P(T_2 - T_1) \tag{2.2-1}$$

where P is the pressure, K is a constant whose value is 0.028 for helium; α_0 is related to the individual accommodation coefficients α_1 and α_2 and the areas A_1 and A_2 of the two surfaces by

$$\alpha_0 = \frac{\alpha_1\alpha_2}{(A_1/A_2)(1-\alpha_2)\alpha_1+\alpha_2} \tag{2.2-2}$$

In our apparatus, A_1, the area of the sample surface, is about 13 cm², and A_2, the area of the surface of the radiation shield, is 420 cm²; thus (A_1/A_2) is about 0.03. Assuming that $\alpha_1=\alpha_2\cong 0.5$ (White 1968), then we get that $\alpha_0\cong 0.5$. Since $P\cong 10^{-7}$ mm Hg, $(T_2 - T_1)\cong 20$ mK, therefore, from (2.2-1), we have

$$q_1 \cong 3 \times 10^{-11}\ \mathrm{W/cm^2} \tag{2.2-3}$$

and

$$Q_1 = q_1 A_1 \cong 4 \times 10^{-10}\ \mathrm{W} \tag{2.2-4}$$

This is the heat leaking from the shield to the sample by conduction through the residual gas.

2.2-2 Heat transfer by radiation

For two plane parallel surfaces areas of which are A_1 and A_2, and emissivities ε_1 and ε_2, and at respective temperatures T_1 and T_2, the heat transfer to A_1 by radiation per unit time is

$$Q_2 = \sigma A_1 F(T_2^4 - T_1^4) \qquad (2.2\text{-}5)$$

where

$$F = \frac{\varepsilon_1\varepsilon_2}{\varepsilon_2+(A_1/A_2)(1-\varepsilon_2)\varepsilon_1} \qquad (2.2\text{-}6)$$

and σ is Stefan's constant, has a value of 5.67×10^{-12} W cm^{-2} deg^{-4}. In our apparatus, the radiation shield is made of polished copper the value of whose emissivity, ε_2, is about 0.02 (White 1968), and we suppose that the value of sample emissivity, ε_1, is 1, then from (2.2-6), F is about 0.4. Assuming that T_2= 4.02 K, and T_1= 4 K, then according to (2.2-5), we get that

$$Q_2(4\ K) \cong 1.5 \times 10^{-10}\ W \qquad (2.2\text{-}7)$$

At the liquid nitrogen temperature range, suppose that T_2= 80.02 K, and T_1= 80 K, we have

$$Q_2(80\ K) \cong 1.2 \times 10^{-6}\ W \qquad (2.2\text{-}8)$$

2.2-3 Heat transfer through solids (wires)

If the ends of a solid bar of uniform cross-section A and length L are at temperatures T_1 and T_2, the heat flow Q_3 through the solid bar is given by

$$Q_3 = \frac{A}{L}\int_{T_1}^{T_2} \lambda(T)\,dT \qquad (2.2\text{-}9)$$

where $\lambda(T)$ is the temperature-dependent thermal conductivity of the solid. For practical calculations, the mean thermal conductivity of a solid bar with certain end temperatures is most often needed., and it is defined as

$$\overline{\lambda} = (T_2 - T_1)^{-1}\int_{T_1}^{T_2} \lambda(T)\,dT\,, \qquad (2.2\text{-}10)$$

then (2.2-8) becomes

$$Q_3 = \overline{\lambda}\,\frac{A}{L}\,(T_2 - T_1)\,. \qquad (2.2\text{-}11)$$

There are ten manganin leads (ϕ=0.075 mm, L=15 cm), one Au-Fe lead(ϕ=0.075 mm, L=25 cm),one chromel lead(ϕ=0.075mm, L=25 cm), and two copper leads (ϕ=0.0625 mm, L=25 cm) which connect the calorimeter with the radiation shield in our equipment. At 4 K and 80 K, we take λ(manganin)= 0.005 and 0.13 W/cm K (Berman 1976), λ(copper)=4 and 4.1 W/cm K (White 1968), λ(Au-Fe)=0.5 W/cm K (Yan and Lu 1985) and 8 W/cm K respectively, and suppose that λ of chromel is the same as that of manganin. Therefore, when the temperature difference between the calorimeter and the shield is 20 mK, according to (2.2-10), we have

$$Q_3(4\ \mathrm{K}) = 0.22\ \mu\mathrm{W}, \tag{2.2-12}$$

and

$$Q_3(80\ \mathrm{K}) = 0.57\ \mu\mathrm{W}. \tag{2.2-13}$$

From (2.2-4), (2.2-7) and (2.2-12), it can be seen that, at 4K, Q_3 is much larger than (Q_1+Q_2), hence

$$Q_1+Q_2+Q_3 \cong Q_3 \cong 0.22\ \mu\mathrm{W}; \tag{2.2-14}$$

and at 80 K, according to (2.2-4), (2.2-8) and (2.2-13), we have

$$Q_1+Q_2+Q_3 \cong Q_2+Q_3 \cong 1.8\ \mu\mathrm{W}. \tag{2.2-15}$$

At 4 K and 80 K, the power which we use to heat sample is about 40 μW and 6 mW respectively, therefore, the ratio of the heat leaking to the heat input is about $0.22/40 \approx 0.6\%$ at 4 K, and about $1.8/6000 \approx 0.03\ \%$ at 80 K.

In Fig. 2.2, we present some data in T vs. t (time) in the vicinity of 4 K which were gotten when the calorimeter was tested. In this figure, it can be seen that before and after the calorimeter was heated, its temperature was very stable, and

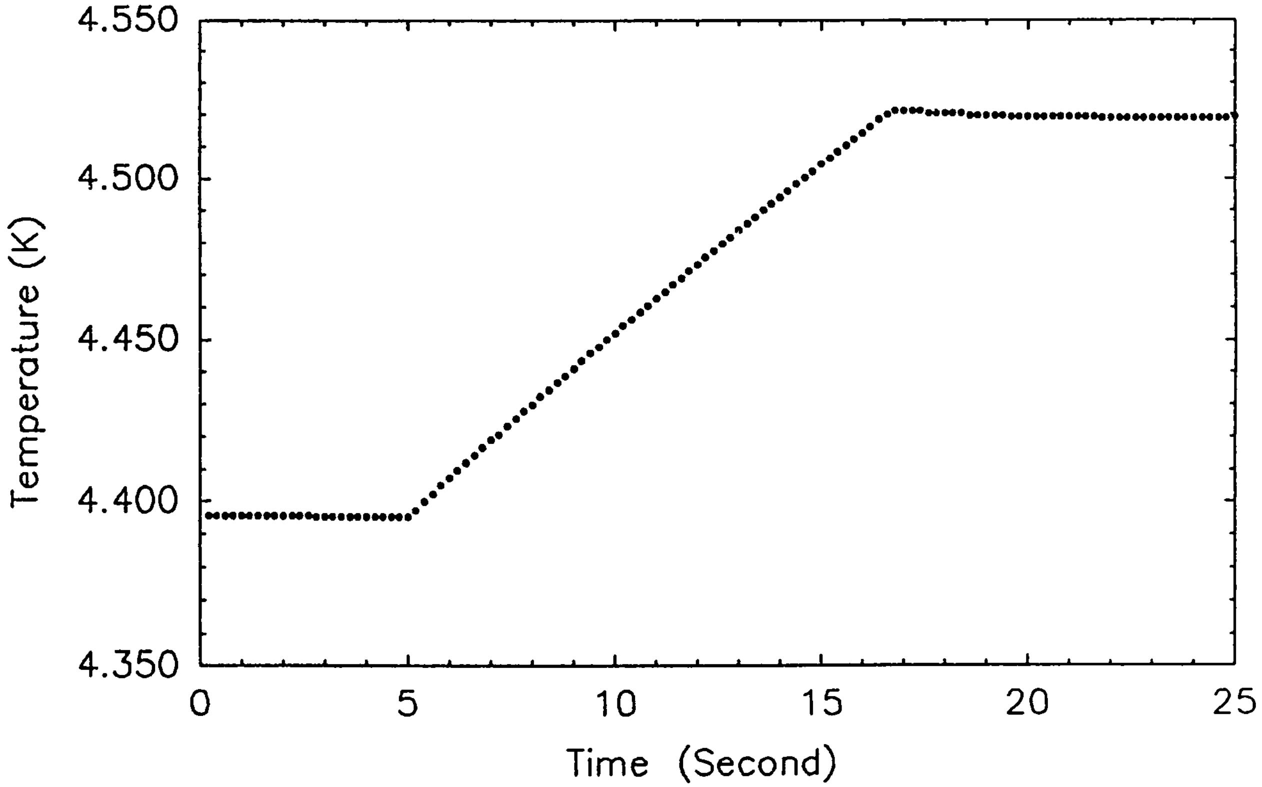

Fig. 2.2 Temperature versus time from a measurement

temperature fluctuation was less than 1mK. It means that the heat leaking is very small and acceptable.

2.3 Thermometry

Two thermometers are used to measure the temperature of the calorimeter. One is a carbon-glass resistance thermometer which is sensitive in the low temperature range, and used between 1 and 50 K. Another one a the platinum resistance thermometer which is used from about 50 K to room temperature.

The carbon-glass thermometer was calibrated by the company (Lake Shore) which made it. The sensitivity (dR/dT) at 4K is 2415 Ω/K , and it decreases by nearly five orders of magnitude from 4K to 300K. The reproducibility at 4.2K is within ± 1 mK. According to the information provided by the company, the temperature of test data for the calibration are those measured with the standard thermometers maintained by Lake Shore Cryotronics, while the resistance values are the measurements recorded on the device being calibrated. The estimated typical error of the calibration which is expressed in deviation from EPT-76 and IPTS-68 is 4 mK at 10 K. A polynomial equation based on the Chebychev polynomial has been fit to the test data. This equation is of the form

$$T = \sum_i A_i \times \mathrm{COS}(i \times \mathrm{ARCCOS}(X)), \qquad (2.3\text{-}1)$$

where A_i represents the Chebychev coefficients, and X is a variable given by

$$X = ((Z-ZL)-(ZU-Z))/(ZU-ZL), \qquad (2.3\text{-}2)$$

where $Z = \mathrm{Log}_{10}(R)$, R is the resistance (Ohms), ZL and ZU designate the lower and upper limit of the variable Z over the fit range. When the fitting range is between 1.40 and 6.90 K, $0 \le i \le 9$; and when the range is from 6.90 to 29.0 K or from 29.0 to 109.9 K, $0 \le i \le 8$. For the three fitting ranges mentioned above, we list values of the Chebychev coefficients, ZL, ZU and RMS error of fit in Table 2.1, 2.2 and 2.3.

The platinum thermometer was calibrated against another platinum thermometer which was calibrated by National Research Council of Canada (NRCC). For convenience, we call the former PT-A, and the latter PT-B. According to the report from NRCC, the PT-B was compared from 10.2 to 90 K with the standard platinum resistance thermometer calibrated in terms of the N.B.S.1955 temperature scale (NBS-55), and maintained by NRCC. The uncertainty of comparison was $\pm 0.1\times 10^{-3}$ ohms. In the temperature range -183°C to +250°C, the resistance-temperature relationship of PT-B is of the form

$$R_t/R_0 = 1+At+Bt^2+C(t-100)t^3 \qquad (2.3\text{-}3)$$

where t is in degrees Celsius, and defined by the International

Practical Temperature Scale of 1960, that is t=T-273.15. In the above equation, R_0=25.530 ohms, A=3.98471×10^{-3}, B=-5.857 ×10^{-7} and C=-4.350×10^{-12}. NRCC reported that, for the PT-B, these values should be accurate enough to permit temperature measurements to within 0.002°C over the range -183°C to +250°C. In order to calibrate PT-A, we compared it with PT-B from 40 K to 300 K, and the uncertainty of comparison was about ±0.5×10^{-3} ohms. The estimated error of the calibration, for the PT-A, is about 10 mK at 80 K, the sensitivity (dR/dT) at 80 K is 0.426 Ω/K.

It should be mentioned that there is a scale difference between NBS-55 and IPTS-68 over the range 13.81 to 90.188 K. The difference is shown in Fig 2.3 from 50 to 90 K. As we know, the specific heat is

$$C = \frac{\Delta Q}{\Delta T} = \frac{\Delta Q}{\Delta R}\,\frac{\Delta R}{\Delta T}. \tag{2.3-4}$$

Therefore, if C_{68} and C_{55} denote the specific heat which is obtained according to IPTS-68 and to NBS-55 respectively, we have

$$\frac{C_{68}-C_{55}}{C_{68}} = \frac{\left(\frac{\Delta R}{\Delta T}\right)_{68} - \left(\frac{\Delta R}{\Delta T}\right)_{55}}{\left(\frac{\Delta R}{\Delta T}\right)_{68}}. \tag{2.3-5}$$

From the above equation, we have calculated the difference between C_{68} and C_{55} for using PT-A to measure specific heat from 50 to 90 K, and the results are shown in Fig. 2.4. The maximum value of $(C_{68} - C_{55}) / C_{68}$ is 0.27% which is at about 88 K.

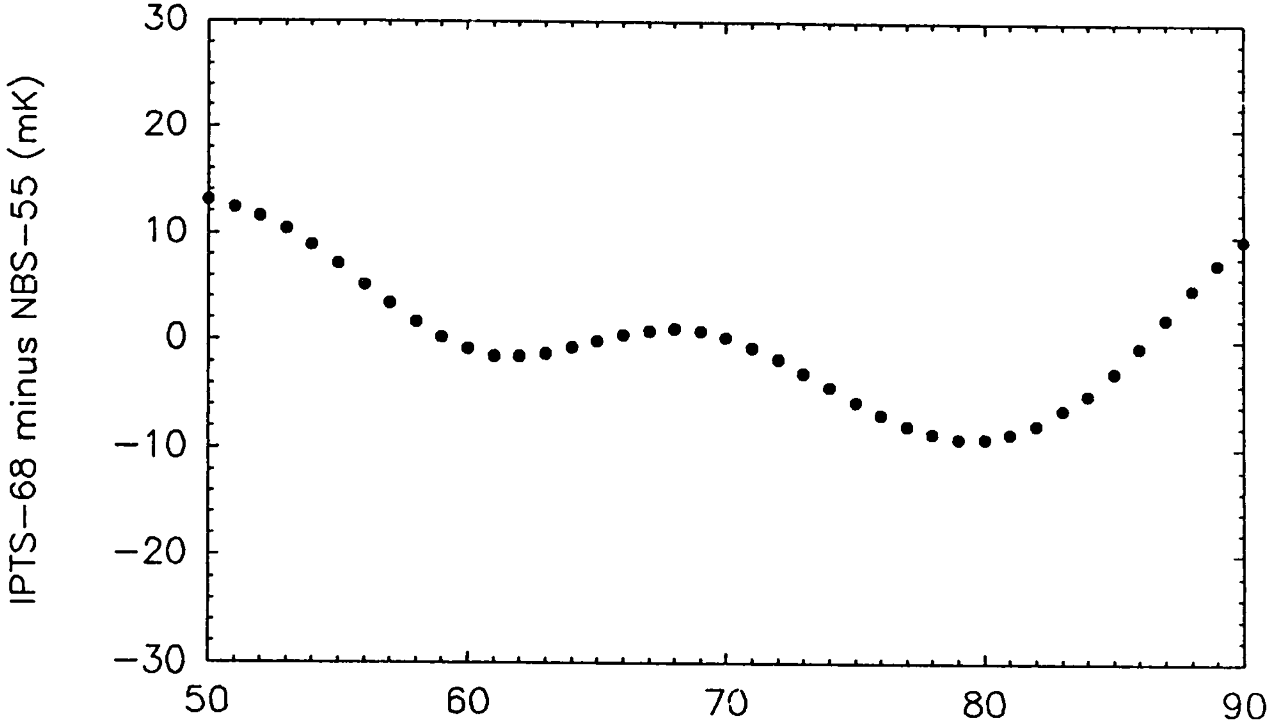

Fig 2.3 Difference of the temperature scale NBS−55 from the IPTS−68. The data are from Bedford et al. 1969.

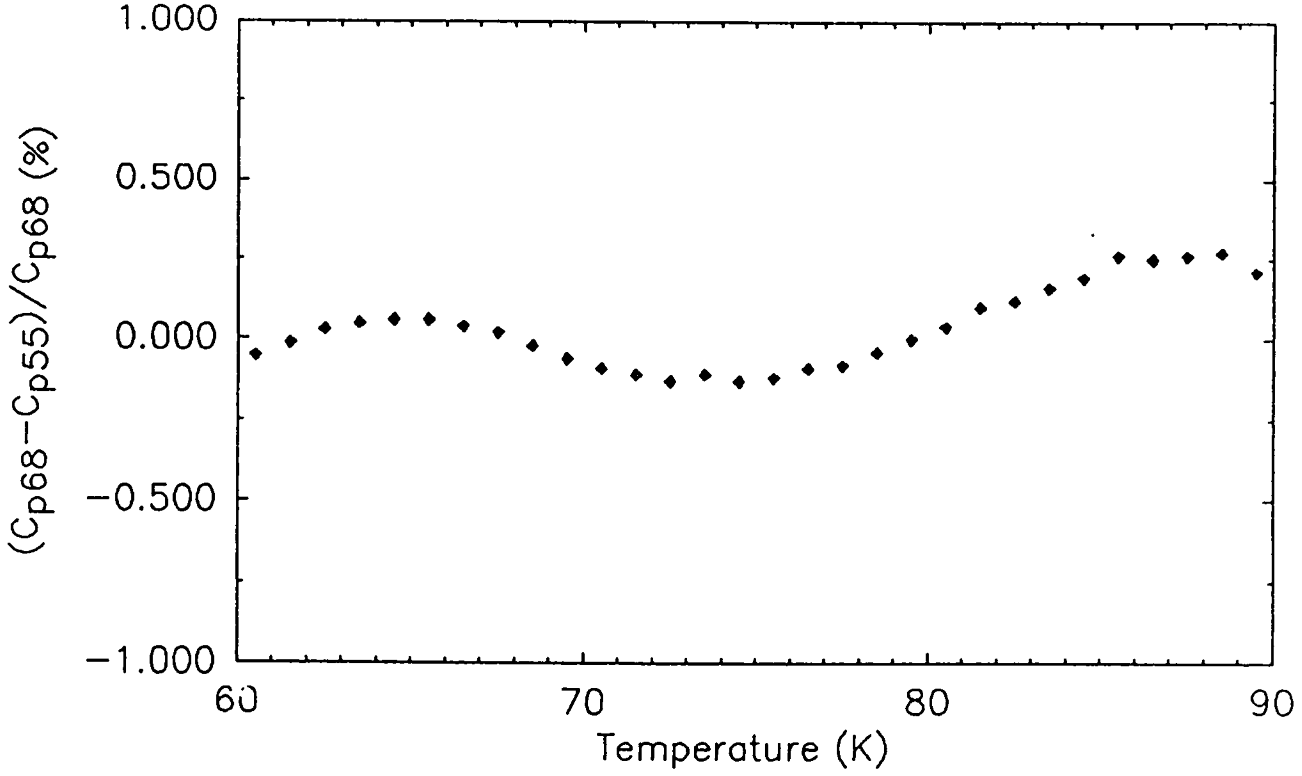

Fig. 2.4 $(C_{p68}-C_{p55})/C_{p68}$ vs T.

Table 2.1 Chebychev coefficients in the temperature range of fit 1.40 to 6.90 K

Order	Coefficient A_i	Std. Dev. of Coeff.
0	3.469587	9.2705×10^{-5}
1	-3.243287	1.5920×10^{-4}
2	1.343478	1.3526×10^{-4}
3	-.519022	1.2278×10^{-4}
4	0.203792	1.0256×10^{-4}
5	-.075711	9.7796×10^{-5}
6	0.028969	1.0777×10^{-4}
7	-.011178	1.2612×10^{-4}
8	0.003808	1.2563×10^{-4}
9	-.001543	1.1480×10^{-4}

ZL = 2.37591103859

ZU = 6.6903185319

RMS error of fit = 0.24 mK

Table 2.2 Chebychev coefficients in the temperature range of fit 6.90 to 29.0 K

Order	Coefficient A_i	Std. Dev. of Coeff.
0	14.208457	5.2253×10^{-4}
1	-12.078669	8.8357×10^{-4}
2	4.431473	7.5375×10^{-4}
3	-1.501479	6.2053×10^{-4}
4	0.477663	5.2431×10^{-4}
5	-.144847	5.5490×10^{-4}
6	0.043369	6.8629×10^{-4}
7	-.011627	7.3106×10^{-4}
8	0.004283	6.3684×10^{-4}

ZL = 1.57062671857

ZU = 2.9355106101

RMS error of fit = 1.27 mK

Table 2.3 Chebychev coefficients in the temperature range of fit 29.0 to 109.9 K

Order	Coefficient A_i	Std. Dev. of Coeff.
0	62.599513	2.2355×10^{-3}
1	-48.148936	3.5372×10^{-3}
2	14.405174	3.2809×10^{-3}
3	-3.727650	3.0353×10^{-3}
4	0.859122	2.8220×10^{-3}
5	-.176478	2.8086×10^{-3}
6	0.032354	2.7860×10^{-3}
7	-.004990	2.7823×10^{-3}
8	-.001799	2.7356×10^{-3}

ZL = 1.18751761718

ZU = 1.67288400316

RMS error of fit = 7.63 mK

CHAPTER 3

SAMPLE PREPARATION

Not long after the superconductor with T_C of about 90 K, whose superconducting phase was later identified as $YBa_2Cu_3O_7$, was discovered by Wu and his colleagues (1987) , it almost became a standard procedure to make it, and therefore, it is quite easy to get a good YBCO superconducting sample. In contrast with this, although almost three years passed after Bi-compound superconductor was reported (Maeda et al. 1988), it is still very difficult to make a good Bi-Sr-Ca-Cu-O superconducting sample, especially, to make a single 110 K phase sample, if it is possible to make now. This is because the properties of the Bi-compound superconductor are affected by so many factors such as composition, heat treatment, cooling rate, oxygen pressure and other preparative conditions (Tarascon et al. 1988, Sumiyama et al. 1988, Kijima et al. 1988, Endo et al. 1988, Koyama et al. 1988, Nobumasa et al. 1989, Endo et al. 1989, Den and Akimitsu 1989, Ishida and Sakuma 1988, Ishida 1989, Majewski et al. 1990), and, so far, people have not really understood what the key point is for making good Bi-compound superconducting sample.

In this chapter, we will describe our sample preparation, mostly, we will focus on the Bi-compound sample preparation, and give some discussion about it.

3.1 Three superconducting phases in Bi-compound system

The Bi-compound superconductor is often expressed as $Bi_2Sr_2Ca_{n-1}Cu_nO_y$, where n is the number of Cu-O layers in half a unit cell, and different n leads to different superconducting phase.The phases which n=1,2 and 3 correspond to are often denoted as the 2201, 2212 and 2223 phase respectively. The transition temperature T_C for all three phases depends on the nominal composition and preparative conditions. However, empirically, T_C increases with increasing number of n up to 3, and decreases for further increase of n (Ihara et al. 1988). Roughly, the transition temperatures of the 2201, 2212 and 2223 phase are between 8 and 25K (Maeda et al. 1990), 65 and 85K (Mohanram et al. 1990) and 100 and 110K, respectively. For the n=4 phase, according to our knowledge, so far, people know very little about it.

With few exceptions, the samples for all three phases have a tetragonal unit cell (Maeda et al. 1990). The lattice parameter a(=b) is approximately 5.4 Å, and changes little when the n changes from 1 to 3 (Tallon et al. 1988, Tarascon et al. 1988, Endo et al. 1988, Maeda et al. 1990). The lattice parameters c of 2201,2212 and 2223 phase are about 24.6, 30.6 and 37.2 Å respectively (Tallon et al. 1988, Raveau et al. 1989 Ramesh et al. 1988, Pierre et al. 1989, Maeda et al. 1990). According to the X-ray diffraction patterns of our samples (radiation: CoK_{α}, wavelength $\lambda=1.79026$ Å), we got that the lattice parameter c is 30.6±0.2 Å for 2212 phase, 36.9±0.2 Å for 2223 phase, and that a=b=5.39±0.01 Å.

From measurements of the Hall effect, it has been found that the carriers in all three superconducting phases are holes, and the transition temperature T_C is strongly affected by the hole concentration (Den and Akimitsu 1989, Maeda et al. 1990, Groen et al. 1990).

It should be mentioned that the ideal composition which was calculated from the crystal structure model based on the X-ray diffraction analysis (Tarascon et al. 1989b) gives the valences completely balanced, indicating $Cu^{+2.0}$, and, therefore, the structure model does not explain the superconductivity (Nobumasa et al. 1989).

It is known that it is difficult for one to get a single 22(n-1)n phase sample if one uses the nominal composition 2:2:(n-1):n to make the sample. Therefore, when people make samples, the composition is often different from 2:2:(n-1):n. For instance, it is reported (Maeda et al. 1988, Tarascon et al. 1989a) that in order to get the single 2212 phase, the nominal composition 2:(2-X):(1+X):2 with X>0 was used instead of 2:2:1:2. For the single 2223 phase, according to our knowledge, it may be impossible to get it using the composition 2:2:2:3.

3.2 Sample Preparation

3.2-1 YBCO Sample

The first sample which we use to measure the specific heat is a $YBa_2Cu_3O_7$ superconductor. We label it as YBCO. The sample was prepared from powders of Y_2O_3, $BaCO_3$ and CuO. The powders were thoroughly mixed, pressed into a pellets, and heated at 920°C for 24 hours in air. Then, the pellet was re-ground, repressed and calcined at 925°C for 10 hours in flowing oxygen. After calcination, the sample was slowly cooled down to room temperature in O_2. Finally, the sample had a diameter of 3/4 inch, and a weight of 17.221 g. The X-ray measurements confirmed that it was a single phase superconductor. Dc-magnetization measured with a SQUID magnetometer showed a single phase transition near 91 K (Fig. 3.1). However, resistance measurements showed a "foot" to zero-resistance at 87 K after a sharp drop near 91 K (Fig 3.2). The origin of the foot is not clear so far.

3.2-2 BSCCO Samples

As mentioned above, so far, it is not known what determines T_C of the Bi-compound superconductors, and what is the real key point for making a good Bi-compound sample. Sometimes, even using the same composition and conditions, people could not get the same results. Therefore, when people make Bi-compound samples, they determine the recipes and preparative conditions mostly according to their experience.

In 1988, we started to make Bi-compound superconducting samples. At the beginning, we used various compositions which did not contain Pb to make samples under various conditions, and tried to get the 2223 phase as much as possible. For a typical Bi-compound sample without lead which we made, there was a sharp drop in resistivity near 110 K, then a tail with zero resistivity temperature at 65-80 K. Some group reported that zero resistance at >100 K could easily be observed, although X-ray diffraction might show that there is only 20-30% of the 2223 phase in a sample (Mohanram et al 1989). Our results, however, do not coincide with theirs. Many non-lead-doped samples made by us do contain more than 25% of the 2223 phase, but there is still a tail, and the zero-resistance temperature was far below 100 K.

The first Bi-compound superconducting sample which we made to measure the specific heat is $BiSrCaCu_2O_y$. We call it BSCCO1. The sample was prepared by the solid-state reaction. Bi_2O_3, $SrCO_3$, $CaCO_3$ and CuO were used, and the purity of all these compounds was larger than 99.99%. The nominal composition of Bi:Sr:Ca:Cu was 1:1:1:2. The powder was well ground and mixed in an agate mortar, and pressed into a pellet. The pellet was calcined at 830°C for 14 hours in air. Then, it was reground, remixed and repressed into a small cylinder with a diameter of 3/4 inch, and subsequently, calcined in air at 872°C for 72 hours. After calcination, it was slowly cooled to 700°C (1 degree/min), and then cooled to room temperature in the oven. We wanted to increase the content of 2223 phase, therefore, the above procedure was repeated. According to the resistivity measurements, however, it seemed that the 2223 phase did not increase, but decreased after the procedure was repeated. Eventually, the sample approximately contains 30% of the 2223 phase and 70% of the 2212 phase according to the low angle part of the powder X-ray spectrum (Fig. 3.4). The resistivity measurements by the standard four-lead method show that there are sharp drops near 110 K and 80 K, with zero resistance temperature at 65 K (Fig. 3.3). The dc-magnetization of the sample was measured in a SQUID magnetometer. The results also show two sharp drops near 110 K and 80 K (Fig. 3.5). The mass of the sample is 9.523 g.

Besides sample BSCCO1, we have performed specific heat measurements on another non-lead-doped sample. We call the sample BSCCO2, and it was made by Hoechst Company, Germany, and its nominal composition of Bi:Sr:Ca:Cu is 2:2:1:2. According to the powder X-ray spectrum, it seems to be a pure 2212 phase sample (Fig. 3.6). However, the resistance measurements reveal that besides a big drop near 91 K, there is another slight drop near 115 K which can be seen in Fig 3.7. This means that the sample still contains some 2223 phase. The dc-magnetization measurements show that the superconducting transition of this sample starts about 90 K, and it is not sharp, but quite broad, and near 76 K second gradual drop is visible (Fig 3.8). The slight drop at 115 K has not been detected by the magnetic measurements. The mass of this sample is 17.815 g.

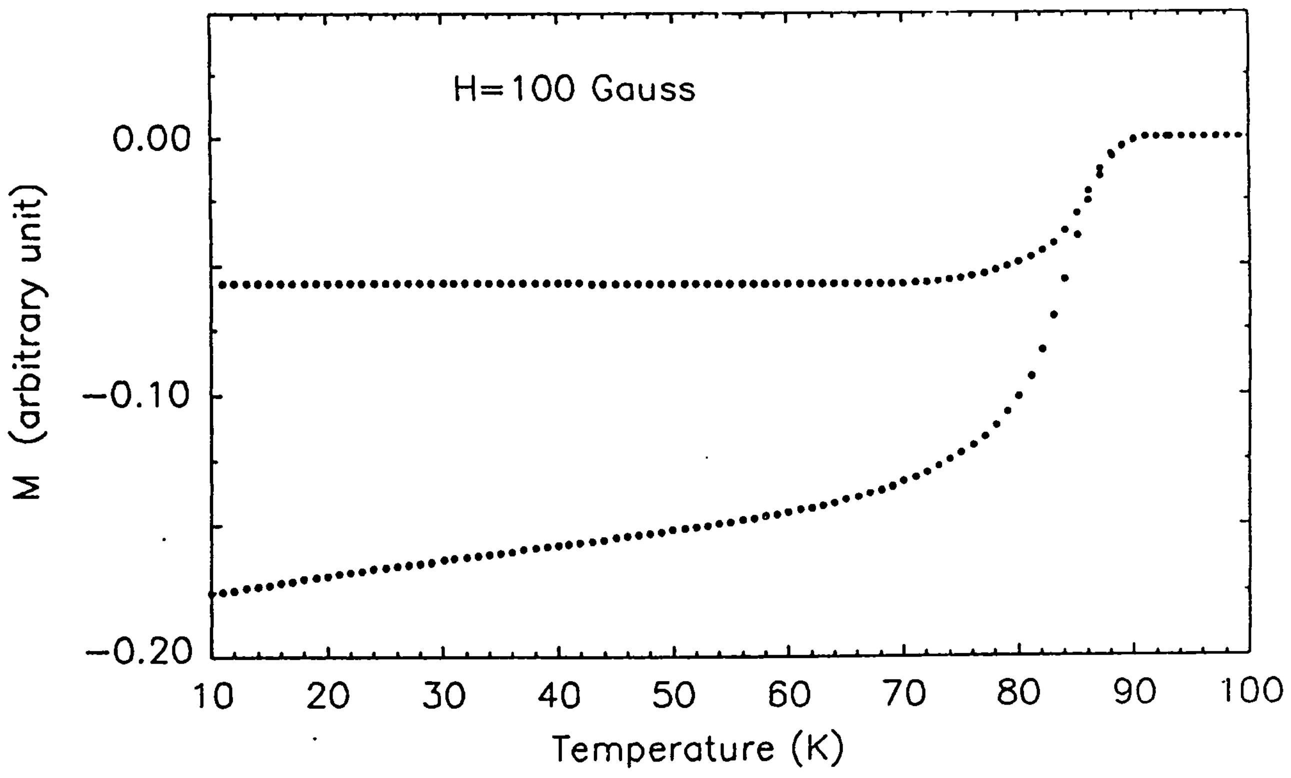

Fig. 3.1 Magnetization versus temperature for Sample YBCO

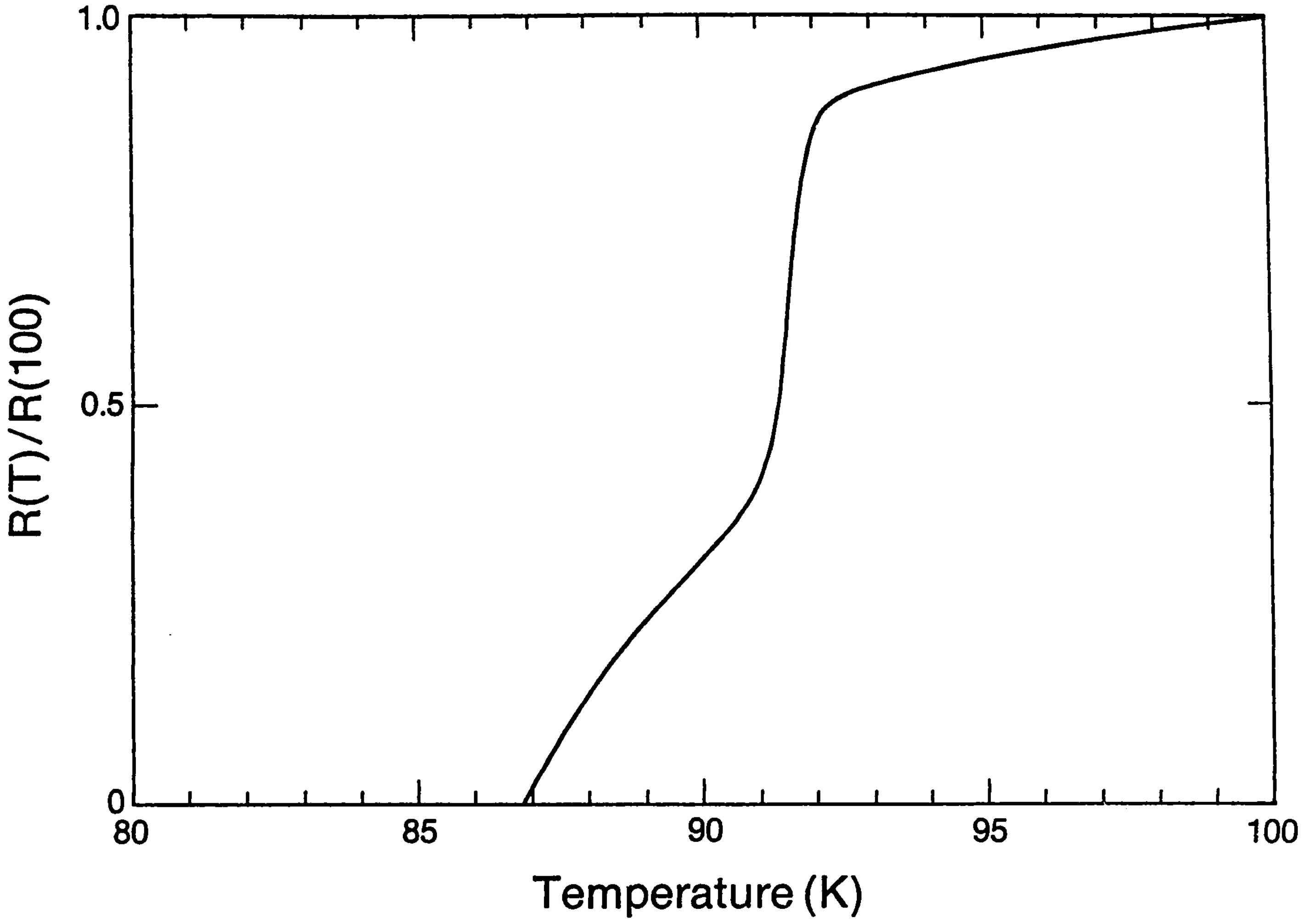

Fig. 3.2. Resistance versus temperature for sample YBCO.

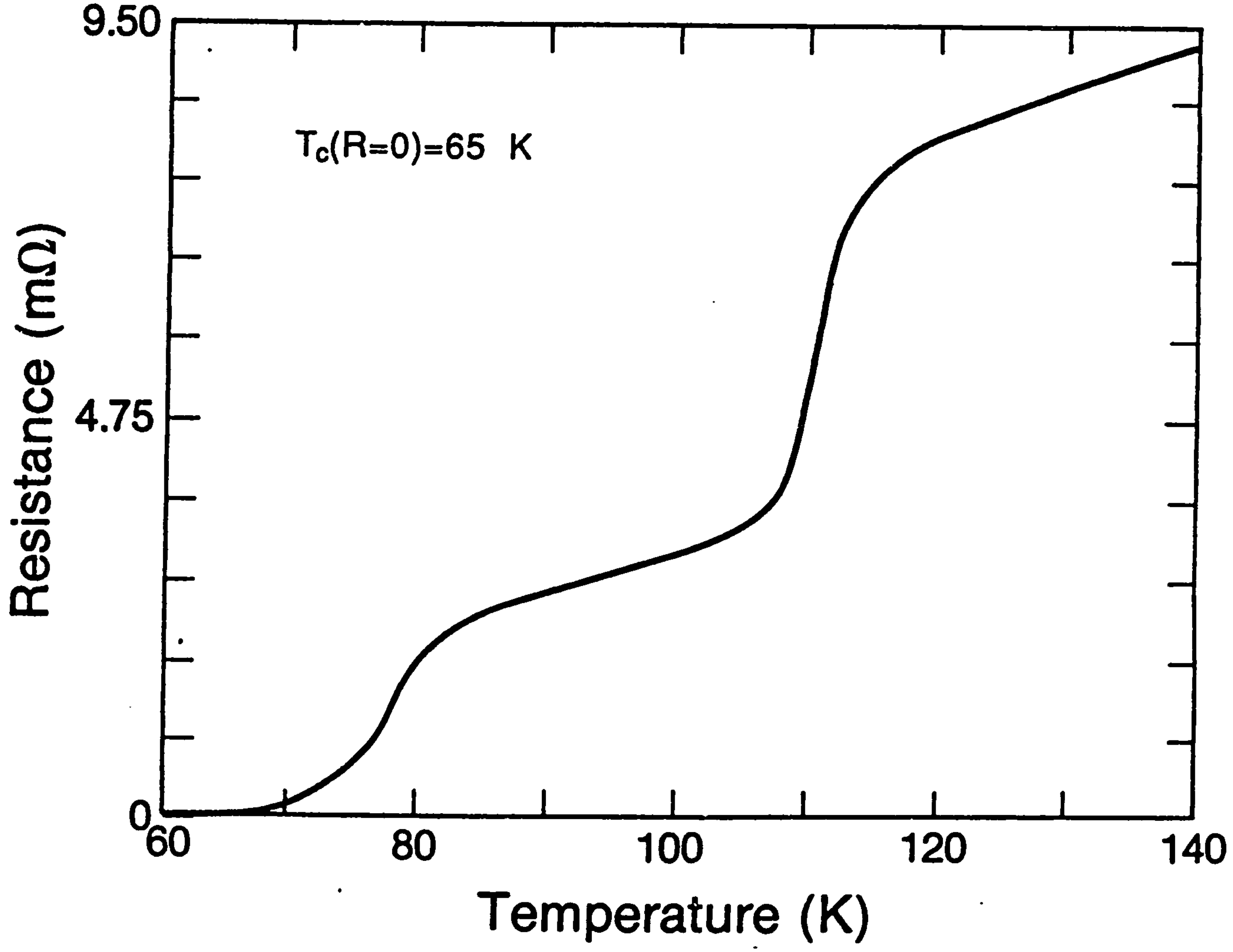

Fig. 3.3 Resistance of BSCCO1 as a function of temperature.

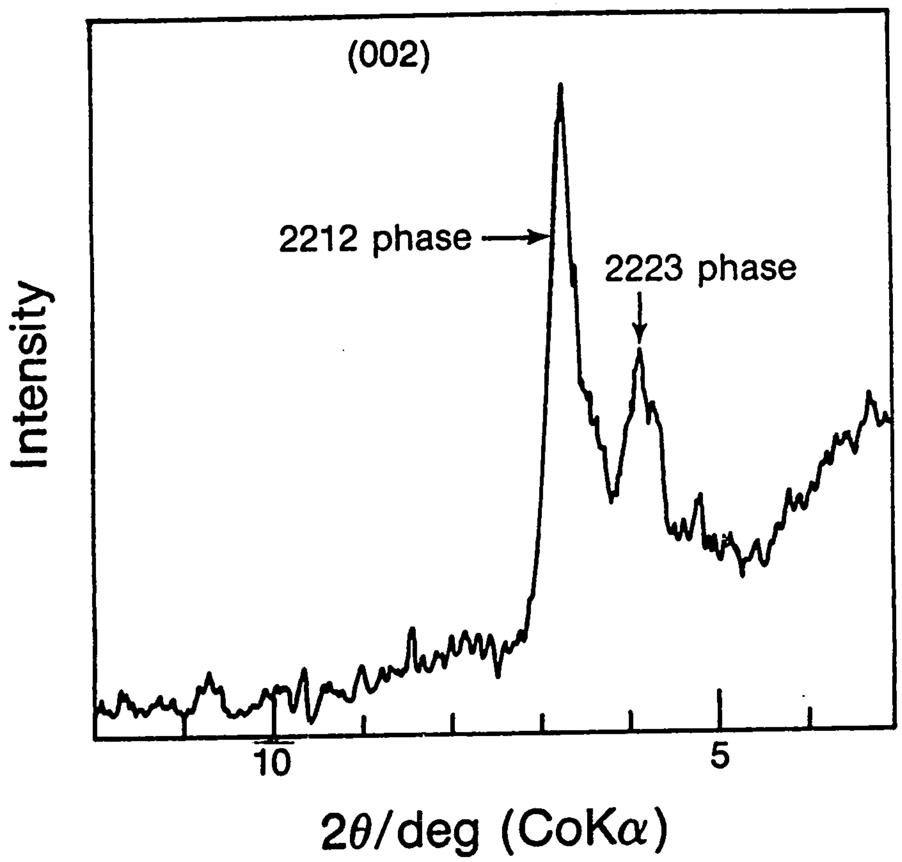

Fig. 3.4. The low angle part of the powder X-ray spectrum for BSCCO1.

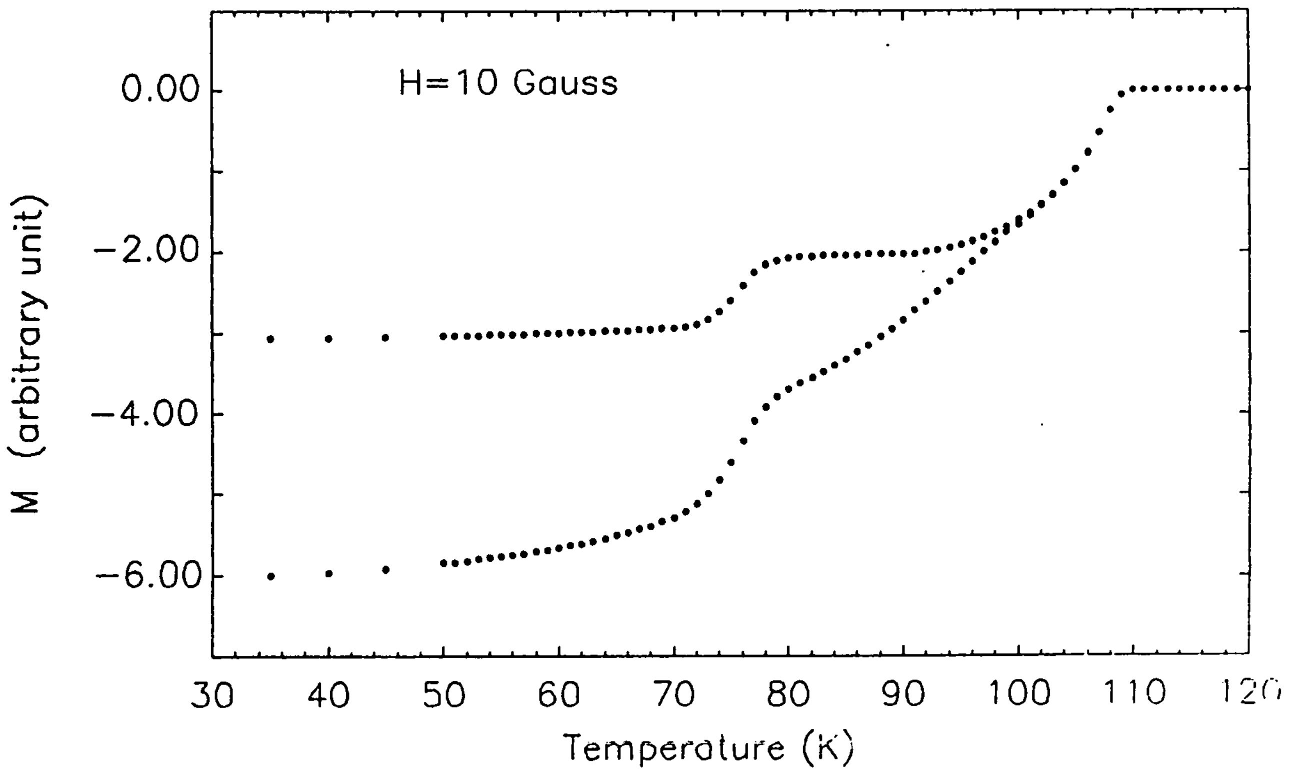

Fig. 3.5 Magnetization versus temperature for Sample BSCCO1

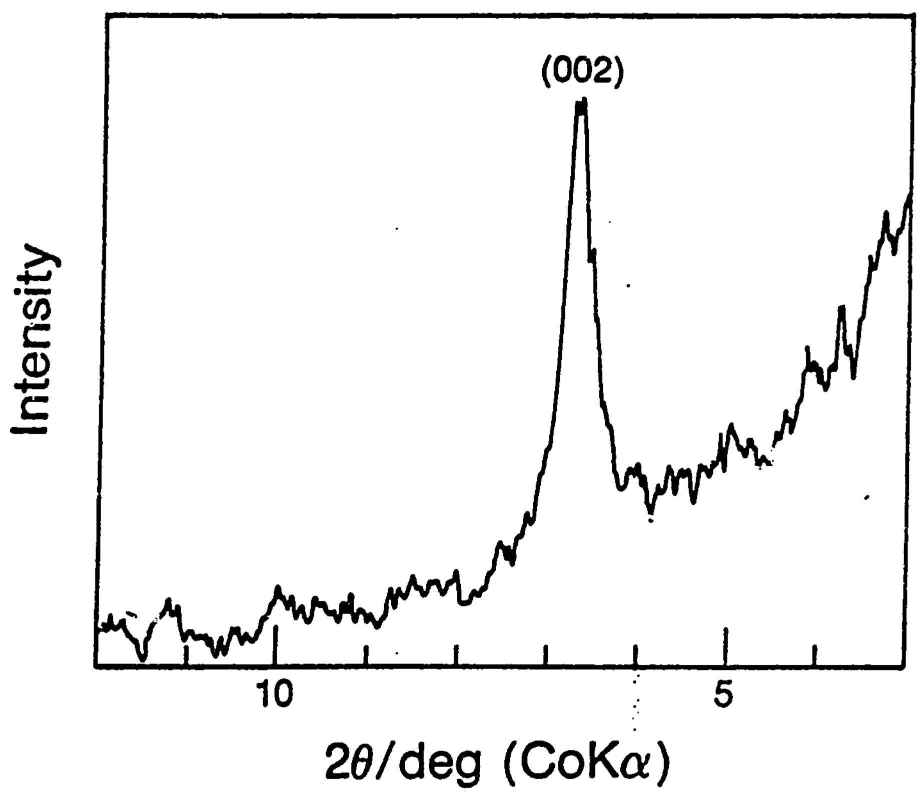

Fig. 3.6. The low angle part of the powder X-ray spectrum for BSCCO2.

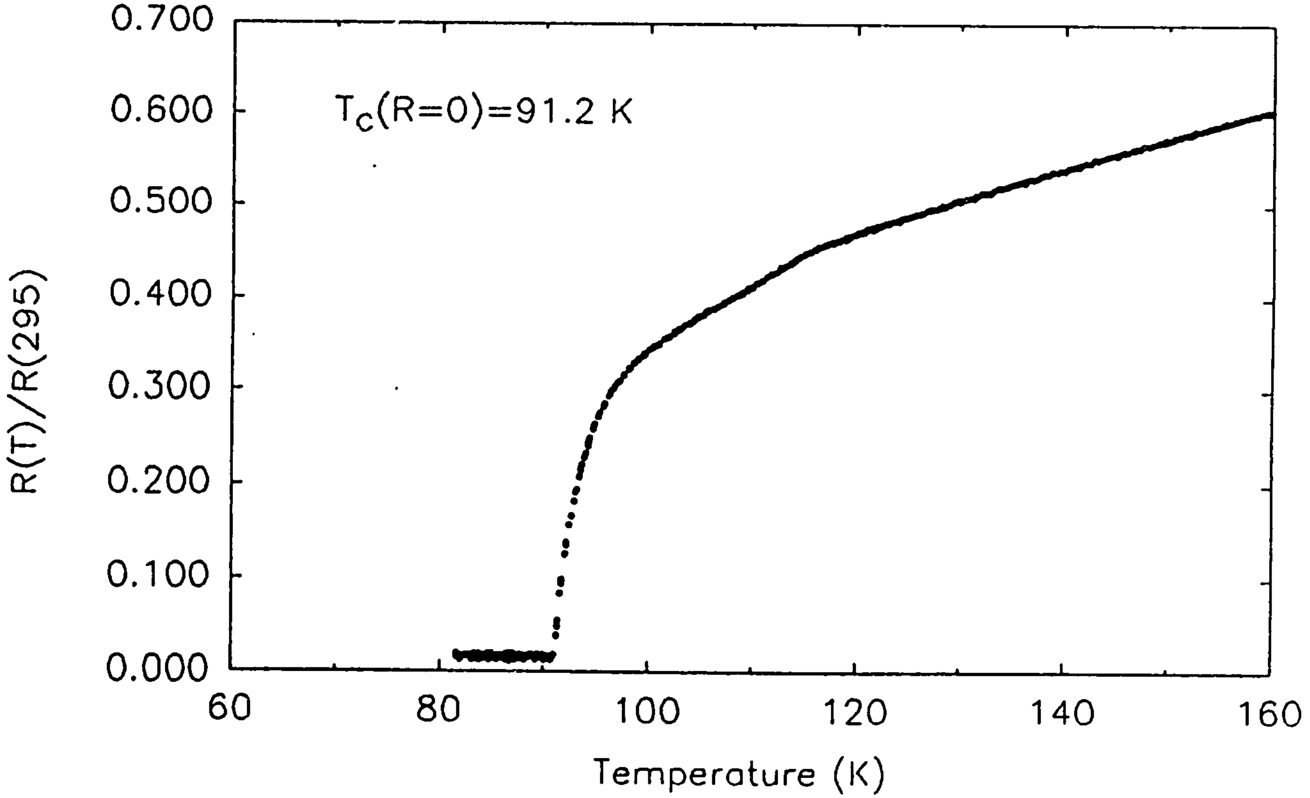

Fig. 3.7 Resistance versus temperature for BSCCO2

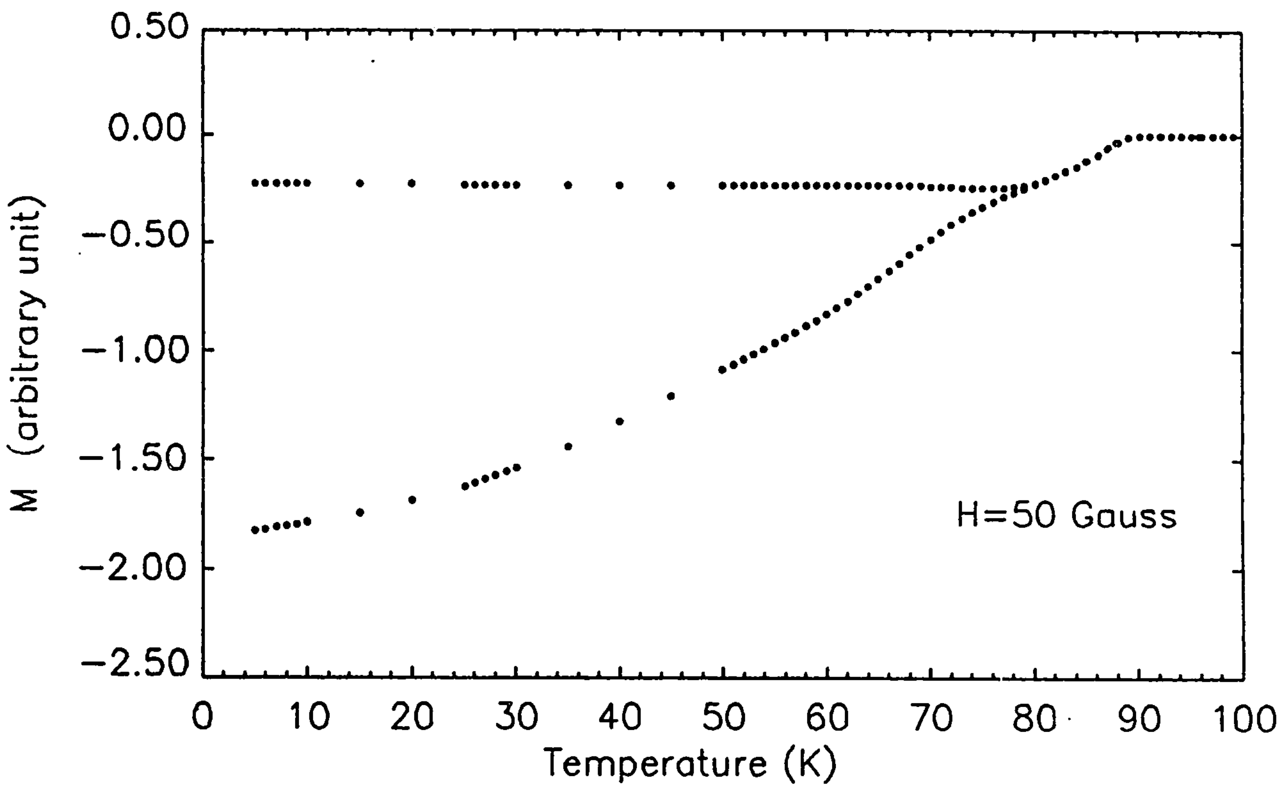

Fig. 3.8 Magnetization versus temperature for Sample BSCCO2

3.2-3 BPSCCO Samples

Since the discovery of superconductivity in Bi-compound system, much effort has been made to increase high-T_C phase (the 2223 phase). In order to do so, an addition of excess Ca, Cu and Sr (Sumiyama et al. 1988, Kijima et al. 1988, Endo et al. 1989), prolonged sintering, low pressure or high pressure oxygen treatments (Endo et al. 1988, Koyama et al 1988 Kuwahara et al. 1988), and partial substitution of Pb for Bi (Sunshine et al. 1988, Takano et al. 1988) have been attempted. Among these efforts, according to our experience and knowledge, the partial substitution of Pb for Bi is the most effective way in increasing the ratio of the high-T_C phase.

It has been observed (Nobumasa et al. 1989) that the Pb atoms are located in Bi-O layers. The valence of Pb is +2, and Bi could have the valence of either +3 or +5, therefore, the substitution of Pb for Bi to occupy its sites will increase the hole concentration. This suggests that the increase of content of the high-T_C phase in Bi-compound samples strongly connects with a proper increase in the hole concentration.

After Pb is added to the Bi-compound system, it becomes easy to make samples with zero-resistance temperature above 100 K. However, in order to raise the percentage of the 2223 phase in samples, it is necessary that samples are sintered for sufficiently long time at a suitable temperature. We have made a group of samples whose nominal composition of Bi:Pb:Sr:Ca:Cu is 1.5:0.5:2:2:3. After being fired at 810°C for 16 hours, the samples have been reground and remixed, then sintered at 845°C for 50, 140, 240 and 340 hours respectively. The X-ray measurements show that these samples contain about 25%, 55%, 65% and 75% of the 2223 phase respectively. However, if there is a further increase in sintering time, the 2223 phase does not increase any more, but decreases. For instance, when the sample mentioned above is sintered at 845°C for 460 hours, the content of the 2223 phase drops to about 65% (see Fig. 3.9). It is because the 2223 phase begins to decompose after an optimum sintering time is exceeded. Other groups have also observed this kind of phenomenon (Shi et al. 1989, Wang et al. 1990).

On the other hand, more intermediate grindings and mixings also are helpful for increasing the 2223 phase. We have compared two samples. One is calcined at 845°C for 340 hours with three intermediate grindings, and another one is calcined at the same temperature for the same hours without any intermediate grinding. The X-ray measurements tell us that there is about 75% of the 2223 phase in the first sample, but only 35% of the 2223 phase in the second one. This may be because more intermediate grinding make the solid-state reaction more uniform.

We would like to point out that, according to our experiments, it is still very difficult to make single 2223 phase after lead is added to the samples, if it is possible now. Very recently, P. Majewski et. al. (1990) also reported that, so far, the 2223 phase could not be prepared without significant amounts of impurity phases, i.e. 2212 phase, copperoxide and

(Ca, Sr)-cuprates.

The sample which is denoted as BPSCCO1 was also prepared by solid reaction method. The initial reagents were Bi_2O_3, PbO, $SrCO_3$, $CaCO_3$ and CuO, all of them were in high purity (>99.99%). The nominal composition of Bi:Pb:Sr:Ca:Cu was 1.6:0.4:1.6:2.0:2.8. After the powder was well ground, mixed and pressed into a pellet, it was first calcined at 810°C for 16 hours in air. Subsequently, the pellet was reground, remixed and repressed into a small cylinder with a diameter of 3/4 inch, and calcined at 845°C for 240 hours in air. Then, the sample was cooled to 500°C slowly (1°C/min.), and further cooling to room temperature naturedly happened in the oven. Finally, the mass of the sample is 12.710 g.

Sample BPSCCO1 shows a single resistive transition to $R = 0$ at 106.3 K (fig. 3.10). The X-ray diffraction patterns of this sample shows, however, that there still is the presence of both the 2223 and the 2212 phase, but, at this time, the 2223 phase is about 70%, and the 2212 phase is roughly 30% (Fig. 3.11). The susceptibility of this sample also show the two superconducting transitions, one is at 108.9 K, and another is near 82 K (Fig. 3.12).

Koyama et al. reported (1988) that the low oxygen pressure treatment was remarkably helpful to increase and single out the 2223 phase. However, the results from our experiments disagree with theirs. A paper by Mohanram et al. (1989) also reported that although the making procedures reported by Koyama

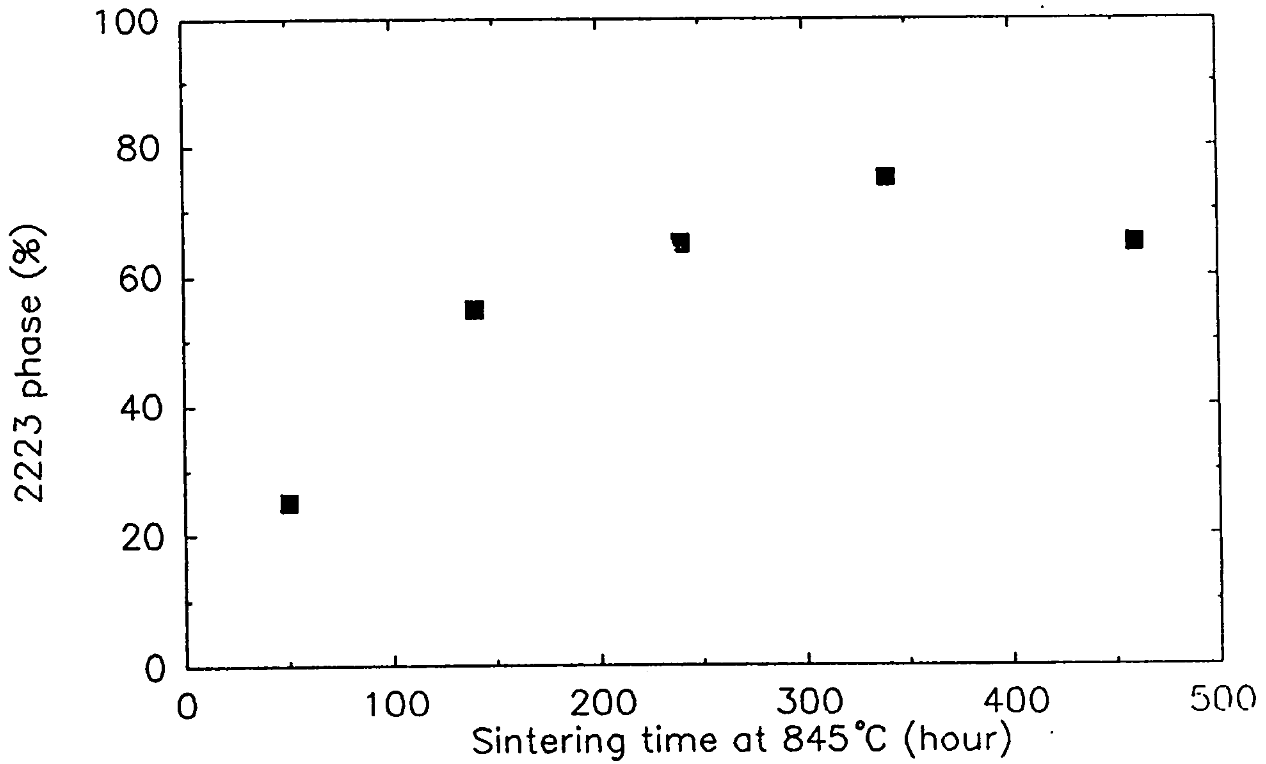

Fig. 3.9 The sintering time vs. the content of 2223 phase for Pb-doped Bi-compound samples ($Bi_{1.5}Pb_{0.5}Sr_2Ca_2Cu_3O_Y$).

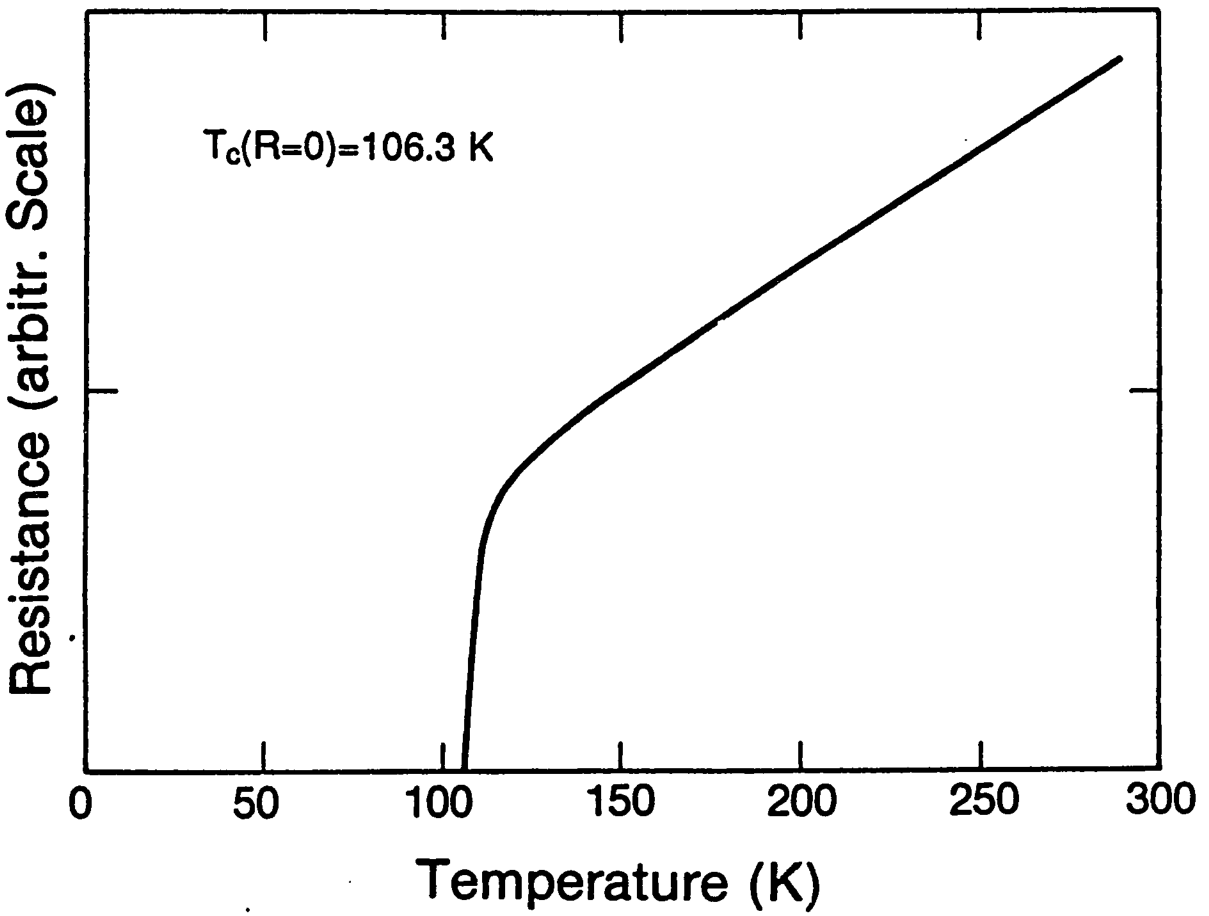

Fig. 3.10 Resistance versus temperature for Sample BPSCCO1.

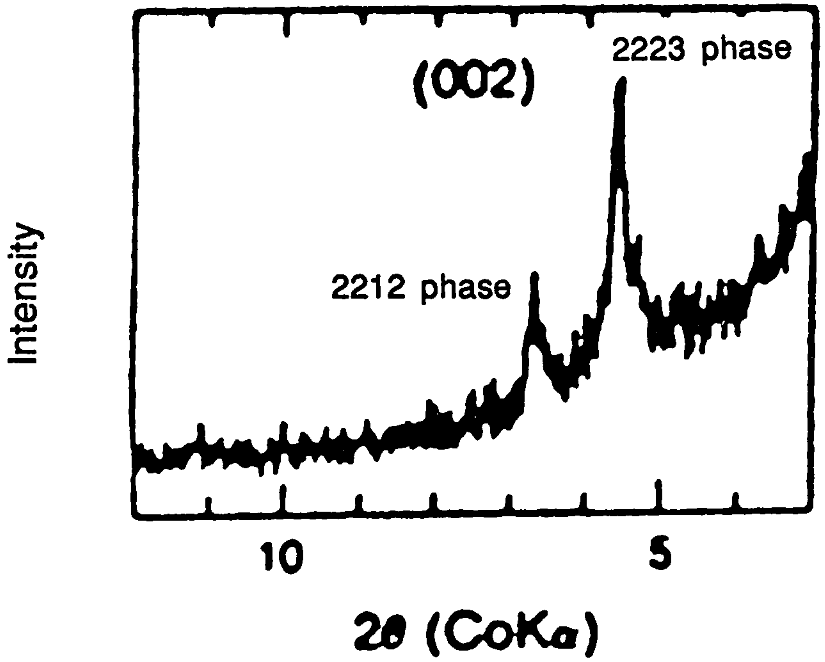

Fig 3.11 The low angle part of the powder X-ray spectrum for BPSCCO1.

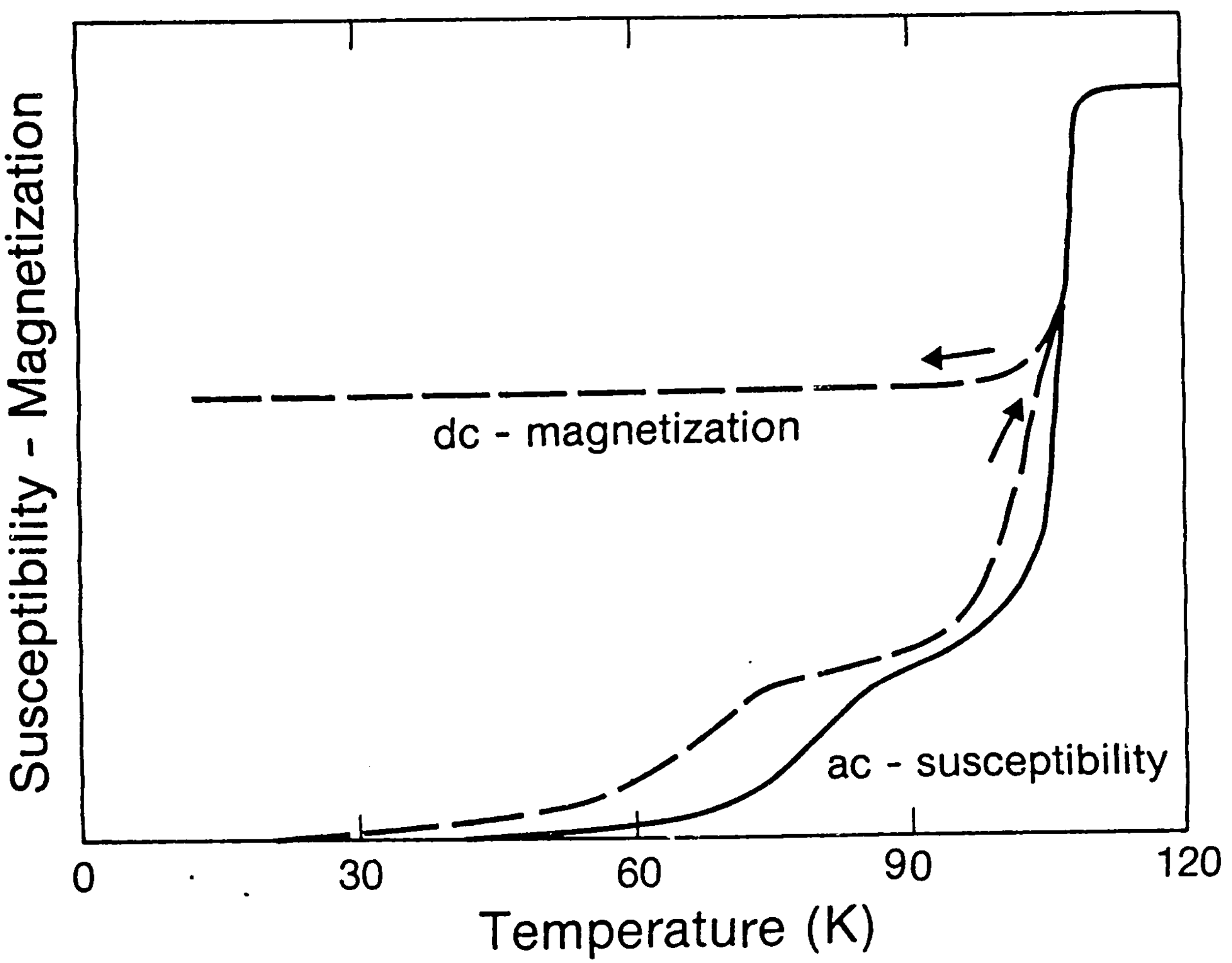

Fig. 3.12 Susceptibility - Magnetization vs. temperature for BPSCCO1, measured by S. Gygax.

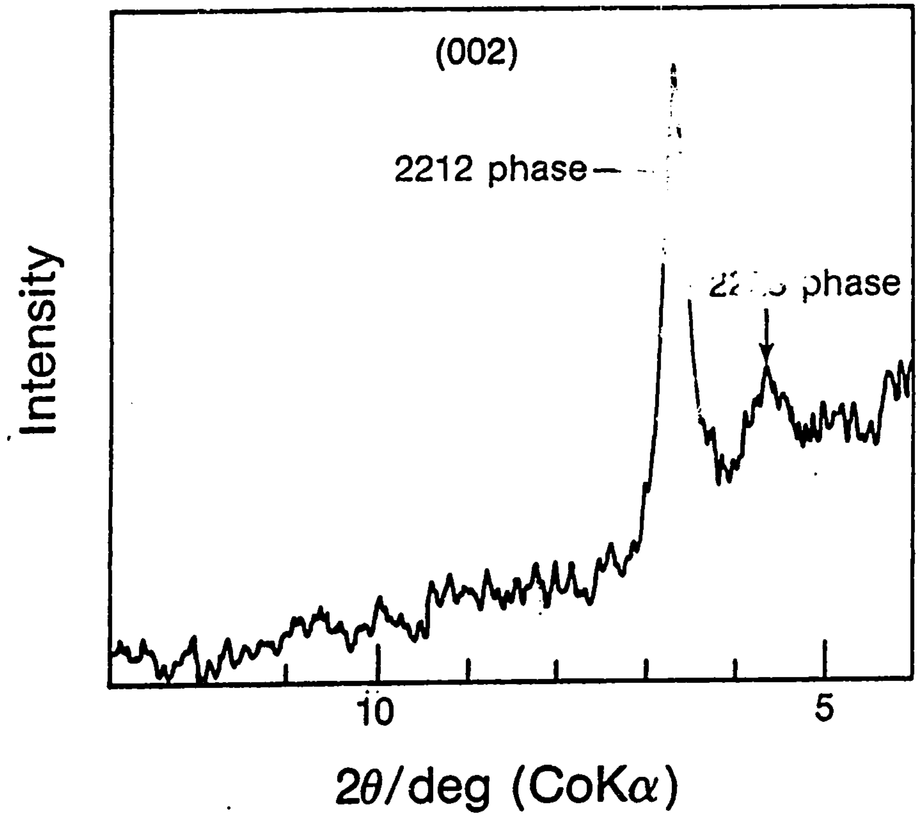

Fig. 3.14. The low angle part of the powder X-ray spectrum for BPSCCO2.

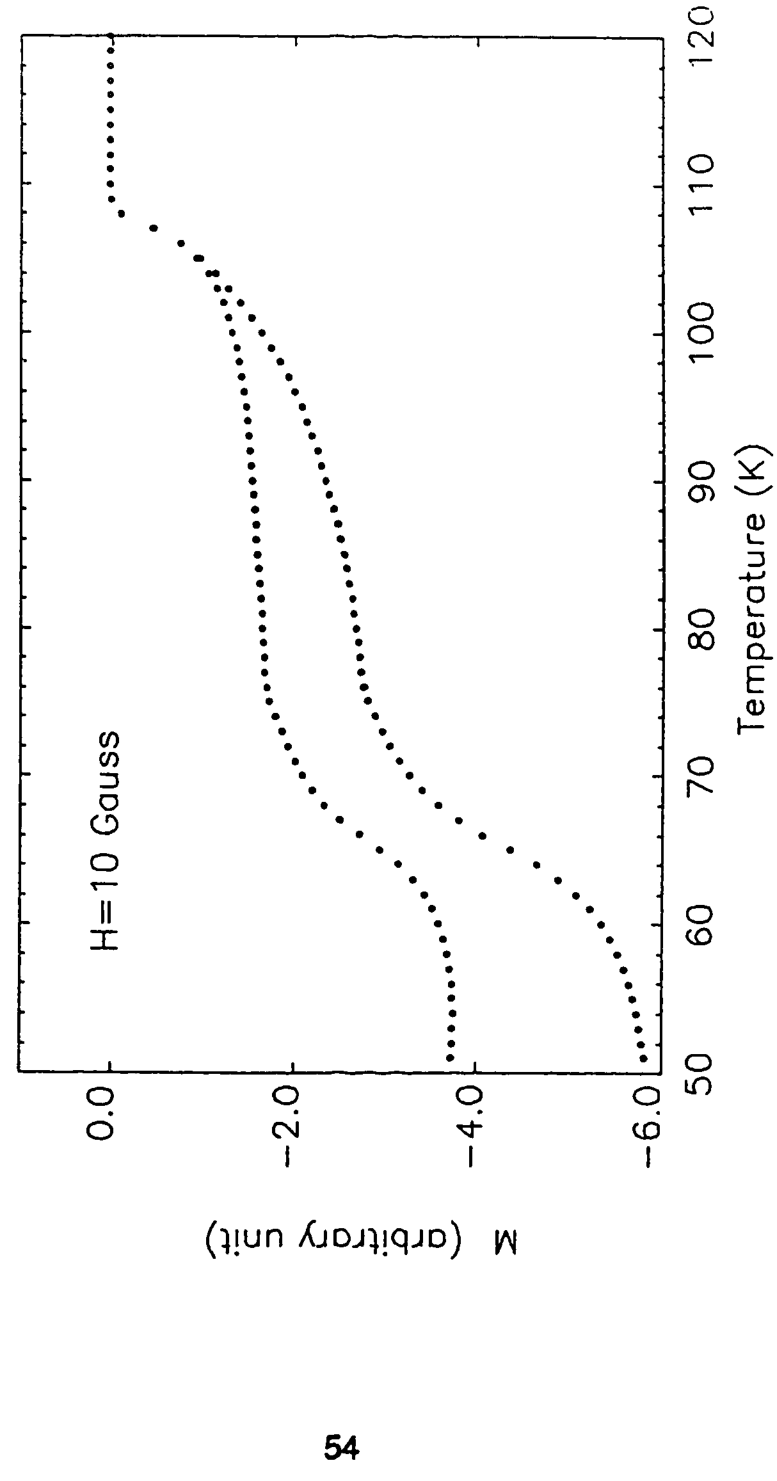

Fig. 3.15 Magnetization versus temperature for BPSCCO2

et al. were exactly followed, they could not get a sample containing the pure 2223 phase, instead of that, the sample only contained about 60% of the 2223 phase.

Sample BPSCCO2 was made under a low oxygen pressure in our laboratory. The nominal composition of this sample was Bi:Pb:Sr:Ca:Cu = 1.84:0.34:1.91:2.03:3.06. The powders were prepared by mixing Bi_2O_3, PbO, $SrCO_3$, $CaCO_3$ and CuO, followed by heating at 810°C for 16 hours in air. Subsequently, they were reground and pressed into a pellet, and refired at 843°C for 170 hours under a oxygen pressure of 1/13 atm. After the firing, the sample was slowly cooled to 500°C (0.5°C/min.), then oven-cooled to the room temperature.

The X-ray powder diffraction of this sample reveals that there still are two phases, the 2223 and the 2212 phase, and the 2223 phase is only about 25% (Fig. 3.14). The dc-magnetization measurements of this sample in a SQUID magnetometer also confirm the existence of the two superconducting transitions, one is near 109 K, and another one is at about 77 K (Fig. 3.15).

The mass of this sample is 14.657 g.

3.3 Sb-doped Bi-compound samples

A paper by Liu et al. (1989) reported that they got superconducting samples with zero-resistance temperature above 130 K, after adding Sb to Bi-Pb-Sr-Ca-Cu system. We followed their procedures exactly, however, could not achieve the results claimed by them. Our experiments show that adding Sb to Bi-compound system does not increase T_C, but decreases T_C if the content of Sb in the Bi-compound superconductor is in excess of a certain value.

With the nominal compositions of Bi:Pb:Sb:Sr:Ca:Cu=1.84:(0.35-X):X:1.91:2.03:3.06 (X = 0, 0.05,0.10,...,0.35), the samples were prepared by the solid state reaction. The powders, Bi_2O_3, PbO, Sb_2O_3, $SrCO_3$, $CaCO_3$ and CuO, were well mixed, then sintered 12 hours at 820°C in air. After they were reground and pressed into pellets, the pellets were refired at 845°C for 150 hours in air, and finally, slowly cooled to room temperature.

The results in T_C, the zero-resistance temperature, vs. X are presented in Fig. 3.16. It is clear from the results that the T_C changes little with increasing X when $X < 0.15$, and then, has a sharp drop when $0.15 < X < 0.30$, finally, T_C almost keeps constant again when $X > 0.30$. It also should be mentioned that when $X \leq 0.15$, each of these samples shows a single resistive transition to R = 0 near 106 K (Fig. 3.17), however, when X = 0.20 (just above 0.15), the sample shows a tail with R = 0 at 80 K after a sharp drop of resistivity near 106 K (Fig. 3.18), and the behavior is very similar to that of samples without lead.

Suppose the valence of Pb is +2, and that of Sb is +3, therefore, substitution of a Sb atom for a Pb atom eliminates a hole in the system. This implies that if the hole concentration lower than a certain level, the T_C will dramatically decrease. As mentioned above, for these Bi-compound superconductors Pb:Sb=

(0.35-X):X, hence X=0.175 means Pb:Sb =1:1. When X=0.20 (just larger than 0.175), the resistance-behavior of sample suddenly changes, and becomes very similar to that of sample without Pb. This fact makes us believe that the hole concentration reaches a critical point when Pb:Sb =1:1. On the other hand, these experiments suggest that adjusting the content of Pb and Sb in composition may be an effective means to control the hole concentration in Bi-compound superconductors.

3.4 The influence of quenching on properties of Bi-compound samples

Some experiments have also been done by us to try to figure out the the effect of quenching on sample properties. Our results are quite similar to those gotten by Ishida, T. (1989), however, do not agree with the results reported by Liu et al. (1989).

Fig. 3.19 shows the data in T_C, the zero resistance temperature, vs. T_q, the quench temperature. The nominal composition of our samples was Bi:Pb:Sb:Sr:Ca:Cu = 1.6:0.3:0.1:2.0:2.0:3.0. After calcination at 865°C for 60 hours, the samples were slowly cooled to various quench temperatures, T_q, from which they were subsequently quenched to air (room temperature).

From Fig. 3.19, it is obvious that quenching has little influence on T_C if $T_q < 700°C$, but, when the quench temperature is larger than 700°C, the influence becomes drastic. On the other hand, the quenching also affects the normal-state properties of the samples. The normal-state resistivity gradually transforms from a metallic temperature dependence to a semiconducting one as the T_q is increased, and when the quench temperature exceeds 800°C, the R-T curve shows semiconducting behavior (Fig. 3.20). The X-ray measurements also tell us that there is no semiconducting phase if we cool samples slowly after calcination, and that the semiconducting phase, whose characteristic peaks are at 8.5° and 20.7° (the wave-length of X-ray λ=1.7903A), appears, when the quench temperature reaches 500°C. It should also be mentioned that, generally speaking, quenching of sample deceases the content of the 2223 phase. However, surprisedly, when the quench temperature equals the calcination temperature (865°C) the content of the 2223 phase increases, though there is a big drop in T_C, the zero-resistance temperature. We list the sample name, T_q (quench temperature), T_C (zero-resistance temperature) and the percentage of 2223 phase in Table 3.1 (see the next page).

In order to explain these phenomena, Ishida, T. assumes (1988b and 1989) that the normal state transport occurs through CuO_2 as well as $(BiO)_2$ layers, and they work as a parallel circuit of two resistors. Furthermore, he supposes that the hole concentration contained in CuO_2 layers play an essential role for determination of T_C in Bi-compound superconductors; holes are supplied from the $(BiO)_2$ layer to the CuO_2 layers, and the extent of hole transfer may be controlled by quenching, hence, the T_C depends on the quench temperature.

At this stage of the research, people need more evidence to judge whether Ishida's hypothesis is correct or not. However, it is clear from their and our experiments that the high temperature quenching of samples drastically decreases T_C, and affects their normal-state properties. In order to make good high-T_C Bi-samples, it is necessary that samples are cooled down slowly after calcination.

Table 3.1 T_q, T_C and the content of 2223 phase for seven Bi-samples

Specimen	T_q	T_C	2223 phase
1-M-190	25°C	92.8 K	50%
2-M-190	250°C	92.0 K	---
3-M-190	500°C	88.0 K	31%
4-M-190	600°C	90.0 K	36%
5-M-190	700°C	91.1 K	32%
6-M-190	800°C	76.3 K	30%
7-M-190	865°C	47.8 K	65%

3.5 Conclusions

In conclusion of this chapter, making good Bi-compound superconducting samples is much more complicated and difficult than making good YBCO samples, because many more factors affect the properties of Bi-compound samples, and so far people still do not clearly know the key point for making good Bi-compound samples. According to our experiments, in order to increase the content of the 2223 phase in samples, so far the most efficient method is the partial substitution of Pb for Bi. However, it is also necessary for raising the percentage of the 2223 phase to sinter samples for appropriately long time at suitable temperatures. This time is about 200 - 300 hours. If the optimum time is exceeded, the 2223 phase starts decomposing. Dopping antimony to Bi-compound samples will not increase the transition temperature, but decrease it. This may be due to a decrease in the hole concentration of samples. Quenching of samples will cause formation of the semiconducting phase. High-temperature quenching drops the transition temperature of samples drastically, while low-temperature quenching does not affect T_c much. It is important for making good high-T_c Bi-superconductors to cool sample slowly after sintering.

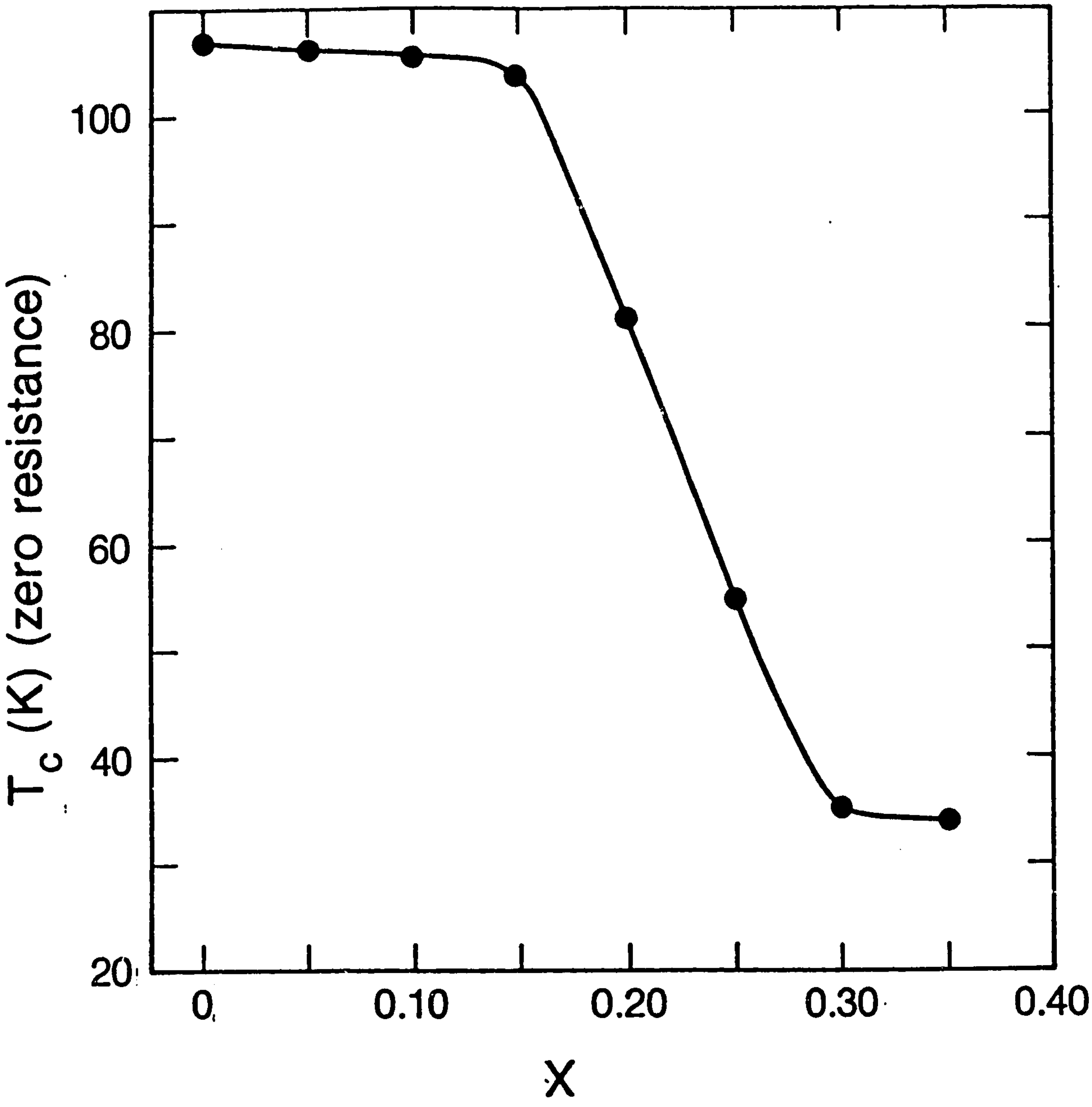

Fig. 3.16 T_c vs. X for $Bi_{1.84}Pb_{0.35-x}Sb_xSr_{1.91}Ca_{2.03}Cu_{3.06}O_y$.

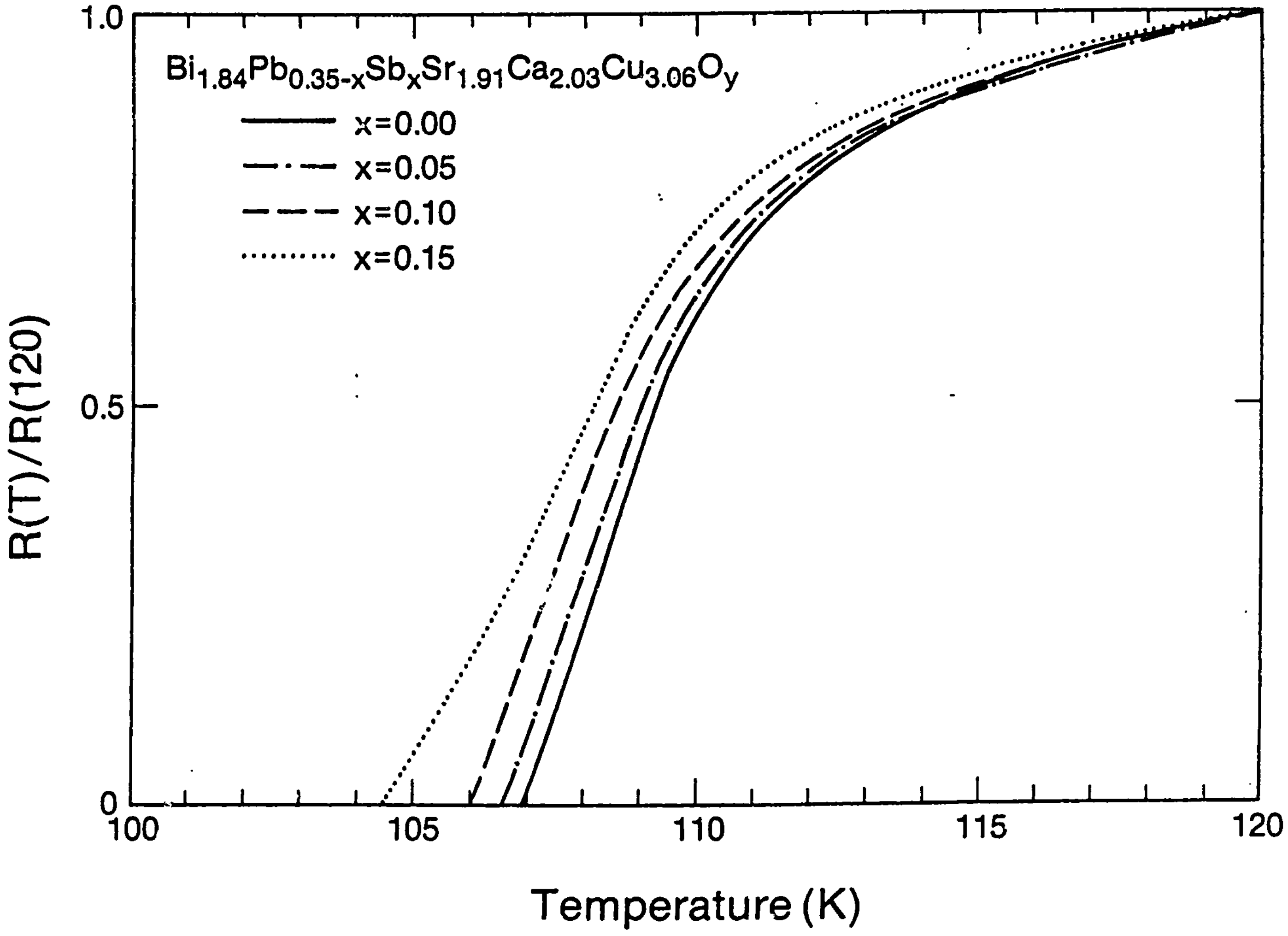

Fig. 3.17. Resistance versus temperature for Sb-doped samples.

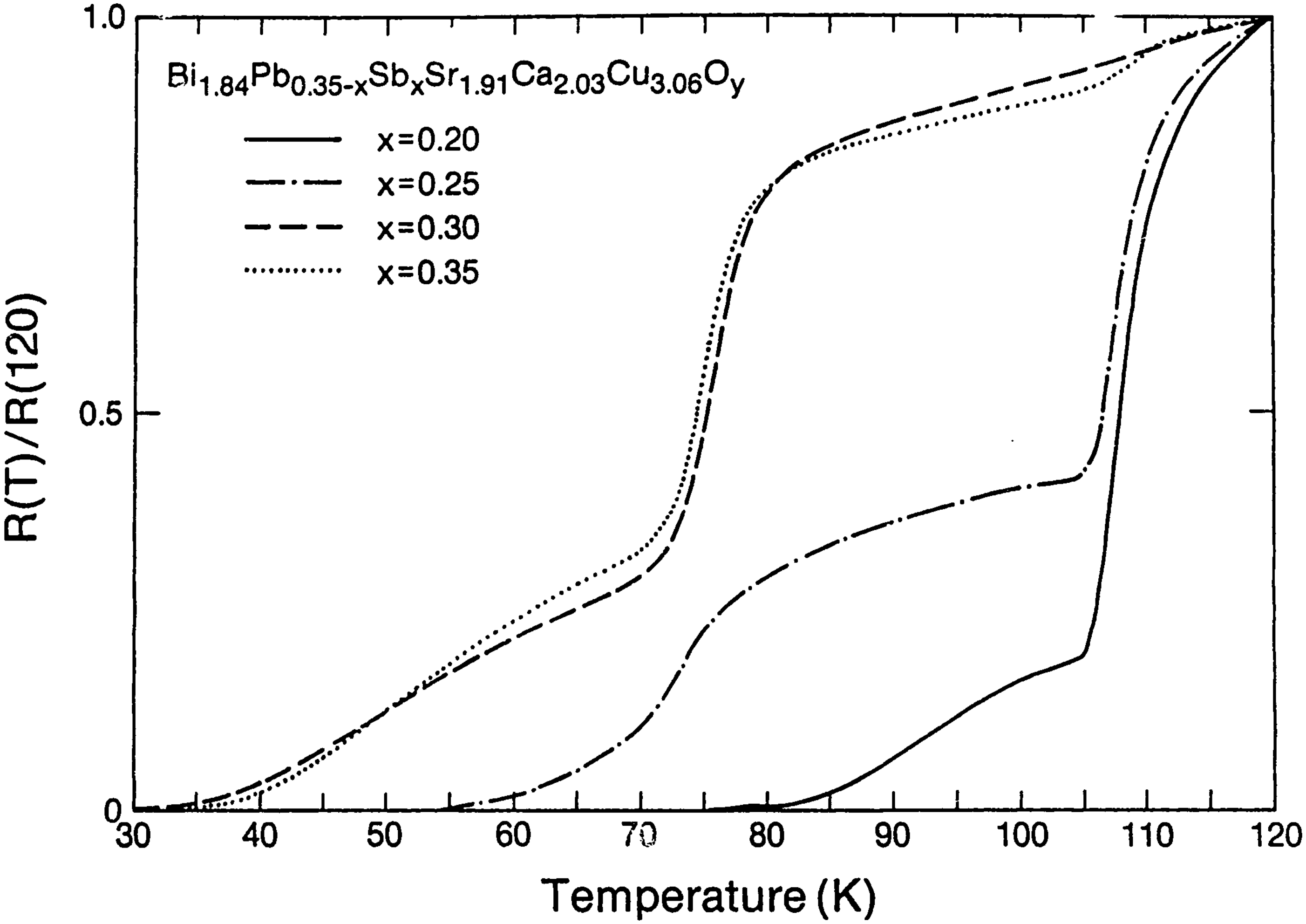

Fig. 3.18. Resistance versus temperature for Sb-doped samples.

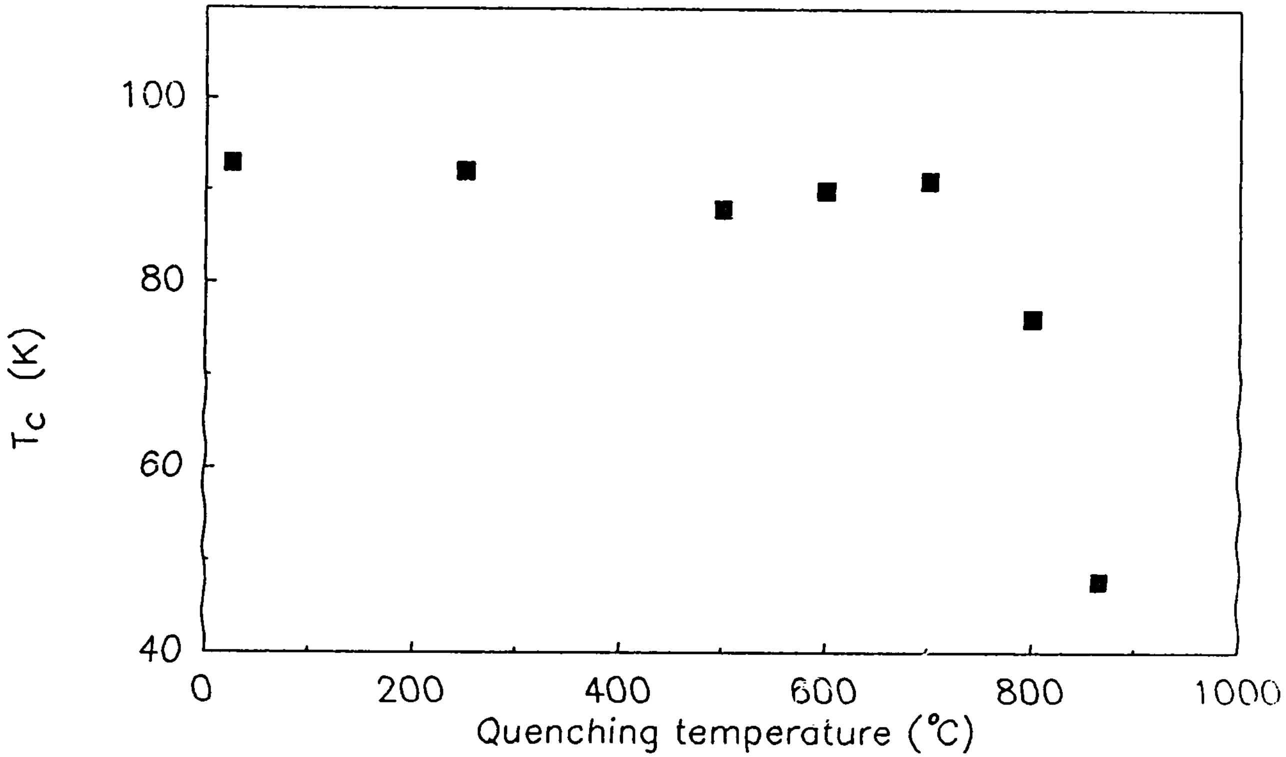

Fig. 3.19 Quenching temperature versus T_c(zero resistance temperature) for Bi–compound samples ($Bi_{1.6}Pb_{0.3}Sb_{0.1}Sr_2Ca_2Cu_3O_y$).

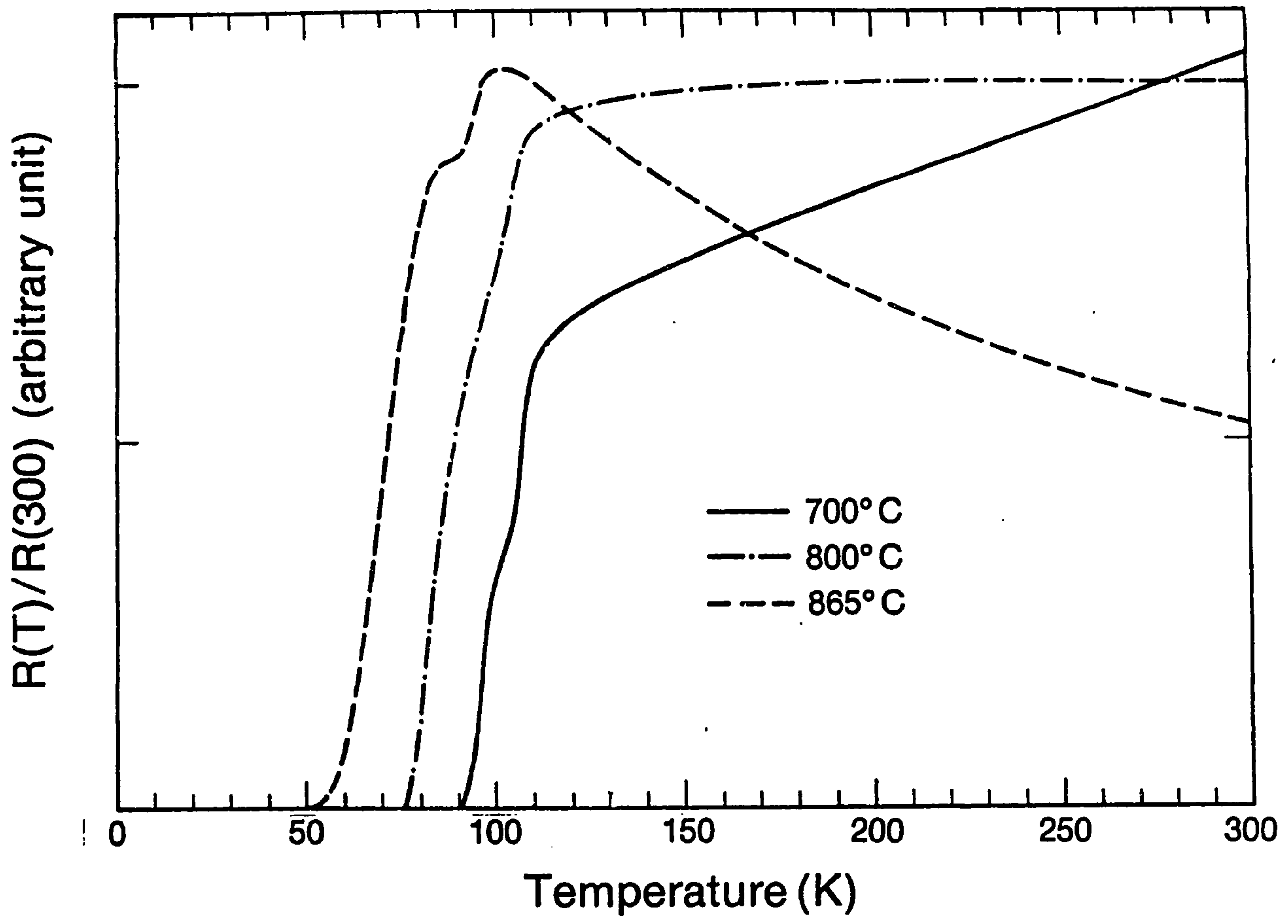

Fig. 3.20. The resistance as a function of T for Bi-compound-samples. The quenching temperatures are indicated in the figure.

CHAPTER 4

SPECIFIC HEAT MEASUREMENTS

In general, scientists focus the specific heat measurements and data analysis on two temperature regions: (1) the vicinity of the transition temperature, (2) the low temperature area; because very most of the interesting and significant information, such as the Debye characteristic temperature θ_0, the Sommerfeld parameter γ and the strength of the electron-phonon coupling, could be obtained from these regions. For the conventional superconductors, the T_c is quite low, hence the two regions often merge into one. However, for the HTSC's, the two regions separate far from each other, and the specific heat measurements are often performed in a large temperature range, but most of the attention is still paid to the two regions, though some anomalies happen in the region which is far above the T_c (Laegreid et al. 1987, Slaski et al. 1989).

In this chapter, we also concentrate most of our attention on the two regions. Section 4.1 will be about the specific heat near T_c, and Section 4.2 focuses on the low temperature specific heat, while the lattice specific heat will be discussed in Section 4.3 which is not only related to the two regions.

4.1 Specific heat near T_c

For the high-T_c superconductors, measurements of $\Delta C(T_c)$ have proved difficult, some of reasons for that have mentioned in Chapter 1: dominant lattice specific heat, broad and possibly incomplete transitions. Furthermore, it needs quite long time (a few minutes in our experiments) for samples to get thermal equilibrium at high temperatures, because of the low thermal conductivity.

If a superconducting transition is incomplete, and the fraction of the sample remaining in normal state is f_n, then BCS relation (1.1-4) should be corrected to

$$\frac{\Delta C(T_c)}{\gamma T_c} = (1- f_n)\alpha = f_s\alpha, \tag{4.1-1}$$

where α is the BCS-ratio, and equal to 1.43 for the weak coupling limit. On the other hand, there should be a T-linear term in C at low temperatures from the normal fraction of the sample, and

$$\gamma_0 = f_n\gamma. \tag{4.1-2}$$

If one wants to determine the BCS-ratio α, one must know γ and f_n first. Unfortunately, so far, it is impossible to obtain γ calorimetrically, because there is no magnetic field large enough to quench superconductivity of HTSC's at low temperatures. Therefore, less direct methods have been used to estimate γ, and we will give some discussion later.

4.1-1 YBCO sample

The first sample on which we performed specific heat measurements was YBCO sample. The results about resistance and magnetic measurements of this sample have been described in Chapter 3. The specific heat measurements showed a clear anomaly in C/T vs. T near 88 K (see Fig. 4.1). The behaviour both below 87 K and above 91.5 K was quasi-linear. Therefore, we made linear extrapolations to estimate the discontinuity $\Delta C(T_c)/T_c$. The temperature of the idealized jump was drawn so as to preserve the entropy balance. Using this way, we got $\Delta C(T_c)/T_c \coloneqq 67$ mJ/mol K^2 ± 15%.

In order to determine the BCS-ratio, we try to obtain the value of γ from the temperature-independent paramagnetic susceptibility above the transition temperature, because

$$\gamma = \frac{1}{3}\left(\frac{\pi k_b}{\mu_b}\right)^2 \chi_p, \qquad (4.1\text{-}3)$$

where k_b is the Boltzmann constant, μ_b is the Bohr magneton, and χ_p is the Pauli paramagnetic susceptibility. Shown in Fig. 4.2 is $\chi(T)$ versus T from 100 to 300 K in an applied field of 4 T. The data are fitted by the two-parameter expression

$$\chi(T) = \chi_0 + B/T, \qquad (4.14)$$

where χ_0 is temperature-independent susceptibility, and the least-squares fit gives $\chi_0 = (2.41 \pm 0.02) \times 10^{-4}$ emu/mol. However,

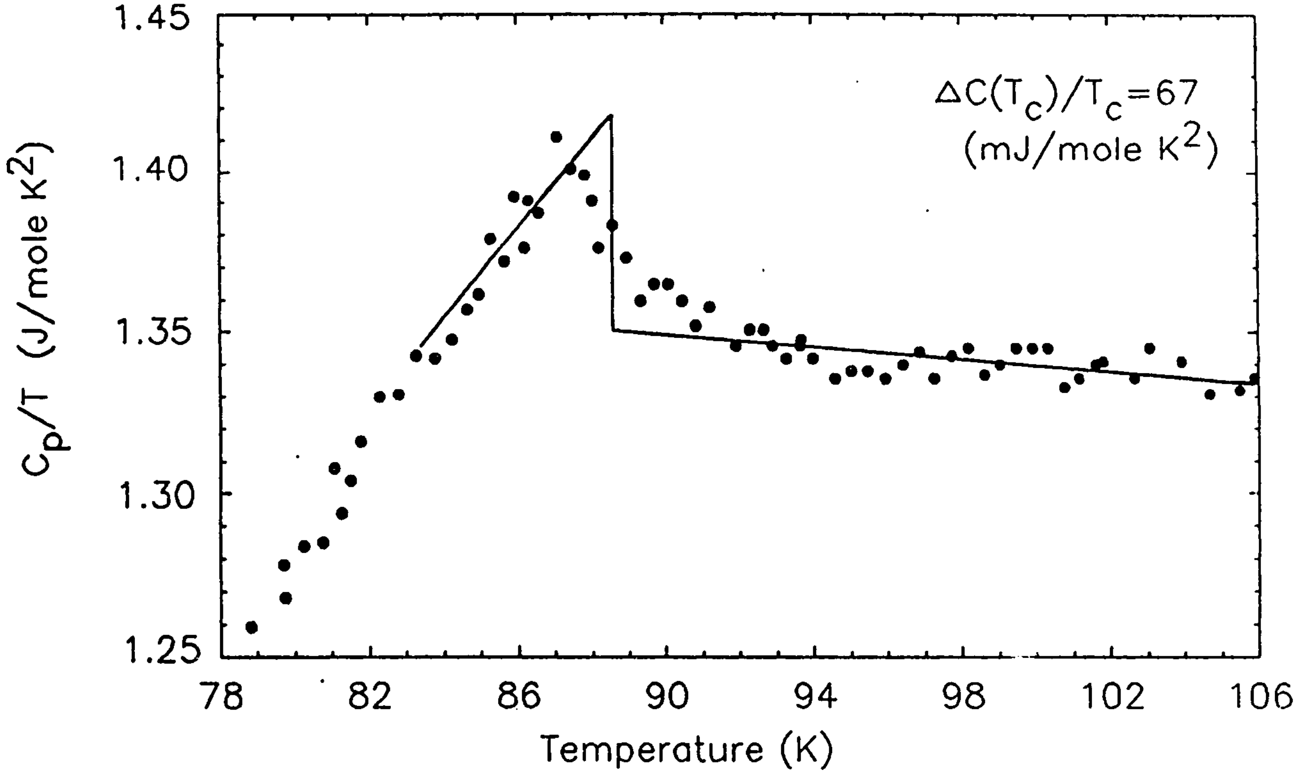

Fig. 4.1 Specific heat of YBCO in the vicinity of T_c

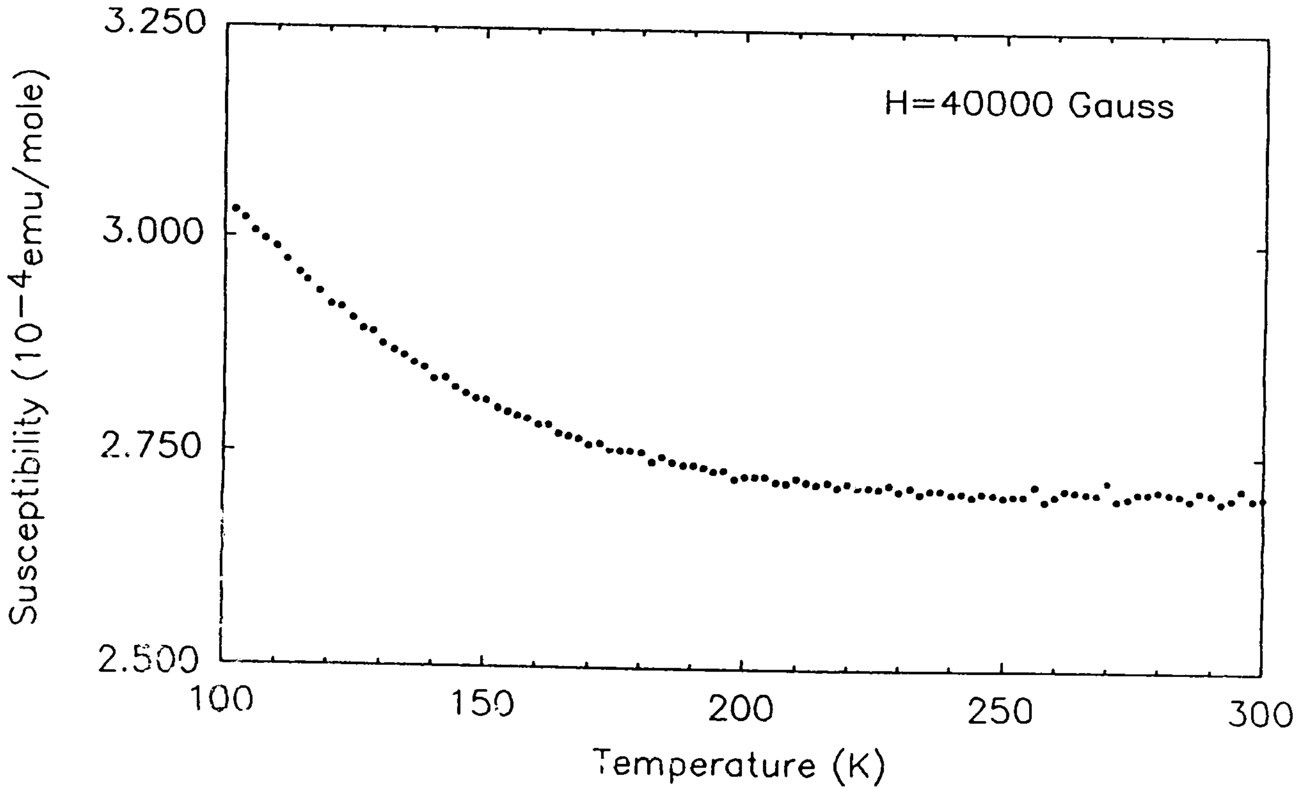

Fig. 4.2 The magnetic susceptibility versus temperature above T_c for YBCO.

the χ_0 contains not only the contribution from the Pauli paramagnetism χ_p, but also the contributions from other sources: the core diamagnetism χ_c, the Van Vleck paramagnetism χ_v, and the Landau-Peierls diamagnetism χ_L. It is very difficult to extract the value of χ_p from χ_0 precisely. The Landau-Peierls diamagnetism, $\chi_L \approx -1/3(m/m^*)^2\chi_p$, is believed to be small compared with χ_p, and can be neglected. Hence, we make corrections for the core diamagnetism χ_c and the Van Vleck paramagnetism χ_v to obtain the approximate value of χ_p from χ_0. For different ions, core diamagnetic contributions are different: $Y^{+3}(-1.2\times10^{-5}$ emu/mol.), $Ba^{+2}(-3.2\times10^{-5})$, $Cu^{+2}(-1.1\times10^{-5})$ and $O^{-2}(-1.2\times10^{-5})$ (Nevitt et al. 1987), therefore, $\chi_c=-1.93\times10^{-4}$ emu/mole. The Van Vleck contribution to χ_0 was calculated by Willis et al. (1991) from Knight shift data on YBCO(123) reported by Barrett et al. (1990), they obtained $\chi_v=1.30\times10^{-4}$ emu/mole. Using this value, we have $\chi_p \approx \chi_0 - \chi_c - \chi_v = 3.04\times10^{-4}$ emu/mol. According to Equation (4.1-3), we get $\gamma \approx 22$ mJ/mole K^2. The values of γ obtained by other groups in this way are from 20 to 42 mJ/mol. K^2 (Inderhees et al. 1987, Nevitt et al. 1987, Gao et al. 1990 and Phillips et al. 1990b). We would like to point out that some groups did not make correction for the Van Vleck contribution, and therefore, the value of γ obtained from χ_0 by those groups was comparatively larger than the actual value of γ. It should be mentioned that Phillips et al. (1990a) estimated the value of γ by extrapolating the $\gamma_2 n_2$ contribution, the contribution from

n_2--the concentration of Cu^{2+} moments located on the YBCO lattice, to γ_0 to the value of n_2 at which superconductivity disappeared, and obtained $\gamma \approx 16$ mJ/mole K^2.

Using $\gamma \approx 22$ mJ/mole K^2, we find that the ratio $\alpha = \Delta C(T_c)/\gamma T_c = 3.0$ for the YBCO sample, and thus appears to be in the strong coupling limit as it is much larger than the weak coupling BCS-value 1.43.

It should be mentioned that measurements by many groups show the sample-to-sample variations in $\Delta C(T_c)/T_c$. For instance, Junod et al. reported in 1988 that every sample measured by them showed different value of $\Delta C(T_c)/T_c$, from smaller than 20 to 57 mJ/mol K^2. Their experiments revealed (Junod et al. 1989) that the oxygen content in samples strongly affected the size of the anomaly, $\Delta C(T_c)/T_c$, and that the anomaly at T_c is largest for $\delta=0$ ($YBa_2Cu_3O_{7-\delta}$), while it can hardly be detected for $\delta \approx 0.20$. Recently, the same group reported (Junod et al. 1990) that $\Delta C(T_c)/T_c$ for their YBCO (123) sample was 67 mJ/mol K^2, and $\gamma \approx 28$ mJ/mol K^2. Hence, it was also in the strong coupling limit.

It was reported that the increase in δ was accompanied by a decrease in the Pauli susceptibility above T_c (Farneth et al. 1989), and a decrease in θ_0 (Gordon et al. 1990). Veal et al. (1989) reported that photoemission spectroscopy showed that there was a decrease of $N(E_F)$ with increasing δ. Therefore, it is reasonable to suggest that the oxygen content in samples affected the size of $\Delta C(T_c)/T_c$ through an effect on $N(E_F)$. Furthermore, there may be a correlation of θ_0 with $N(E_F)$ for high-T_c superconductors.

Phillips et al. (1989 and 1990a) point out that the discontinuity in C at T_c, $\Delta C(T_c)$, is strongly sample dependent, and is correlated with n_2, which act as pair-breaking centers limiting the transition to the superconducting state. Therefore, they interpret the sample-to-sample variations in $\Delta C(T_c)/T_c$ as measures of a corresponding variation in the volume fraction of superconductivity. A sharp transition does not necessarily mean that there is a high value of f_s for the sample, and that the sample is good. For example, f_s for some single crystals with very sharp transitions is about 50%. Phillips et al. believe that the value of $\Delta C(T_c)/T_c$ could be 77 mJ/mol K^2 for an "ideal", fully superconducting sample. According to this interpretation, the values of $\Delta C(T_c)/T_c$ obtained by current experiments may be smaller than actual values of $\Delta C(T_c)/T_c$ because of incomplete superconducting transition, therefore, actual value of α could be larger. However, this does not change the conclusion that the YBCO sample is in the strong coupling limit.

4.1-2 Bi-compound samples

We have measured the specific heat near T_c on four Bi-compound samples: BPSCCO1, BPSCCO2, BSCCO1 and BSCCO2 which have been described in Chapter 3. BPSCCO1, BPSCCO2 and

BSCCO1 are obviously multiphase samples, while X-ray measurements show that BSCCO2 seems to be a single 2212-phase sample. However, the resistivity measurements reveal that the sample still contain a little 2223 phase.

In Fig. 4.3 and 4.4, we show the specific heat in the vicinity of the two transitions for sample BSCCO1 and BPSCCO1. It can be seen that there is an anomaly for each transition. However, besides these anomalies, other anomalies have also been observed. For BSCCO1, they are: one near 64 K and another lambda-like anomaly at 56 K; for BPSCCO1, other three anomalies are at 68, 63 and 55 K.

It should be mentioned that, for some HTSC samples, more than one anomaly in the vicinity of T_c -- at either a higher or a lower temperature -- have been observed by several groups (Li et al. 1987, Junod et al. 1987, Ishikawa et al. 1988, Inderheels et al. 1988, Lazarev et al. 1988, Wang et al. 1989). For instance, Ishikawa et al. (1988) observed two maxima in C/T vs. T between 84 and 92 K for their YBCO sample which showed a two step transition in both $\rho(T)$ and $\chi_{ac}(T)$ curves. Junod et al. reported (1987) that one of their YBCO samples showed two discontinuities in specific heat near T_c. Lazarev et al. (1988) reported that their $HoBa_2Cu_3O_{6.75}$ sample exhibited two anomalies in the vicinity of T_c, as well as a double maximum in the 50-70 K region, one of which was a large lambda-like anomaly. Even some single crystal sample showed more than one anomalies in the vicinity of T_c. Wang et al. reported that their superconducting single crystal $GdBa_2Cu_3O_{7-\delta}$ showed two

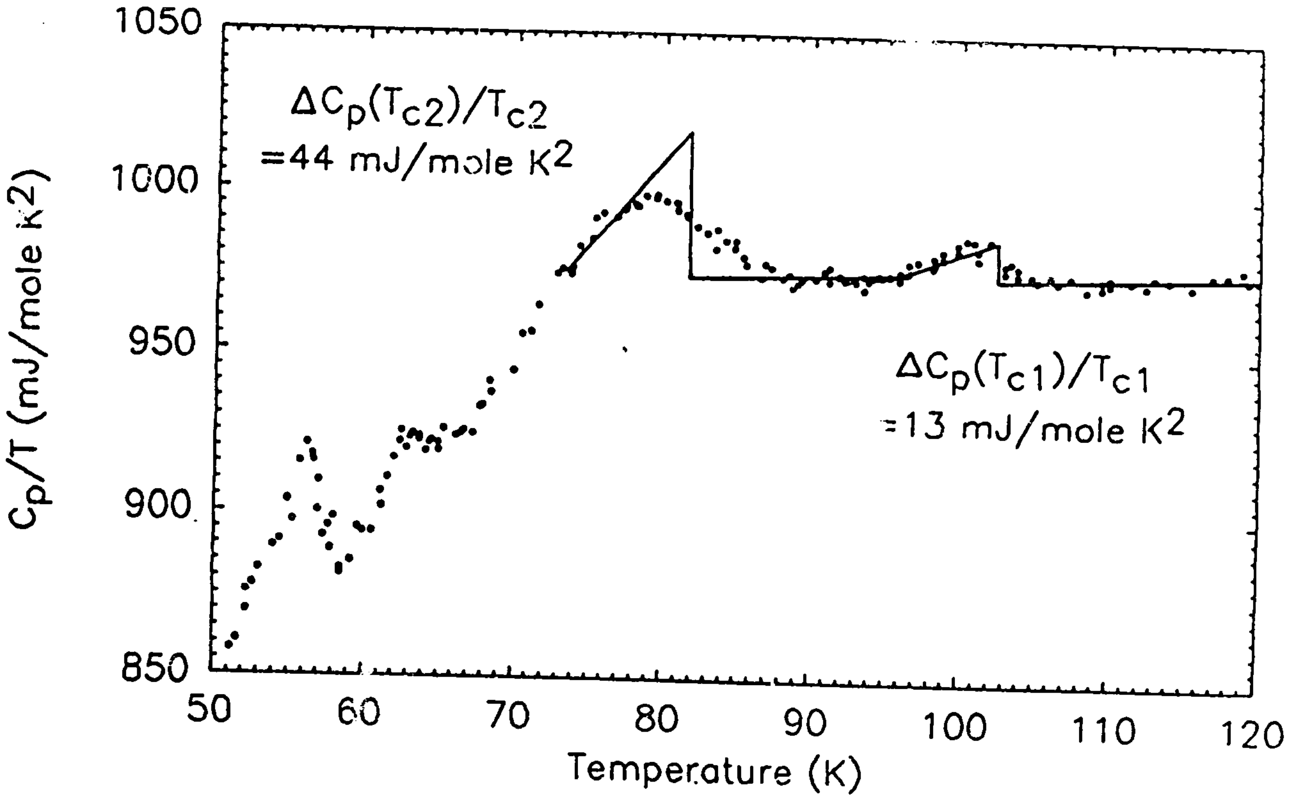

Fig. 4.3 Specific heat of BSCCO1

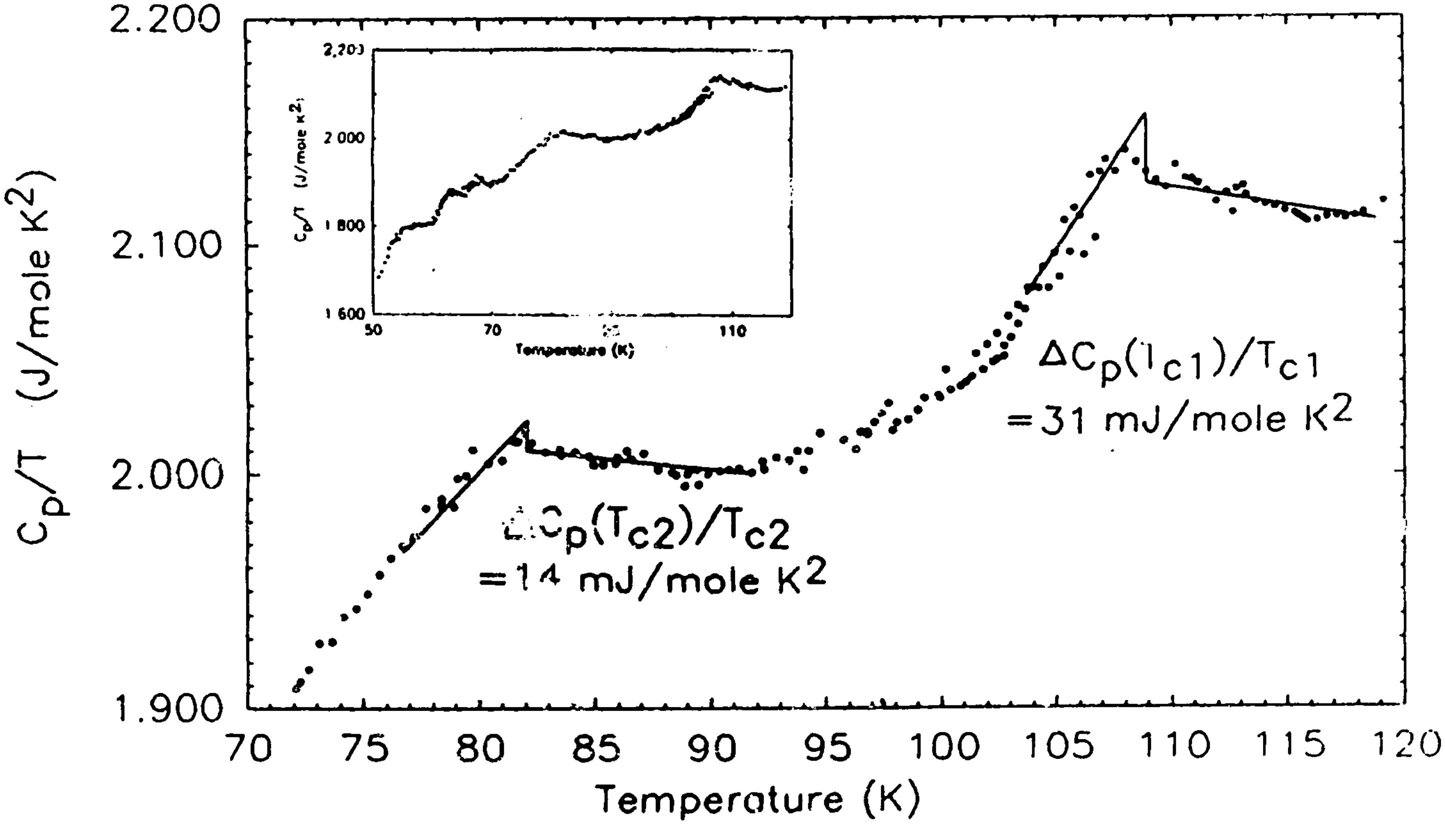

Fig. 4.4 Specific heat of BPSCCO1 in the vicinity of T_c The other three anomalies at 55, 63 and 68K are shown in the inset.

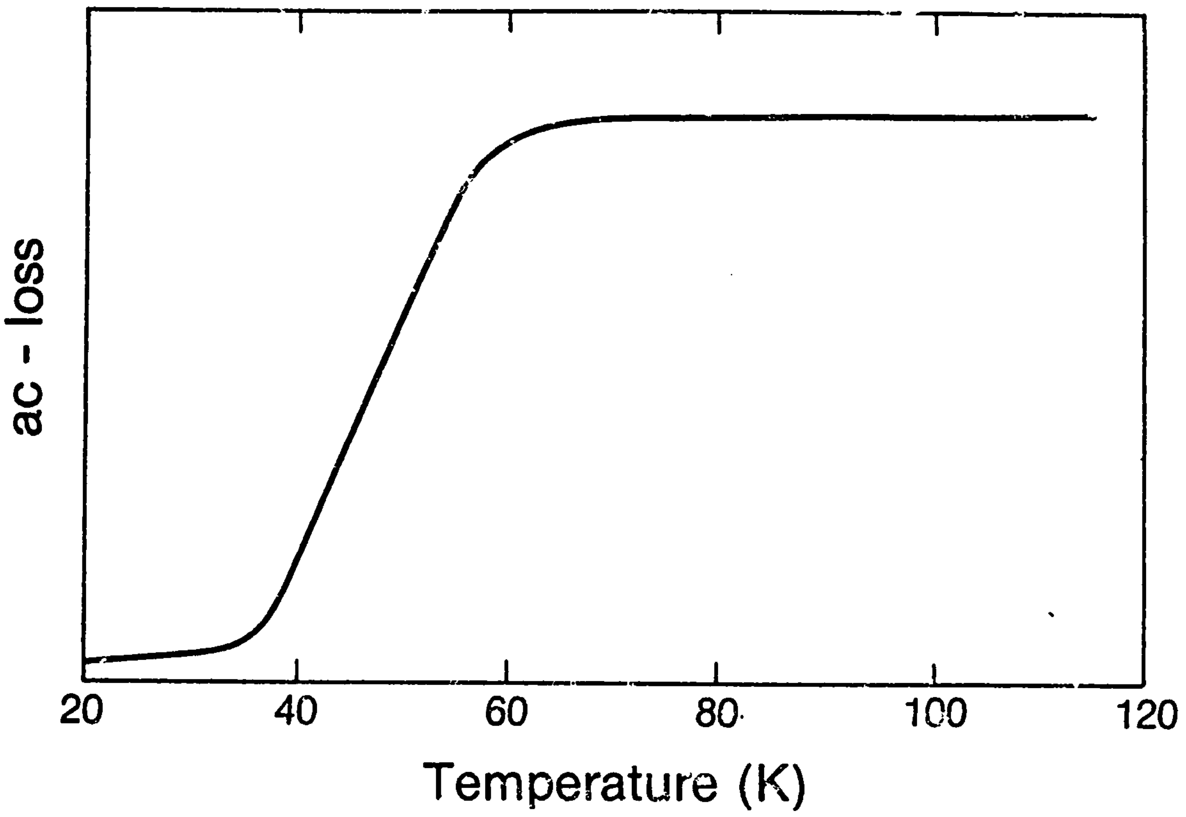

Fig. 4.5. ac-loss (0.010e, 160Hz) for BSCC01,
measured by S. Gygax.

anomalies in specific heat between 80.7 and 87.5 K. Junod (1990) suggested that gases trapped in pores in samples may be associated with these anomalies. However, some of anomalies are difficult to explain.

For sample BSCCO1 in our experiment, the lambda-like anomaly at 56 K may be attributed to some magnetic transition, because ac-loss shows a big change between 35 and 62 K (see Fig. 4.5).

For the anomaly at superconducting transition, we estimate the discontinuity $\Delta C(T_c)$ by using linear extrapolations from above and below the T_c in a plot of C/T vs. T as mentioned above. In this way, we obtain $\Delta C(T_c)/T_c = 44$ mJ/mole $K^2 \pm 25\%$ (BSCCO1) and 14 mJ/mole $K^2 \pm 50\%$ (BPSCCO1) at the 2212 phase transition; $\Delta C(T_c)/T_c = 13$ mJ/mole $K^2 \pm 30\%$ (BSCCO1) and 31 mJ/mole $K^2 \pm 30\%$ (BPSCCO1) at the 2223 phase transition.

Sample BPSCCO1 and BPSCCO1 are multiphase superconductors, therefore the actual discontinuity should be $\Delta C(T_c)/T_c f_s$ according to Equation (4.1-1). Powder X-ray spectra show that, f_s is roughly 70% (the 2212 phase) and 30% (the 2223 phase) for BSCCO1, and that 30% (the 2212 phase) and 70% (the 2223 phase) for BPSCCO1. Hence, for BSCCO1, the actual discontinuity is 62 mJ/mole K^2 at the low transition, and 43 mJ/mole K^2 at the high transition; for BPSCCO1, they are 47 and 44 mJ/mole K^2 respectively.

For sample BSCCO2, which may contain more than 95% of the 2212 phase, no anomaly in C has been observed in the vicinity of the superconducting transition (Fig. 4.6). This may result from that the Meissner fraction of this sample is smaller than those of other samples, and from that its transition is broader than those of other samples (see Fig. 3.1, 3.5, 3.8 and 3.12). Estimating the field expulsion from the difference between the ZFC and the FC curves far below the transition temperature and attributing the ZFC curve to total field expulsion (χ=-1), we find the Meissner fraction of sample BSCOO2 to be only about 13%, comparing with about 50% (BSCCO1), 40% (BPSCCO1) and 32% (YBCO). Phillips et al. reported (1990a) that, for a Zn-doped YBCO sample, which showed a small Meissner effect, there was no measurable $\Delta C(T_c)$. They point out (1990b) that a small Meissner fraction suggested that $\Delta C(T_c)$ was not detectable because it was small and the transition broad, but that it was not really zero. The fact that the Debye characteristic temperature θ_0 of this sample is lower than other sample's (see Section 4.2) may also provide some clue why no anomaly has not been detected for this sample. As mentioned above, some groups have observed that decrease of $\Delta C(T_c)$ is associated with decreasing θ_0 for YBCO samples (Gordon et al. 1990).

The results from magnetic susceptibility measurements above T_c should also be mentioned hero. The temperature dependence of the susceptibility of the Bi-compound sample above T_c is complicated, and not similar to that of YBCO sample.

The common feature for our Bi-compound samples is that there is a broad peak between 170 K and 240 K (Fig. 4.7 and 4.8). Maeda et al. (1989) also observed this feature in their Bi-compound samples, and the peak exists around 170 K. For this kind of temperature dependence, it is difficultly to extract Pauli paramagnetic susceptibility from total susceptibility, and therefore, it is hard to use these results to determine γ, the coefficient of the electronic specific heat. However, from Fig. 4.7 and 4.8, it is clear that the paramagnetism of BPSCCO1 above T_c is much larger than that of BSCCO2. According to our calculation, the core diamagnetic susceptibility of BPSCCO1 and BSCCO2 are -2.65×10^{-4} and -2.17×10^{-4} emu/mole respectively. These facts may mean that the Pauli paramagnetic susceptibility of BSCCO2, which is proportional to $N(E_F)$, is much smaller than that of BPSCCO1. Therefore, the $N(E_F)$ of BSCCO2 may also be much smaller than that of BPSCCO1. This could be the main reason why the size of $\Delta C(T_c)/T_c$ of BSCCO2 is so small, and cannot be detected.

So far, specific heat measurements on Bi-compound samples are much less than those on other HTSC's. However, the results also strongly show sample-to-sample differences. We list values of $\Delta C(T_c)/T_c$ (in mJ/mole K^2) for some of Bi-compound superconductors in Table 4.1 (see page 84).

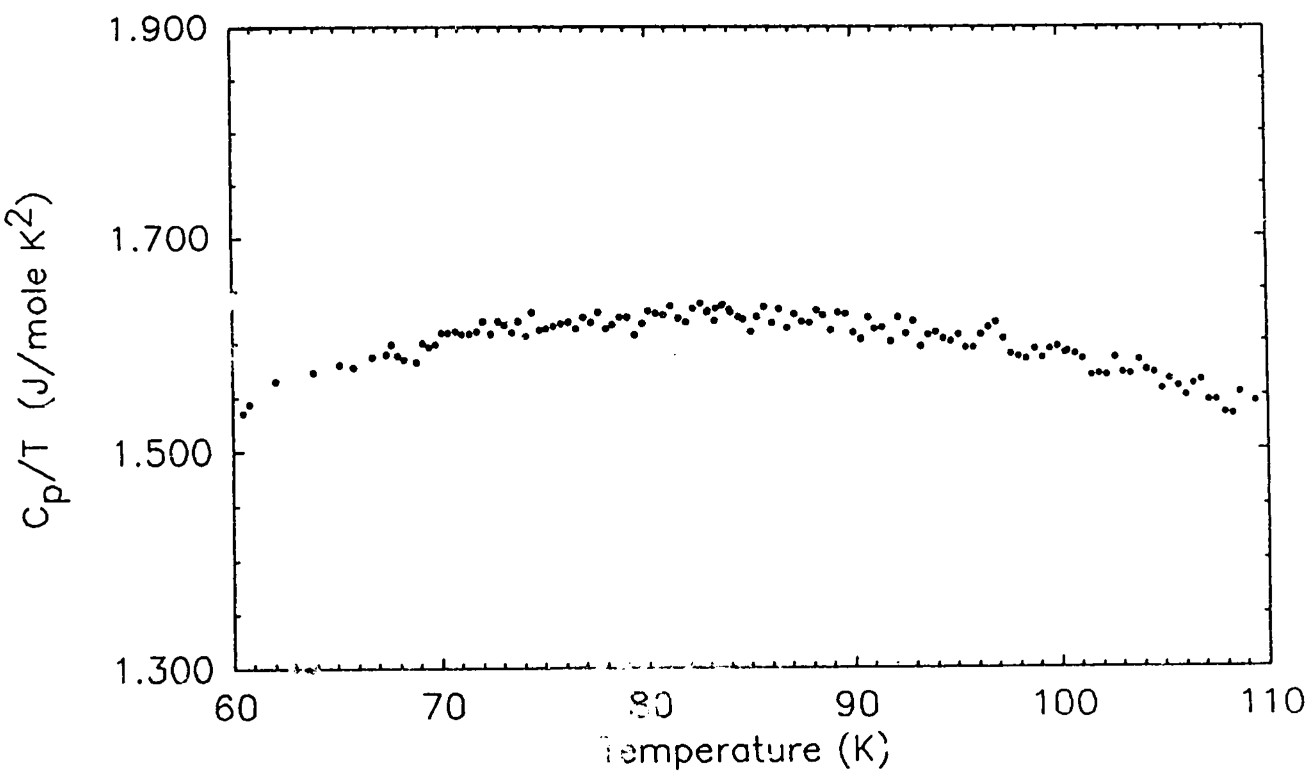

Fig. 4.6 Specific heat of BSCCO2 in the vicinity of T_c.

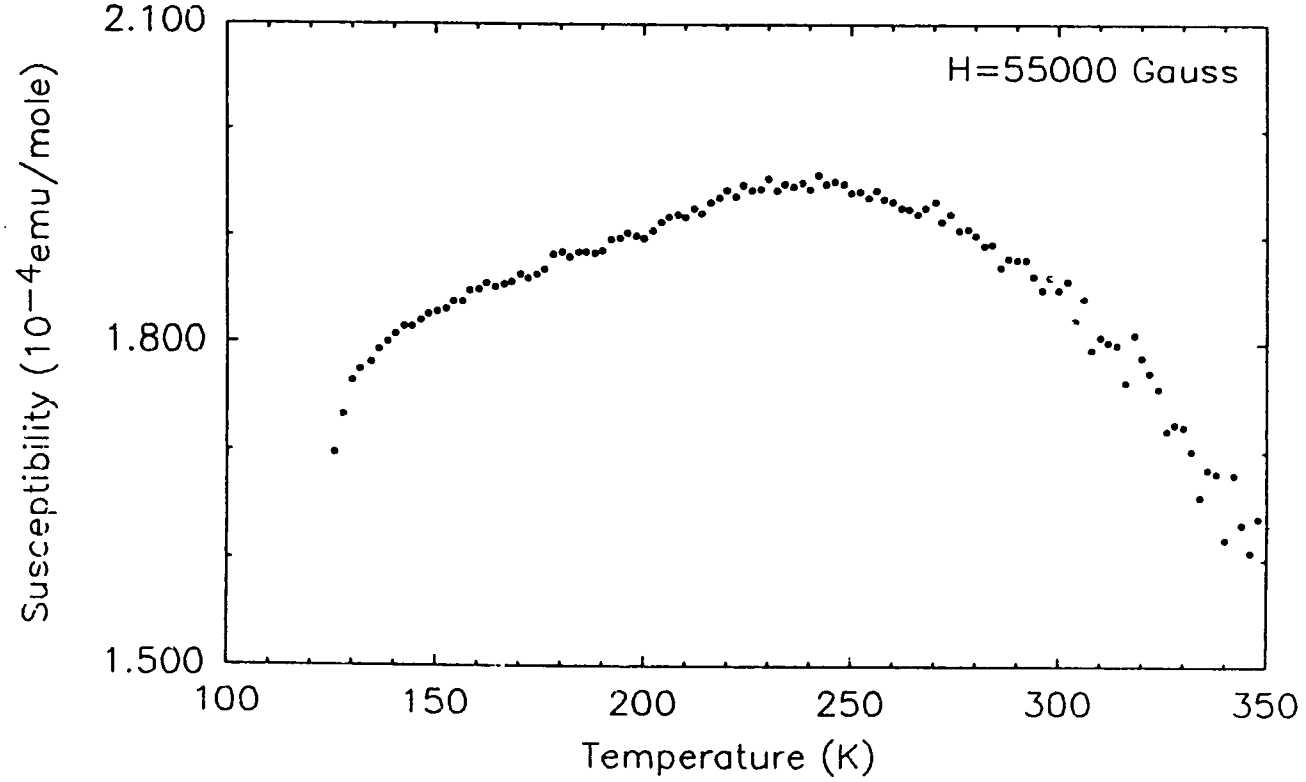

Fig. 4.7 The magnetic susceptibility versus temperature above T_c for BPSCCO1.

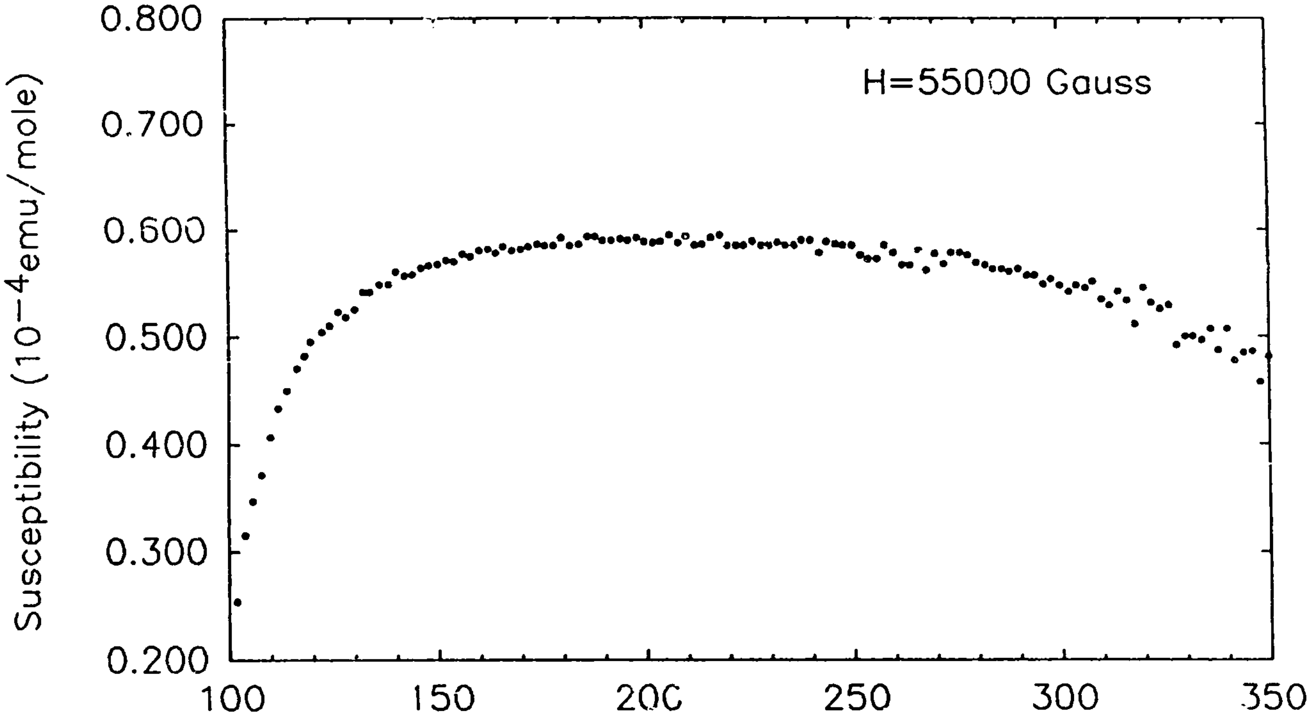

Fig. 4.8 The magnetic susceptibility of BSCCO2 as a function of temperature.

Table 4.1

A review of $\Delta C(T_c)/T_c$ values for some Bi-compound superconductors

2212 PHASE		2223 PHASE	
44 (62)	BSCCO1	57	Gao et al. 1990
20	Bischof et al. 1989	49.5	Jin et al. 1989
16	Fisher et al. 1988	37	Fisher et al.1989
14 (47)	BPSCCO1	31 (44)	BPSCCO1
0	Seidler et al. 1989	16	Schilling et al. 1989
0	BSCCO2	16	Okazaki et al. 1990
		13 (43)	BSCCO1
		0	Seidler et al. 1989

(the values in brackets are obtained from $\Delta C(T_c)/T_c f_s$, where f_s is the percentage of the 2212 phase or the 2223 phase in a sample).

4.2 Low temperature specific heat

Before the Bi-compound superconductors were discovered, almost all specific measurements at low temperatures on HTSC's showed two common features: an upturn in C/T and a T-linear term in C which has received most attention. The upturn can be probably attributed to magnetic impurities. However, the origin of the γ_o has not been known clearly, and is difficult to explain. It might be attributed to various sources which act separately or in combination:

1. The superconducting transition is not complete, and there is still some normal part in the sample even at very low temperatures. Thus, a linear term $\gamma_o T = f_n \gamma T$ should be observable as mentioned above, where f_n is the fraction of the volume which remains in the normal state.

2. If the sample were a gapless-superconductor, a T-linear term would appear in the specific heat. But, for the HTSC's, this possibility seems to be small, because numerous tunneling experiments indicated that the high-T_c superconductors are not gapless. For example, the energy gap in the La-Sr-Cu-O superconducting samples is about 8-15 meV (Kirtley et al. 1987a, Pan et al. 1987, Hawley et al. 1987), and that in the YBCO is about 30-40 meV (Kirtley et al. 1987b, Crommie et al. 1987).

3. The possible presence of the two level systems (TLS) with low energy atomic tunneling which might be created by oxygen vacancies could produce a T-linear term in C. This possibility has been indicated by some thermal measurements (Wenger et al. 1987, Collocott et al. 1987, Nunez Regueiro et al 1988, Lasjannias et al 1988).

4. Various impurity phases in the materials could causes a considerable amount of the linear term in the specific heat. R. Kuentzler et. al. (1988) reported that some of possible impurity phases in the YBCO system, in particular the phase of $BaCuO_{2+X}$, have large pseudo-linear term in C. Some measurements show (Sasaki et al.1988) that the value of γ_o for $BaCuO_{2+X}$ can be as

large as 98 mJ/mol K^2, and therefore, there is a considerable linear term in C even for the sample including less than 5 wt% of $BaCuO_{2+x}$ which could not be detected by X-ray analysis. Another fact that the LaBaCuO samples which contain Ba impurities have a larger γ_0 than the LaSrCuO samples (Fisher et al. 1988b) also suggests that Ba compounds may be the main sources from which the linear term could arise.

5. Temperature-linear term was predicted, as an intrinsic property of HTSC, by the RVB theory of Anderson (1987).

We have performed low-temperature specific heat measurements on three multiphase Bi-compound superconducting samples (BPSCCO1, BPSCCO2 and BSCCO2). The most significant difference between Bi-compound samples and other HTSC's is that Bi-compound samples have no linear term in their specific heat, while the upturn in C/T still exists for these samples. For the lattice part of the specific heat, these samples show a common feature that it deviates from the T^3-dependence above 5 K, and then has a maximum in C/T^3 vs. T which is around 11 K. This fact mirrors that the Debye temperature θ_D (T) reaches a minimum around this temperature, and that there may be the first singularity in the density of states distribution of the phonons. We will discuss that in Section 4.3.

In Fig. 4.9, 4.10 and 4.11, we present the data in C/T vs. T^2 in the low temperature range for the three samples. It was the first attempt that the data were graphically fitted to $C/T = \gamma_0+\beta T^2$ in order to derive γ_0 and β. It can be seen in Fig. 4.9, 4.10

and 4.11 that, in this kind of fit, the data show a relatively-wide linear range in C/T, but, then the straight line extrapolates to $\gamma_0<0$ for all three samples. For instance, we obtain γ_0 = -9 mJ/mol K^2 and β = 2.35 mJ/mol K^4 from the graphical fit for the BPSCCO2, and the data show a linear range between about 4 and 8 K. The result that γ_0 = -9 mJ/mol K^2 is obviously unreasonable. Therefore, we use an analytical fit instead of the graphical fit. Before we discuss the analytical fit, we would like to point out that the line which corresponds to the T and T^3 terms from a least-squares fit of the data is almost everywhere lower than the experimental data except in a very small temperature range. This kind of phenomenon has been also observed for the YBCO superconducting samples (Fisher et al. 1988).

In diagrams of C/T^3 vs. T (Fig. 4.12, 4.13 and 4.14), two feature can be clearly identified: the upturn below about 4 K mentioned previously, and the broad peak at higher temperature which is at 12.2 K for the BPSCCO1, while those are at 11.0 K and 10.5 K for the BPSCCO2 and BSCCO2 respectively. Therefore, we try to fit the data from about 2.6 K to the temperature at which the broad peak occurs with the function

$$C(T) = A/T^2+\gamma_0T+\beta T^3+mC_E(T), \qquad (4.2\text{-}1)$$

were $C_E(T)$ is an Einstein term, m represents the number of oscillators per unit cell, and

$$C_E(T) = R\,(T_E/T)^2 \frac{\exp(T_E/T)}{[1-\exp(T_E/T)]^2}, \tag{4.2-2}$$

R is the universal gas constant, and T_E is the Einstein temperature which characterizes the Einstein term.

In expression (4.2-1), the first term represent the upturn, and the third and the fourth term are used to deal with the lattice specific heat which deviates from the simple T^3-behavior.

The least-squares fits gave $\gamma_0 = -0.6 \pm 0.8$ mJ/mol K^2 (BPSCCO1), -0.1 ± 0.3 mJ/mol K^2 (BPSCCO2) and 0.5 ± 0.7 mJ/mol K^2. These values of γ_0, which are in agreement with other works (Fisher et al. 1988a and 1989, Muto et al.1988, Sera et al. 1988, Urbach et al. 1989, Bombik et al. 1989, Sasaki et al. 1989, Chakraborty et al, 1989, Gao et al. 1990), mean that there is no T-linear term within the experimental uncertainty for these Bi-compound samples. Therefore, we believe that the T-linear term in low-temperature specific heat is not a general feature for all high-T_c superconductors.

It is well known that the Tl-Ba-Ca-Cu-O superconducting sample has the same structural relationship as that of the Bi-compound sample, but Ba is contained in the former, and not in the latter. Experiments have shown that there is a linear term in C for TBCCO, and γ_0 could be as large as 16 mJ/mol K^2 (Fisher

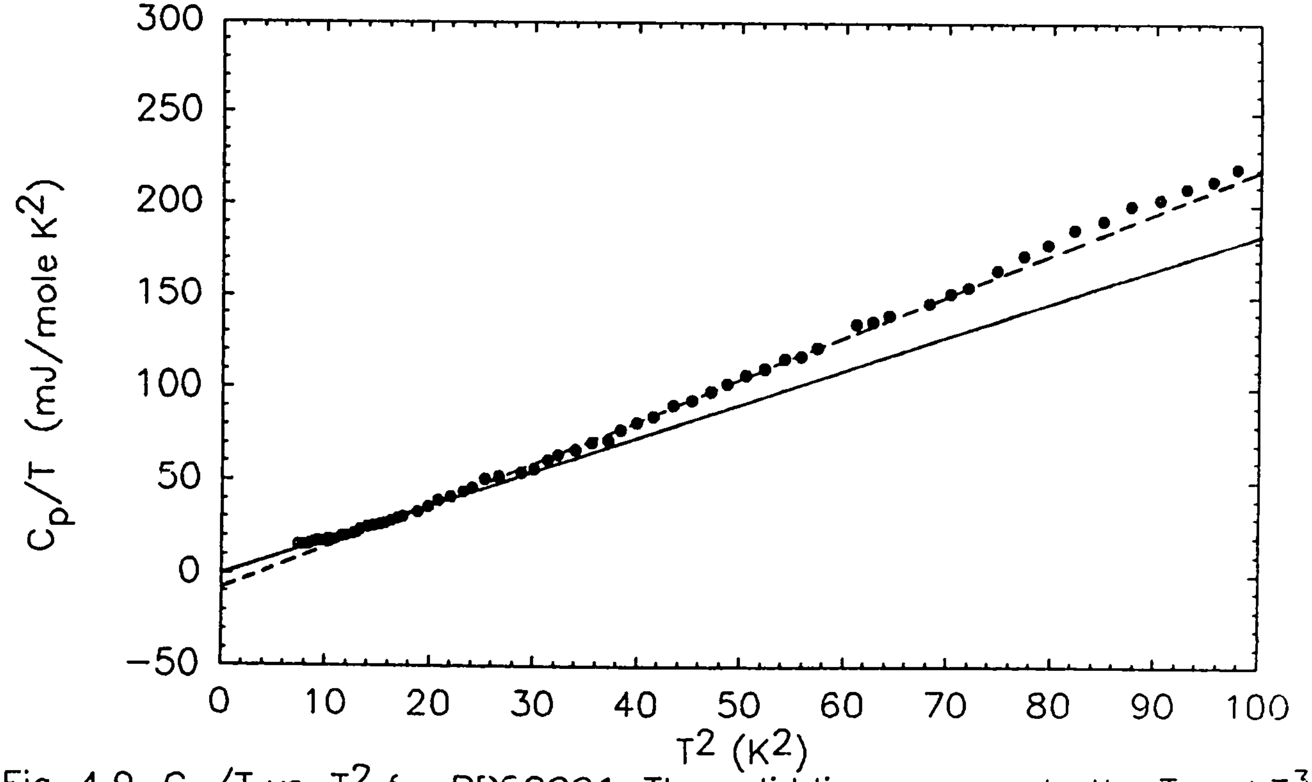

Fig. 4.9 C_p/T vs. T^2 for BPSCCO1. The solid line represents the T and T^3 terms from the least-squares fit of the data, while the dashed line represents the kind of fit obtained by fitting a straight line visually.

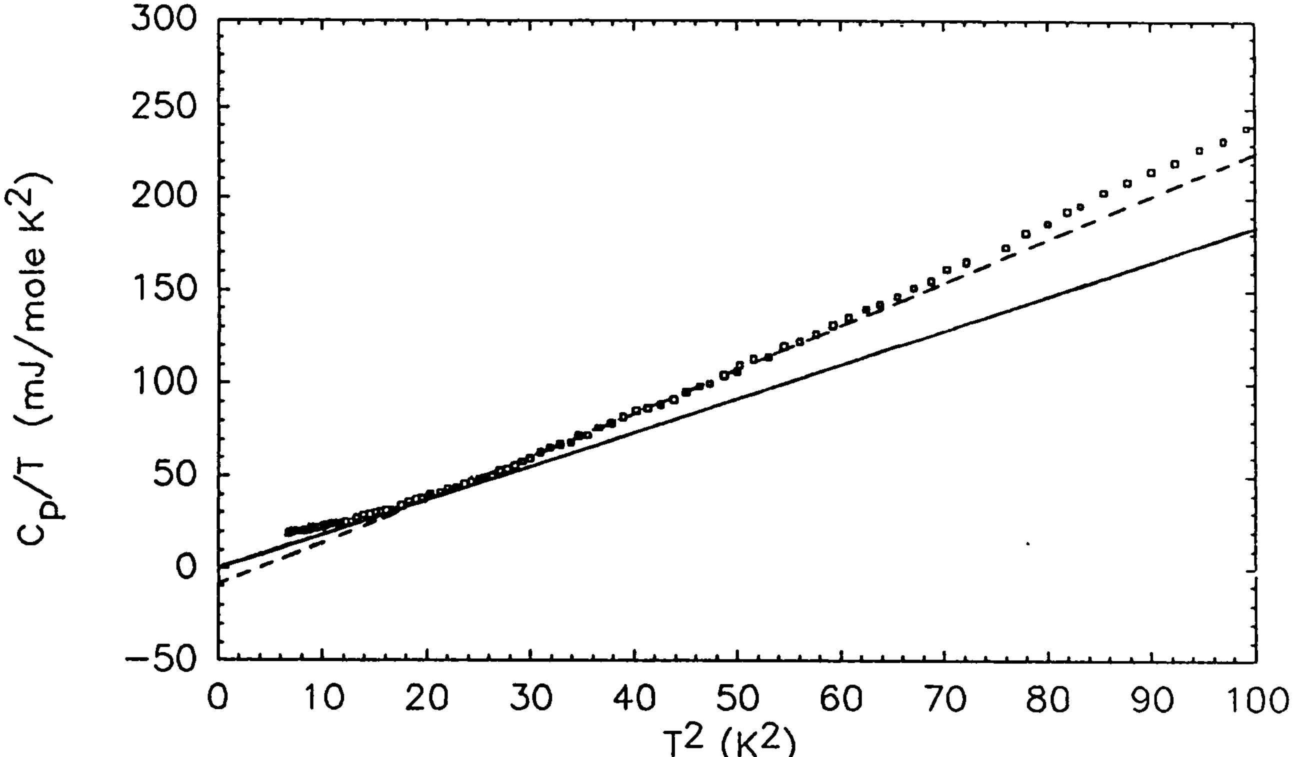

Fig. 4.10 C_p/T vs. T^2 for BPSCCO2. The solid line represents the T and T^3 terms from the least−squares fit of the data, while the dashed line represents the kind of fit obtained by fitting a straight line visually.

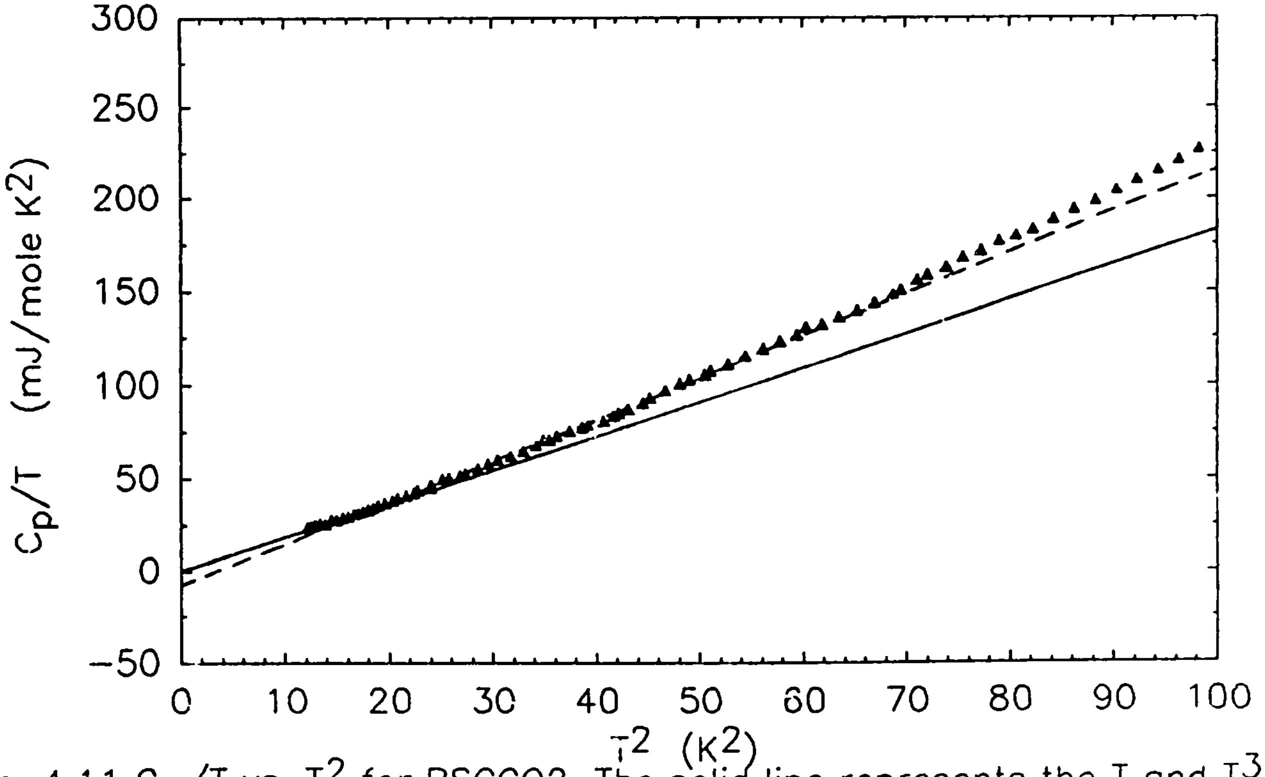

Fig. 4.11 Cp/T vs. T^2 for BSCCO2. The solid line represents the T and T^3 terms from the least−squares fit of the data, while the dashed line represents the kind of fit obtained by fitting a straight line visually.

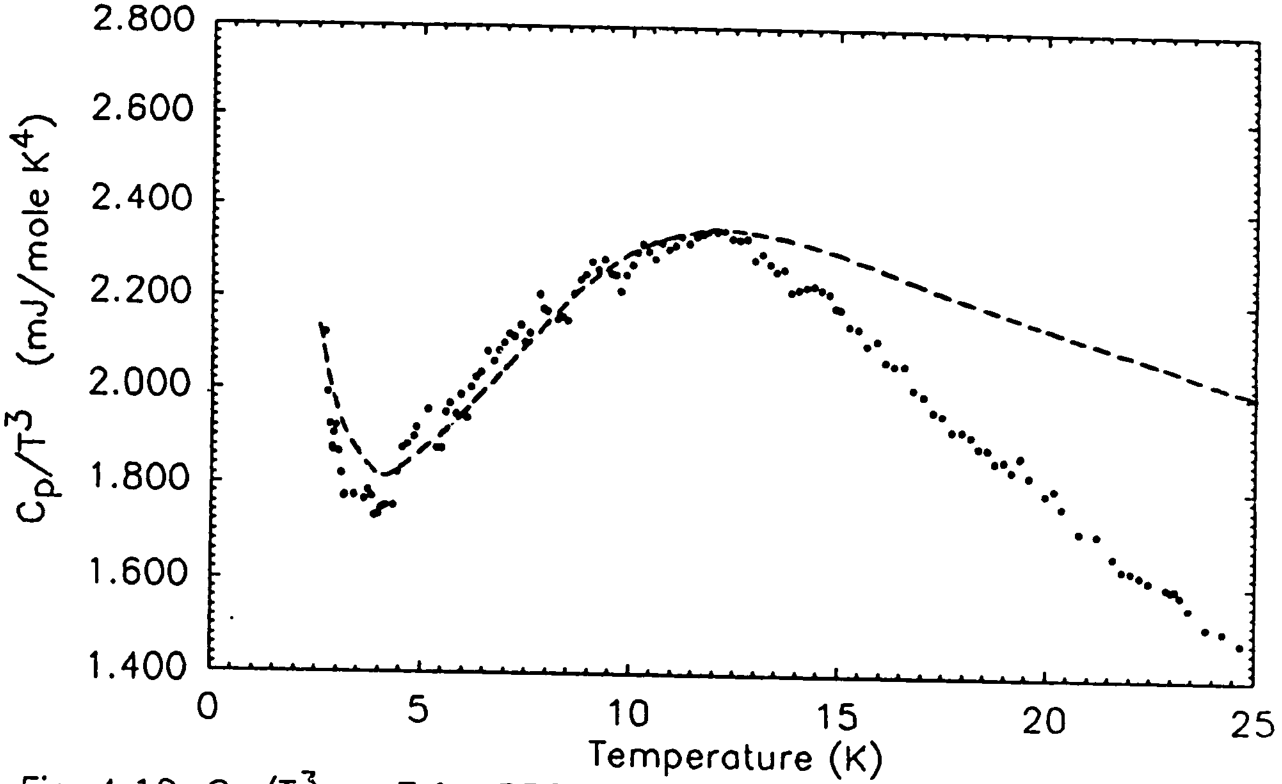

Fig. 4.12 C_p/T^3 vs. T for BPSCCO1. The dashed line is the fit to Eq.(4.2-1)

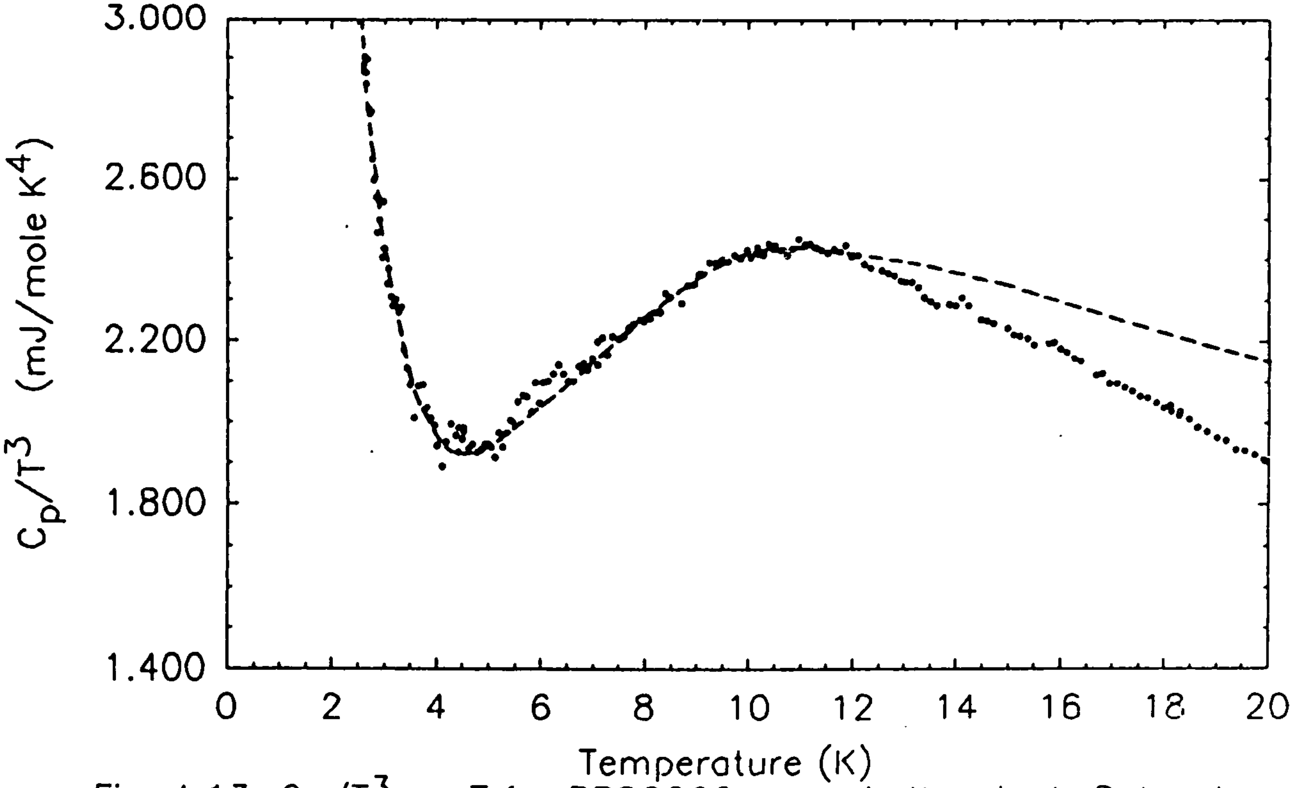

Fig. 4.13 C_p/T^3 vs. T for BPSCCO2. --- is the single Debye temperature fit (Eq. 4.2-1)

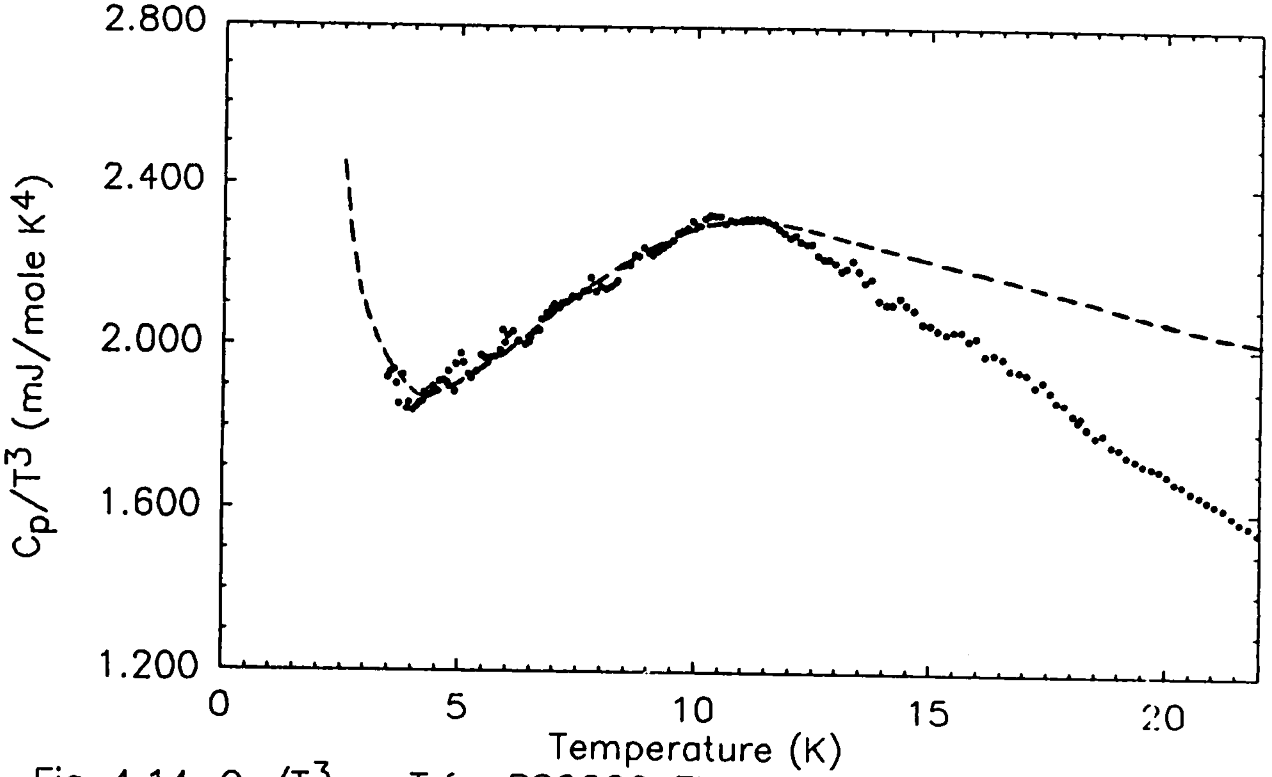

Fig. 4.14 C_p/T^3 vs. T for BSCCO2. The dashed line is the fit to Eq.(4.2−1).

et al. 1988a). This fact suggests once again that Ba-compounds may be the dominant impurity phases which contribute to the nonzero value of γ_0.

It should be mentioned that some nonzero values of γ_0 have been reported by several groups (Collocott et al. 1988, Muto et al. 1988, Sasaki et al. 1989). They might arise from impurity phases, or some internal "defects" which cause normal regions even at the lowest temperatures. However, so far, other possibilities cannot be excluded, and final answer for this problem also depends on improvement of sample quality and characterization.

4.3 Lattice Specific Heat

It is well known that the Debye characteristic temperature at T=O, θ_0, a very important parameter, can be determined from the coefficient of the cubic Debye term, because at the very low temperature ($T< \theta_D/50$)

$$C_L = n(12\pi^4R/5)\times T^3/\theta_0^3 = \beta T^3, \qquad (4.3\text{-}1)$$

where R is the gas constant, n is the number of atoms per molecule. Fitting the experimental data with Equation (4.2-1), we get that β of BPSCCO1 , BPSCCO2 and BSCCO2 are 1.83±0.08, 1.84± 0.06 and 1.81±0.18 mJ/mole K^4 respectively, therefore θ_0 for these sample are 274±4, 273±4 and 253±9 K.

On the other hand, we can get θ_D (T) at any temperature from comparison between the Debye theory and the experimental value of the lattice specific heat:

$$C_L\ (T/\theta_D) = 9nR\left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} \frac{x^4 e^x dx}{(e^x-1)^2} = C_{Lexp}(T), \qquad (4.3\text{-}2)$$

were $C_{Lexp}(T)$ is the experimental value of the lattice specific heat at T, $x = h\nu/k_bT$, and ν is the phonon frequency. For the high temperature superconductors, unfortunately, so far C_L and C_e cannot be determined independently from each other as it is the case for the conventional superconductors. In the high temperature region, however, the electronic specific heat is only a few percent of C_L, therefore we can approximately determine C_L by making small correction to the total specific heat, and then use relation (4.3-2) to calculate the $\theta_D(T)$. Gao et al. reported (1990) that the value of the Sommerfeld coefficient for their Bi-sample was 43 mJ/mole K^2. Roughly, we borrowed this value to calculate the electronic specific heat, and then subtracted the electronic specific heat from the total specific heat to get rough values of C_L of our samples at high temperatures. By this way, we obtained that θ_D(100 K) was about 463 K for BPSCCO1, and 474 and 466 K for BPSCCO2 and BSCCO2 respectively. Comparing these values with those of θ_0, one can see a big difference between θ_0 and θ_D(100 K). However, this is not unusual. Debye theory is not perfect and the fundamental deficiency in this theory is the inadequate treatment of the effects arising from the discreteness of atomic arrangements in the crystal. The fact that the value of θ_D is not constant reflects that phonon contributions cannot be entirely described by this simple theory. E. Gmelin et al. (1982) reported that the rather steep increase of θ_D from low to high temperature was rather normal for complicated molecular structures rather than out of ordinary.

Another common feature should also be mentioned, it is that, for almost all solids, a minimum of θ_D is observed near $0.05 < T/\theta_D < 0.1$. Consistent with this behaviour of $\theta_D(T)$ is the expectation that there is a maximum in C_L/T^3 vs. T. Such a maximum has been observed and indicated above for all samples which we used to measure the specific heat at the low temperature, and according to our knowledge, also for most of high-T_c superconductors. A. Junod et al. (1983) point out that C_L/T^3 is an image of the spectrum $G(h\nu)/\nu^2$ for $\nu=4.93k_bT/h$. In other words, features in $G(h\nu)$ at a particular value of ν show up in C_L/T^3 at a temperature $T=h\nu/4.93k_b$. Therefore, a peak in C/T^3 means that there may be a singularity in the phonon density of states at a phonon frequency

$$\nu \approx 5k_bT/h. \qquad (4.3\text{-}3)$$

It has been reported (Ramirez et al. 1987, Reeves et al. 1987b, Junod et al. 1987 and Rosenberg et al. 1987) that, for

Y-Ba-Cu-O, Gd-Ba-Cu-O, Y-(BaK)-Cu-O, La-Cu-O, (LaSr)-Cu-O and (LaBa)-Cu-O superconductors, a characteristic peak in C/T^3 at a temperature between 20 and 25 K has been observed. In order to deal with the departures from a simple T^3-behavior, some groups use a Debye function and an appropriate Einstein term to fit the lattice specific heat, and get the characteristic temperature of T_E is about 120 K. It indicates that there might be an anomaly in the PDOS near $h\nu$=10 meV. Such low lying phonon anomalies have been successfully detected from PDOS determinations by neutron scattering experiments for Y-Ba-Cu-O, Nd-Ba-Cu-O, Pr-Ba-Cu-O, Y-Ba-(CuZn)-O and (LaSr)-Cu-O (Ramirez et al. 1987, Rhyne et al. 1987, Renker et al. 1988, Gompf et al. 1988 and Rietschel et al.1988).

For Bi-samples, as mentioned above, our measurements showed that the maxima in C/T^3 for BPSCCO1, BPSCCO2 and BSCCO2 are at 12.2, 11.0 and 10.5 K respectively. Urbach et al. (1989) reported a broad peak in C/T^3 at about 9 K, and Gao et al. (1990) observed a peak near 10 K for their Bi-sample. As mentioned above, we used Equation (4.2-1) to fit low-temperature specific heat data. We obtained that T_E for BPSCCO1, BPSCCO2 and BSCCO2 were 60, 56 and 55 K, the oscillator strength m for all three samples was approximately the same, and was about 0.5. Consistent with these values of T_E was the expectation that there would be an anomaly in the PDOS near 5 meV. PDOS determinations by neutron scattering experiments (Renker et al. 1989) showed the ω^2-background and an anomaly in the low frequency range for Bi-samples, however, the anomaly was not near 5 meV, but near 10 meV. The reason for that, so far, we have not clearly known.

It can be seen in Fig. 4.12, 4.13 and 4.14 that the fit based on Equation (4.2-1) is well consistent with the experimental data until a little bit above the maximum in C/T^3, and that then, however, it becomes increasingly inaccurate. Urbach et al. also reported (1989) that this kind of fit could not be extended to higher temperatures. The analysis of the broad peak in C/T^3 at higher temperatures depends on a correct treatment of the lattice part of the specific heat. The reason for that is that the Debye model is not perfect as mentioned above, and it well represents the lattice specific heat only in very low temperatures, therefore, the Debye temperature θ_0 obtained near T=0 is not a good parameter for the higher temperatures.

For a complicated compound containing various elements, it is reasonable to assume that different atoms have different contributions to the specific heat, for instance, for heavy atoms, the contribution to the specific heat starts at low temperatures, and, for light atoms, the contribution starts at higher temperatures. Therefore, we suppose that the lattice specific heat can be understood with the assumption of several separated sets of lattice vibrations, and we have attempted to fit the lattice specific heat in a wide temperature range by assigning an individual Debye temperature θ_{Di} to each constituent in this way:

$$C_L = \sum_i n_i C_D(\frac{\theta_{Di}}{T}) + mC_E(T), \qquad (4.3\text{-}4)$$

and, therefore, Equation (4.2-1) becomes

$$C(T) = A/T^2+\gamma_o T+\sum_i n_i C_D(\frac{\theta_{Di}}{T}) + mC_E(T), \qquad (4.3\text{-}5)$$

where $C_D(\theta_{Di}/T)$ is the Debye specific heat function, and n_i denotes the number of atoms for the ith elements per formula, hence

$$\sum_i n_i = n, \qquad (4.3\text{-}6)$$

where n is the total number of various atoms per formula. Furthermore, because the light and the heavy atoms correspond to the set of high and low frequency modes respectively, we suppose that the individual Debye temperatures depend on the atomic mass as

$$\theta_{Di}/\theta_{Dj} = (M_j/M_i)^{1/2}, \qquad (4.3\text{-}7)$$

as a first approximation.

At low temperatures, we have

$$\sum_i n_i(12\pi^4 R/5)T^3/\theta_{Di}^3 = \beta T^3. \qquad (4.3\text{-}8)$$

Therefore, by fitting to the low temperature T-cubic term we obtain the following atomic Debye temperatures θ_{Di}:

Table 4.2

The values of individual Debye temperatures from Eq. (4.3-7), the first approximation, for BPSCCO1, BPSCCO2 and BSCCO2

SAMPLE	θ_D(Bi)	θ_D(Pb)	θ_D(Sr)	θ_D(Ca)	θ_D(Cu)	θ_D(O)
BPSCCO1	153	154	236	349	277	552
BPSCCO2	155	156	240	354	281	561
BSCCO2	150	---	231	342	272	541

After these atomic Debye temperatures are used, the fits are improved at higher temperatures, deviation from the measured value is approximately 20% at 100 K, comparing with about 70% in the single Debye temperature fit.

On the other hand, according to the Debye model, the phonon frequency spectrum can be taken as

$$\begin{aligned} G_{Di}(h\nu) &= 3n_iN\frac{\nu^2}{\nu_{Di}^3} \qquad \text{for } \nu\leq\nu_{Di} \qquad (4.3\text{-}9) \\ &= 0 \qquad \text{for } \nu>\nu_{Di}, \end{aligned}$$

where N denotes Avogadro's number, and $\nu_{Di}=k_b\theta_{Di}/h$. Therefore, we can calculate the total frequency spectrum by using atomic Debye temperatures

$$G_D(h\nu) = \sum_i G_{Di}(h\nu). \qquad (4.3\text{-}10)$$

Fig. 4.15 shows the phonon frequency spectrum obtained in this way. Comparing it with the phonon frequency spectrum of some Bi-compound sample measured by inelastic neutron scattering (Renker et al. 1989), we find that some atomic Debye temperatures θ_{Di} indicated in Table 4.2 should be adjusted to higher values. In order to make the adjustment, we correct relation (4.3-7) to

$$\theta_{Di}/\theta_{Dj} = (M_j/M_i)^{\delta}, \qquad (4.3\text{-}11)$$

where δ is not simply equal to 1/2, because there should be some degree of coupling when different atoms combine into a compound, δ is considered as the coupling coefficient among different sets of lattice vibrations, and it is different from compound to compound.

Taking $\delta = 0.650$, 0.670 and 0.695 for BPSCCO1, BPSCCO2 and BSCCO2 respectively (these values of δ make deviation of fits by Eq. (4.3-5) from experiment data smallest), the atomic Debye temperatures of the three samples are adjusted to the values in the following table

Table 4.3

The values of individual Debye temperatures from Eq. (4.3-11) with $\delta = 0.650$, 0.670 and 0.695 for BPSCCO1, BPSCCO2 and BSCCO2

SAMPLE	θ_D(Bi)	θ_D(Pb)	θ_D(Sr)	θ_D(Ca)	θ_D(Cu)	θ_D(O)
BPSCCO1	146	146	256	426	316	773
BPSCCO2	145	146	259	437	321	809
BSCCO2	140	---	256	441	320	835

After this adjustment, the fits are reasonably good over the whole temperature range in which we perform specific heat measurements. This can be seen in Fig. 4.16, 4.17 and 4.18, in which we present the experimental data and fitting curves of C/T^3 vs. T from 2.6 to 120 K. The deviation from the experimental value is only a few percent at high temperatures. We list some experimental data and the data from different fits to make a comparison in Table 4.4, 4.5 and 4.6.

We would like to point out that all of atomic Debye temperatures are not independent of each other, and determined by δ and β (the coefficient of the cubic Debye term). This means that there is only one more independent parameter, δ, in Equation (4.3-5), comparing with Equation (4.2-1). However, the fits are greatly improved. Therefore, we believe that, for a complicated compound, maybe the lattice specific heat can be understood with the assumption of several sets of lattice vibrations, every of which has its own Debye temperature determined by

Equations (4.3-8) and (4.3-11).

Table 4.4.

A review of some values of specific heat at high temperatures from experiments and different fits for BPSCCO1

T(K)	C_{exp}(J/mole K)	C_{fs}(J/mole K)	C_{fa}(J/mole K)
60	109	209	110
80	160	290	155
100	203	343	196
110	234	365	215

(C_{exp}, C_{fs} and C_{fa} denote the experimental data, the data from the single effective Debye temperature fit and the data from the fit based on Eq. (4.3-5) in which the individual Debye temperatures depend on the atomic mass as $\theta_{Di}/\theta_{Dj} = (M_j/M_i)^{\delta}$ with δ=0.65.)

Table 4.5.

A review of some values of specific heat at high temperatures from experiments and different fits for BPSCCO2

T(K)	C_{exp}(J/mole K)	C_{fs}(J/mole K)	C_{fa}(J/mole K)*
60	105	209	107
80	152	291	151
100	196	346	191
110	208	366	209

*(With δ=0.67)

Table 4.6.

A review of some values of specific heat at high temperatures from experiments and different fits for BSCCO2

T(K)	C_{exp}(J/mole K)	C_{fs}(J/mole K)	C_{fa}(J/mole K)*
60	91.8	181	91.9
80	130	244	125
100	159	284	154
110	170	298	167

*(With δ=0.695)

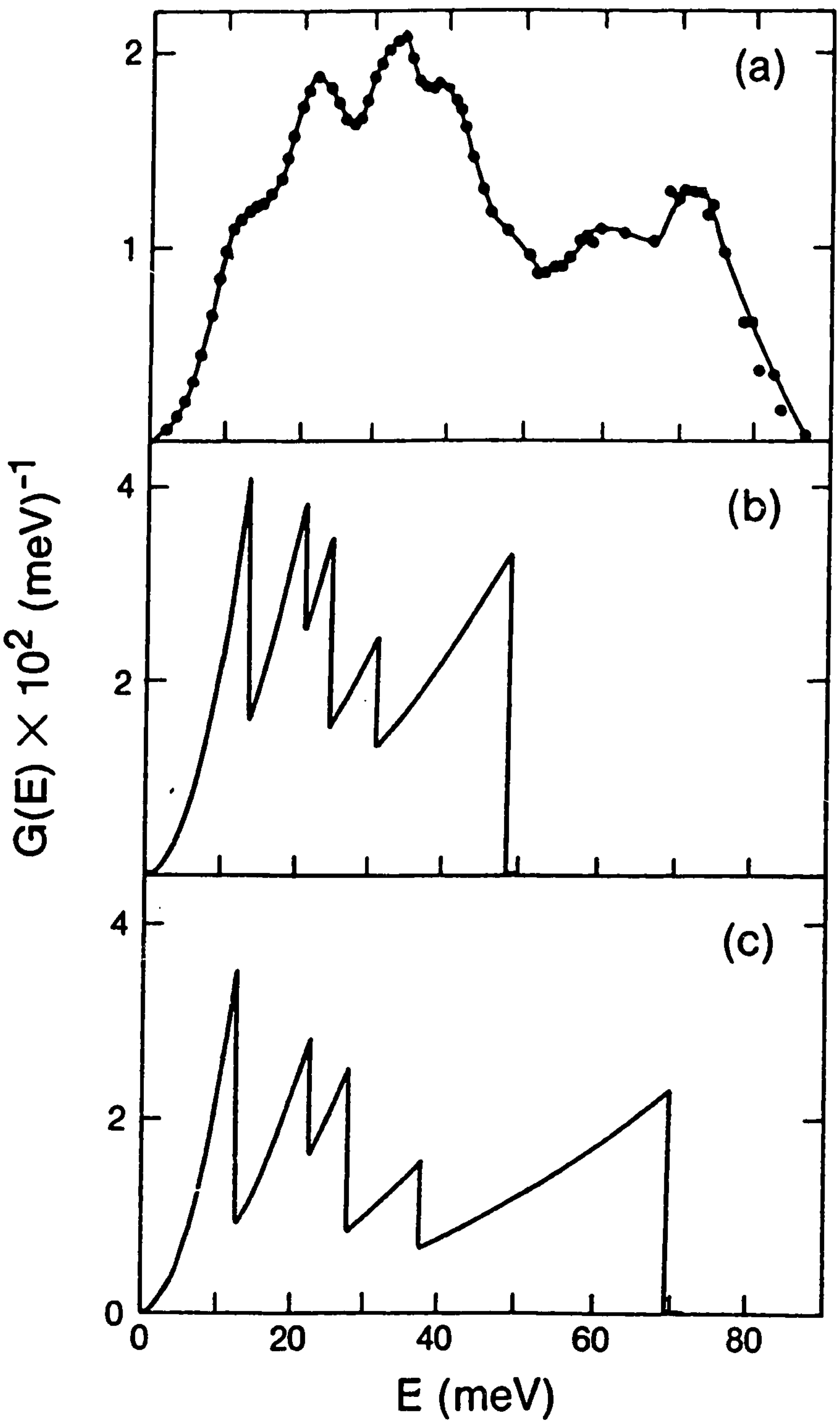

Fig. 4.15 a) The phonon density of states of $BiSr_2CaCu_2O_{8+\delta}$ (T_c~80K). The results are from B. Renker et al. (1989). b) The calculated PDOS of BPSCCO2 obtained according to atomic Debye temperatures in Table 4.2. c) The PDOS of BPSCCO2 obtained from atomic Debye temperatures in Table 4.3.

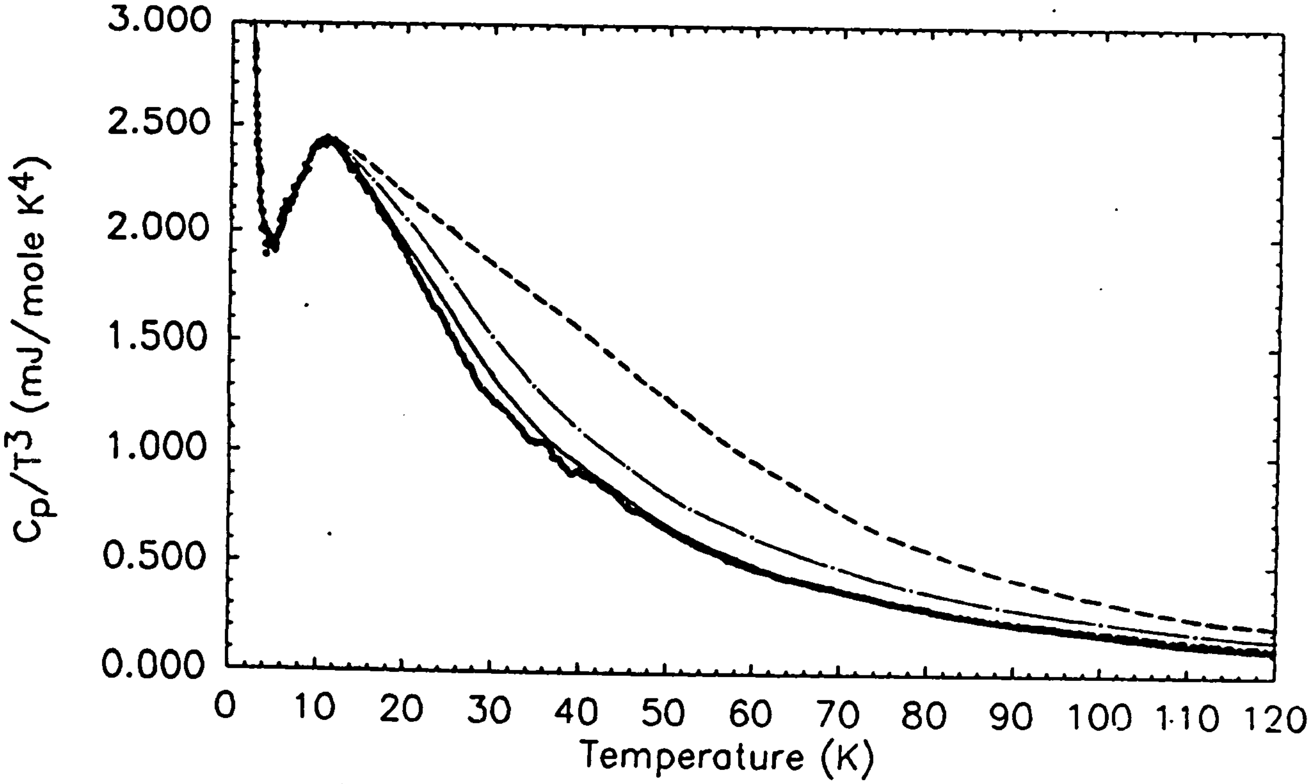

Fig. 4.16 C_p/T^3 vs. T for BPSCCO2. The data–point line is from the experiments. —— The fit to Eq. (4.3–5) with $\Theta_{Di}/\Theta_{Dj}=(M_j/M_i)^{\delta}$, δ=0.670. —·— The fit to Eq. (4.3–5) with $\Theta_{Di}/\Theta_{Dj}=(M_j/M_i)^{1/2}$. --- The single effective Debye temperature fit.

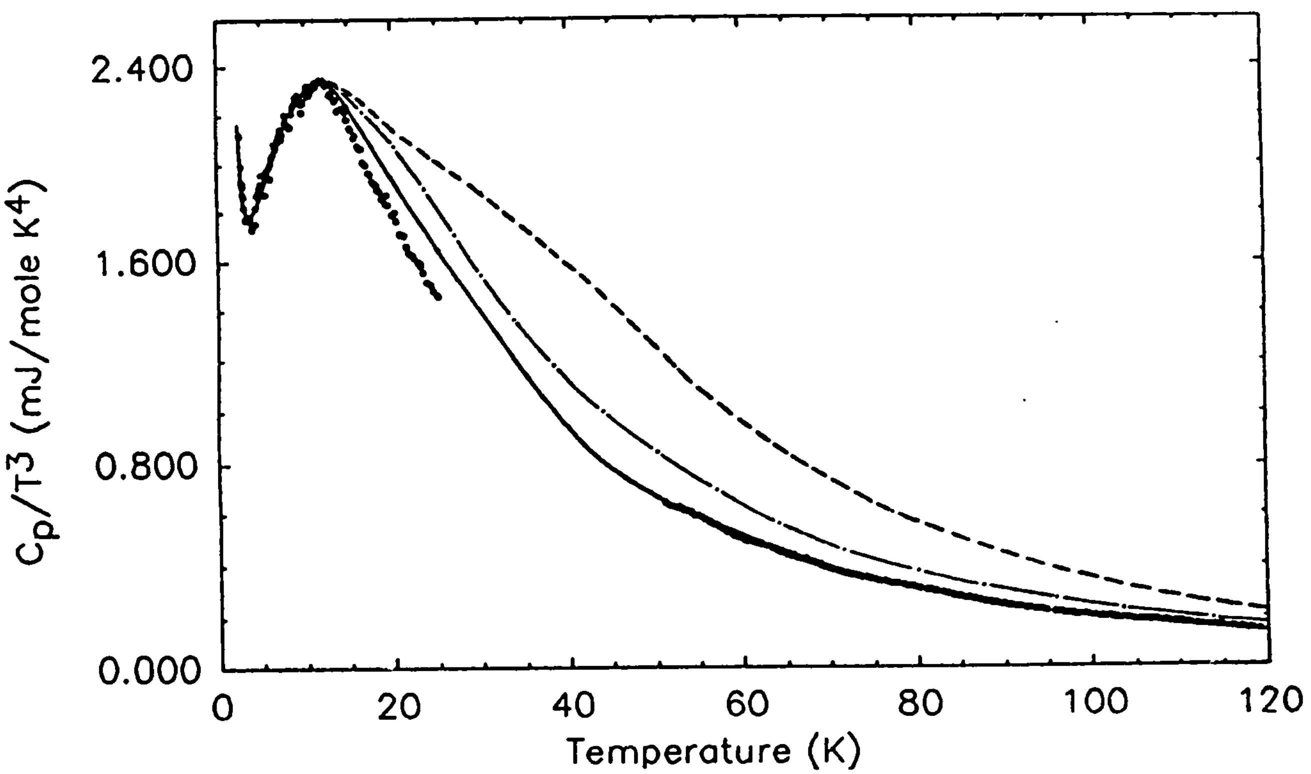

Fig. 4.17 Cp/T^3 vs. T for BPSCCO1. The data–point line is from the experiments. ——— The fit to Eq. (4.3–5) with $\Theta_{Di}/\Theta_{Dj}=(M_j/M_i)^{\delta}$, $\delta=0.650$. —·— The fit to Eq. (4.3–5) with $\Theta_{Di}/\Theta_{Dj}=(M_j/M_i)^{1/2}$. – – – The single effective Debye temperature fit.

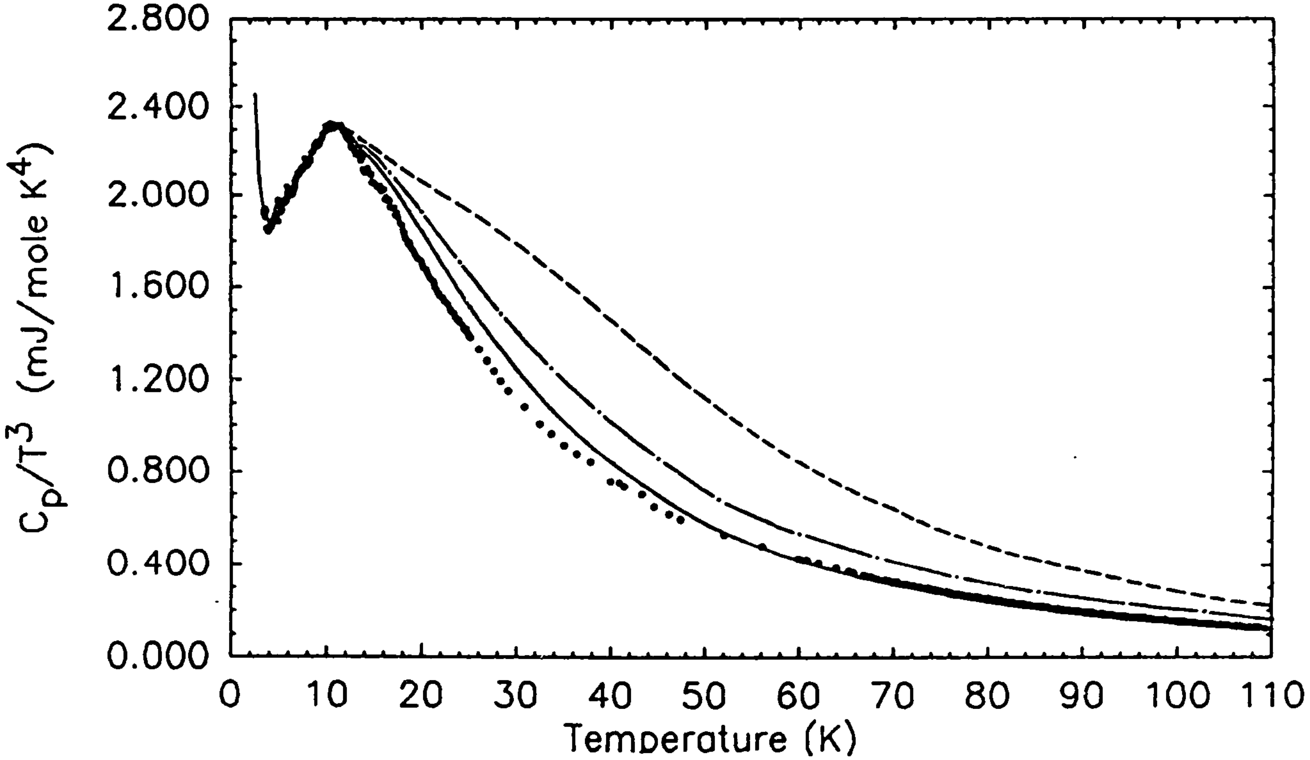

Fig. 4.18 C_p/T^3 vs. T for BSCCO2. The data−point line is from the experiments. ——— The fit to Eq. (4.3−5) with $\Theta_{Di}/\Theta_{Dj}=(M_j/M_i)^{\delta}$, δ=0.695. —·— The fit to Eq. (4.3−5) with $\Theta_{Di}/\Theta_{Dj}=(M_j/M_i)^{1/2}$. — — —The single effective Debye temperature fit.

CHAPTER 5

CONCLUSIONS

1. From our measurements, the ratio $\frac{\Delta C(T_c)}{\gamma T_c}$ is larger than 3.0 for the YBCO sample, and is in the strong coupling limit.

2. For some Bi-compound superconducting samples, the specific heat jumps at two transition temperatures have been observed. However, the sizes of anomalies are different from sample to sample. We believe that sample quality and different content of 2212 and 2223 phase cause these differences. For the sample whose Meissner fraction is small, whose θ_0 is lower and whose $N(E_F)$ may also be much smaller, the anomaly at the transition temperature cannot be detected.

3. The low-temperature specific heat data of Bi-compound superconductors can be fitted with the equation

$$C(T) = A/T^2+\gamma_0 T+\beta T^3+mC_E(T).$$

The least-squares fits give us that there is no temperature-linear term in the low-temperature specific heat within the experimental uncertainty. Therefore, the T-linear term is not a general feature for all high-temperature superconductors.

4. For Bi-compound superconductors, there are big differences among Debye temperatures which are obtained from low temperatures and from high temperatures. This is not related to the properties of high-T_c superconductors, but just

because the Debye theory is not a good theory for complicated compounds. Perhaps the lattice specific heat can be understood with the assumption of several sets of lattice vibrations, every of which has its own individual Debye temperature θ_{Di}, and

$$\theta_{Di}/\theta_{Dj} = (M_j/M_i)^{\delta},$$

where δ is considered as the coupling coefficient among different lattice vibrations.

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