CHAPTER 2

SYNTHESIS AND CHARACTERIZATION OF THE SUPERCONDUCTOR $Ba_2HoCu_3O_7$

2.1 INTRODUCTION

Even after the discovery of so many HTSC in the recent years, there remained many unresolved questions concerning the exact composition and the crystal structure of the phase and whether the superconductivity really occurs in a bulk state. To answer these important questions, a detailed investigation focusing on the determination of the right composition and the crystal structure of the superconducting phase is needed. This can be achieved by means of X-ray diffraction , differential thermal analysis with the aid of a.c. susceptibility and resistivity measurements. Here, a brief description on the sample preparation methods of ceramic superconductors and the methodology of the various experimental techniques employed to study their physical properties are presented with a typical example, $Ba_2HoCu_3O_7$. The pressure dependence on T_c is also studied.

2.2 METHODS OF PREPARATION

Ceramic superconductors do not occur naturally and they have to be synthesized. These HTSC are generally La or Y based, as mentioned earlier with a composition $RBa_2Cu_3O_7$ with x varying from 0 to 1 (R stands for a rare earth). The crystal structure attained with this particular composition with vacant oxygen sites and the presence of copper ions in a higher valence state brought about by barium are found to be crucial to the occurrence of superconductivity in these materials.

A number of factors should be taken into account during the synthesis of ceramic oxide superconductors: the control of stoichiometry, the subtle geometrical features that govern the crystal structure of the final compound, concentration of defects, homogeneity of the product and its single phase nature. All these parameters have a profound bearing on the superconducting characteristics of the end product. There are many methods for synthesizing these HTSC:

1. Preparing an alloy from the constituent metals and oxidizing it subsequently at controlled high-temperatures and gas pressures to get the final oxide material. However,

this is not a very convenient route in view of the problems relating to the homogeneity of the final product and the high cost of materials.

2. Starting with a solution containing these oxide materials as solutes, one can prepare the desired compound by first obtaining a precipitate by a suitable chemical treatment. This co-precipitate is then heat-treated to attain the desired compound which on further heat and oxygen treatment attains the optimum superconducting characteristics. This particular method, although laborious, gives the most homogeneous product because of the small particle sizes in the precipitate and hence is supposed to show best results.

3. The Solid State Reaction method is the widely used method and in this , the appropriate stoichiometeric proportions of the starting materials are mixed thoroughly in an agate mortar and pestle for small quantities (10-15 gms). For larger quantities, a ball mill is used. The well mixed powder is then heated at a suitably high temperature below the melting point. The appropriate condition that lead to the completion of the reaction can be determined only by trial and error. Intermittent grinding between heating cycles can be done to hasten the reactions and to ensure a

total conversion to the desired product. This powder is then shaped into the desired form using a suitable die and plungers by applying pressure. Sintering is done at optimised conditions. The optimum temperature at which the ground powder is heated and the time of heating are the two most crucial factors that are to be mainly considered during the preparation. Either alumina or platinum crucibles can be used during preparation for heating and sintering, depending on the temperature.

2.3 CHARACTERIZATION

The various aspects of characterization namely, structural characterization, determination of physical properties and chemical properties give the complete descriptions of all the informations needed. Structural characterization includes diffraction, microscopic and spectroscopic methods. Physical properties,as characteristic tool deal with the study of crystal structure and variations in electrical resistivity, susceptibility, specific heat, Hall effect while chemical characteristics include the determination of stoichiometry, presence of the major and minor phase concentration, impurities and homogeneity.

2.3.1 X-Ray Diffraction

A complete description of the structure of a superconductor requires the determination of the crystal structure, unit cell dimensions and space group. One of the main problems in the preparation of superconducting materials is to find out whether the product obtained from a soild state reaction has a single phase or multiphase. The different crystal structures that make up the mixture can be identified by X-ray diffraction. In addition to this, crystal imperfections such as,the presence of impurity (which can be obtained from the line broadening) can also be detected from X-ray diffraction pattern.

There are three diffraction methods, namely, 1.Laue method, 2.rotating crystal method and 3. powder diffraction method. Among these methods, powder diffraction method is the widely used method for polycrystalline samples.In this technique, the sample is kept stationary and is irradiated by a beam of monochromatic X-ray radiation.

The characterization of the samples in the present work is done using the computer controlled X-ray diffractometer with

structure (software) packages. Here, a monochromatic beam of X-rays is allowed to irradiate a small specimen of the substance ground into a fine powder. The X-ray tube is operated at a voltage of 35kV and the tube current is of the order of 20-30 mA. The intensities of the diffracted beam are measured with the help of a photon counter. The photons in the scattered radiation are counted by means of the scintillation counter (0.9kV). Now, from the X-ray diffraction pattern, the (hkl) values and in turn the lattice parameters are obtained by the method of least square fitting. This powder diffraction method, with the counter as detector, gives the information regarding the phase identification in addition to the information about the crystal system and unit cell lattice parameters.

2.3.2 Characterisation by Physical Technique

2.3.2.1 Coil test for superconductivity with T_c>77K

This test is used to check whether the sample's transition temperature is equal to or greater than liquid nitrogen temperature (77K). This method of testing is quick and reliable for establishing superconductivity of the sample [1].

The basic principle involved is that the coil inductance is affected by the susceptibility of the sample introduced into the coil. When a substance which has a magnetic phase transition (para to ferro or para to dia) is placed at the centre of the core of the coil, the inductance changes. It gets summed up when the sample is magnetic and decreases for diamagnetic - superconducting materials. A shematic diagram of the coil test set up is shown in Figure 2.1

Two coils each having 400 turns of copper wire with diameter 50 μm are mounted on a perspex base. These form the two arms of the bridge circuit connected to a carrier frequency amplifier. To start with, the two coils are dipped in liquid N_2 bath and are balanced for null deflection at 77K. Now the sample to be tested is precooled and introduced into one coil. An imbalance is produced because of a change in the inductance of the coil which is due to the transition of the sample. This change from para to dia is indicated by the deflection of the needle to one side of the zero in the scale. On the other hand, when a sample which changes from para to ferro magnetic state on cooling is introduced into the core of the coil, the needle will move in the opposite

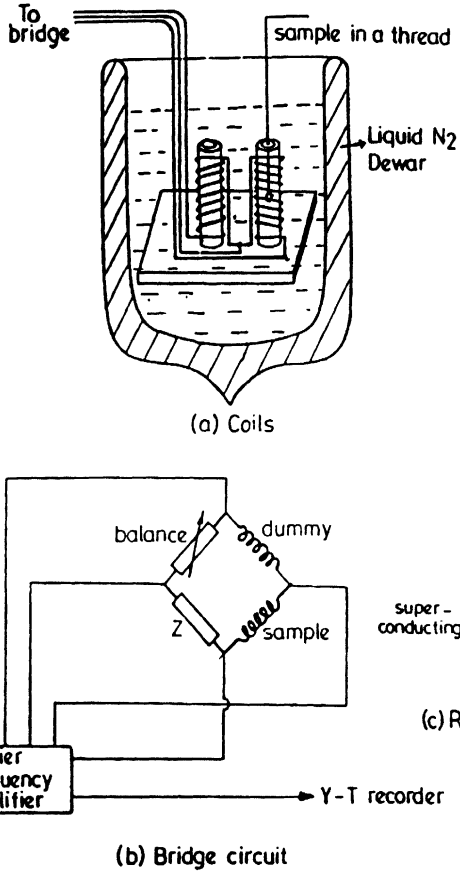

FIG 2.1 COIL TEST SET UP FOR ESTABLISHING SUPERCONDUCTIVITY ABOVE LIQUID NITROGEN TEMPERATURE (> 77K)

direction of the zero. The strength of the signal (extent of deflection from zero) is an indication of the superconducting phase in the given sample. Though there is a slight change in the resistance of the coil when they are cooled to liquid N_2 temperature, this can be off set by balancing the null deflection under those conditions before introducing the sample. If the sample is in powder form, then they can be either packed into small packets or loosely pressed into discs.

2.3.2.2 Electrical Resistivity `ρ'

The variation of resistivity, ρ , of a sample as a function of temperature is one of the methods used for establishing superconductivity. The onset of superconductivity in a substance is indicated by the total loss of resistance in it at a particular temperature and below that. If the temperature coefficient of resistivity is positive, the behaviour is metallic; if it is negative, the behaviour is semiconducting. The T_c at which ρ becomes zero need not always be represented by a sharp discontinuity. For homogenous single crystals of pure metals and well annealed alloys, the width of transition is narrow, i.e, 0.001K; it

gets broadened for polycrystalline or impure metals. The temperature interval over which the transition occurs from normal to superconducting state (transition width ΔT_c) can vary from few degrees to several degrees of kelvin (10^{-5}K-5K). In such cases, the midpoint between the 90% and 10% drop in ρ value is taken as T_c.

a. Four probe method

The electrical resistivity measurements are made on well sintered pellets using van der Pauw-Montgomery Four Probe Method [2]. The principle behind the resistivity measurement is explained as follows; an anisotropic sample of uniform thickness with four measuring point contacts on the top surface arranged in the form of a rectangle ABCD is taken. The distance between the contacts AB is L_1 and between BC is L_2 and the thickness is L_3. Let R_1, R_2 are voltage to current ratios along the two perpendicular directions. Current is sent through BC and the potential difference is measured across CD. Then the ratio of voltage to current gives R_1. Now,the current is passed through AD and the potential difference is measured across BC and thus, the ratio of voltage to current gives R_2. Now, the

resistivity in the two perpendicular directions is given by $\rho_1 = HER_1$ and $\rho_2 = HER_2$ where H is the geometric parameter. It is a function of L_2/L_1 for ρ_1 and L_1/L_2 for ρ_2 and E is the effective thickness. The effective thickness E plotted in dimensionless form against L_3, the actual thickness of the specimen, is a curve that depends on L_2/L_1. However, E is almost equal to the actual thickness for thin samples provided $L_3 << (L_1L_2)^{1/2}$ and the ratio $L_3/(L_1L_2)^{1/2}$ is less than 0.4 and in such case, E does not depend on (L_1/L_2) significantly. Montgomery [2] has given a graph of R_2/R_1 as a function of L_2/L_1 and another graph showing the behaviour of L_2/L_1 with H . The value of H, E and hence T_c can be calculated using the values of R_1/R_2, L_1/L_2 from the graph.

b. Measurement of Electrical Resistivity from 77K to 300K

The experimental set up to measure electrical resistivity is shown in Figure 2.2 . The electrical contacts are made with indium at four points in rectangular shape and the fine copper wire leads are connected to the sample to ensure ohmic contacts at all temperatures. Now, this sample is mounted on a sample holder (a small copper metal strip of length 5.5 cm) but insulated from it by a thin layer of insulating material (GE varnish). This sample holder is

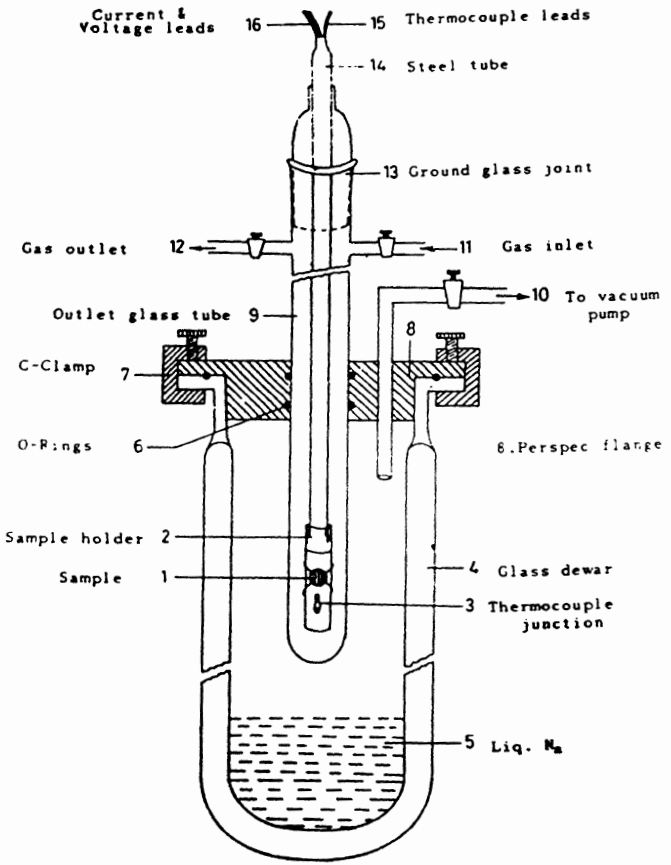

FIG 2.2 APPARATUS FOR THE MEASUREMENT OF RESISTIVITY BY FOUR PROBE METHOD

suspended at one end of a thin walled steel support tube.This steel tube with sample assembly is then placed inside a glass tube which has two openings (one acts as a inlet while other as an outlet) for the passage of hydrogen. This glass cell is then fitted into a dewar containing liquid N_2 which acts as a refrigerent. The temperature is measured with a chromel alumel thermocouple, which has an accuracy of ± 0.5K.

Initially, pure and dry hydrogen is flushed into the glass cell and a hydrogen atmosphere is maintained throughout the experiment. H_2 gas serves as a good exchange gas because of high thermal conductivity (446.3×10^{-6} at 300K) and it prevents condensation of gases and water vapour. The temperature of the sample in the range to be measured is controlled by adjusting the position of the sample cell in the dewar which has a small quantity of liquid N_2 at the bottom. The other junction of the thermocouple is kept immersed inside the liquid N_2 serving as a 77K reference point i.e., the cold junction. Using the standard tables and from the thermo emf developed,the temperature can be calculated. The circuit used for this measurement is shown

in Figure 2.3. The two leads from the current source pass a constant current of 10 mA. The voltage drop is measured by a nanovoltmeter. Now, to get the two values of resistance in the two perpendicular directions, the current and voltage terminals are interchanged using a switch arrangement. Specific resistance is calculated using the formula $\rho_i = HER_1$. A set of values at temperature T namely V_1, V_2, R_1,R_2, R_1/R_2, H and are then calculated. The sample is considered to be superconducting when a voltage drop, as measured by the nanovoltmeter is of the order of < 100 ± 8 nv and this should remain constant when the input current polarity is changed.

2.3.3 Magnetic Susceptibility 'χ'

The superconductor, is a perfect diamagnet (at low magnetic fields) and should show a negative susceptibility, when cooled below the transition temperature T_c. The measurement of magnetic fields at low applied fields is a reliable and a good method of measuring the transition temperature accurately. Above T_c, χ can exhibit positive values and show an abrupt change to negative values at T_c.

The superconducting transition of a sample is measured by SQUID Model 1822 Magnetometer. SQUID is the most sensitive

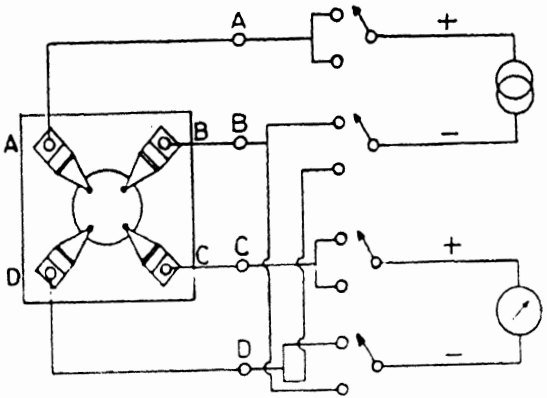

FIG 2.3 CIRCUIT DIAGRAM FOR THE MEASUREMENT OF RESISTIVITY BY FOUR PROBE METHOD

device available to measure magnetic fields, magnetic field gradients and magnetic susceptibilities. It consists of two Josephson junctions mounted on a superconducting loop. The device used is constructed using thin films. The junctions are formed with Nb-NbO-Pb thin films. A constant current greater than the critical current (maximum zero-voltage current) of the two junctions biases the SQUID at a non zero voltage.

The critical current and the voltage across the SQUID are periodic in the external magnetic flux, Φ_e, applied to the loop, with a period of one flux quantum, Φ_0. A change in flux $\Delta\Phi_0$, that is much smaller than Φ_0 can be detected with the flux locked SQUID. The feedback circuit generates a current in a coil inserted in the SQUID so that the flux in the SQUID is maintained at a constant value. To measure the magnetic susceptibility, the sample is placed in one of the pickup loops. The application of a magnetic field produces an output from the flux locked SQUID that is proportional to the susceptibility of the sample.

2.4 HIGH PRESSURE STUDIES OF HTSC

The pressure dependence of T_c for HTSC has been investigated

extensively since a large pressure effect on the superconducting transition temperature T_c of La-Ba-Cu-O compounds was revealed by Chu et al [3]. It was showed that by applying a pressure of 1.5 GPa the critical temperature T_c could be increased from 30K to values above 40K. This large pressure effect led to the very successful idea of replacing La by the smaller Y, resulting in a critical temperature for $YBa_2Cu_3O_7$ above 90K. Other substitutions including those with Sr, were tried but with no significant increase in T_c. Many new superconducting Cu-O oxide compounds, such as an electron-doped Nd-Ce-Sr-Cu-O and a highly hole-doped Tl-Ba-Cu-O compounds have been synthesized and a new feature of the pressure dependence of T_c has been found [4,5].The crystal structure of some Cu-O oxide superconductors have been investigated by means of a neutron diffraction technique under pressure [6] and some of the results strongly suggest that with increasing pressure a charge transfer takes place to CuO_2 plane. It is the general perception, that there exists an intimate correlation between T_c and the hole concentration in the CuO_2 planes [7]. Apart from this, pressure experiments can be used to test theoretical models for high temperature superconductivity. The basic idea is that a model should not

only predict critical temperatures of the right order of magnitude, but should also correctly predict the pressure dependence of T_c. High pressure can also be used to synthesize compounds that are otherwise unobtainable and/or that are unstable at ambient pressure.

For the study of HTSC , a wide range of standard high pressure equipments have been used, from classical pressure bombs to diamond anvil cells. Various techniques have been used to generate pressure and to measure T_c under pressure. A piston cylinder high-presure apparatus can be used for the hydrostatic pressure experiment. Using the piston cylinder apparatus, the temperature dependence of the resistivity from 77K to 300K is measured. In each case, kerosene contained in a teflon capsule is used for the liquid pressure medium. The pressure in the capsule is determined by a magnin gauge and the temperature is measured by a copper-constantan thermocouple. The resistivity of the sample is measured by a four-probe method with the electrodes connected to the sample by using silver paste for ohmic contact. During cooling and heating, the press load is held constant.

2.5 PREPARATION AND CHARACTERIZATION OF $Ba_2HoCu_3O_7$

Samples of $Ba_2HoCu_3O_7$ are prepared by the method of powder calcination. The prescribed amounts of high purity $BaCO_3$, Ho_2O_3 and CuO are mixed and pressed into pellets. They are pre-sintered at 900°C for one hour in air. These presintered materials are subsequently well ground and cold-pressed into bar samples with typical dimensions of $1x2x5mm^3$ at a pressure of 2-2.5 ton/cm^2 and then sintered for 950°C for 24 hours in oxygen atmosphere. Cooling is done at a rate of 150°C/hour.

2.6 RESULTS AND DISCUSSION

The X-ray pattern of the superconducting oxide with a metal ratio Ho:Ba:Cu of 1:2:3 shows that the obtained powder consists of single oxygen deficient perovskite phase. As for the structure of the present compound, it is essentially the same as that of $YBa_2Cu_3O_7$. It has a perovskite related structure possibly with orthorhombic symmetry where $a=a_p$, $b=b$ and $c=3a_p$ with a_p being the lattice constant of cubic perovskite cell. The X-ray pattern is used to check for the presence of a secondary phase. The lattice parameters of this compound are as follows: a = 3.885 Å; b = 3.899 Å;

c = 11.677 Å .These values agree well with the values reported in the literature [8].

Resistivity measurements are made in the bar samples in a standard four-probe configuration using silver paste contacts. The temperature is measured by a calibrated Si-thermometer. It is found that this compound showed superconductive transitions upon cooling at transition temperature (T_{co}) of 94K. The resistivity begins to decrease towards zero at critical temperatures where mid point (T_{cf}) is 93K for Ho compound.

Pressure shift of T_c is determined by measuring the electrical resistance as a function of temperature at various pressures. Kerosene is used as a pressure transmitting medium, which ensured hydrostatic pressures over the measuring temperature range. The specimen is immersed in kerosene with a teflon capsule. Pressure is applied by using a piston cylinder type press.

The temperature dependence of electrical resistance is measured under pressures of 0,1,2,3 and 4 Gpa. The resistance versus temperature graphs at 0,1,2,3 and 4 Gpa

are shown in Figure 2.4 and the following observations are made.

1. All resistance versus temperature curves have slight shoulder in the transition temperature range.

2. The pressure shift of T_{co} and T_{cf} is very small. Careful temperature control of sample is done for the precise determination of the transition temperatures. Therefore, heating and cooling runs are carried but the resistance versus temperature curves on heating and cooling coincide with each other.

3. The superconducting transition of this compound terminates at 93K at atmospheric pressure.

4. dR/dT changes with increasing pressure.

The variation of transition temperature with pressure is shown in Figure 2.5. T_{co} and T_{cf} are determined and plotted to observe the pressure dependence. The pressure dependence of T_{co} and T_{cf} is not so large when compared with that of La-Ba-Cu-O system. The pressure shift for a small positive pressure in the normal state may be due to the effective carrier concentration which is independent upon pressure

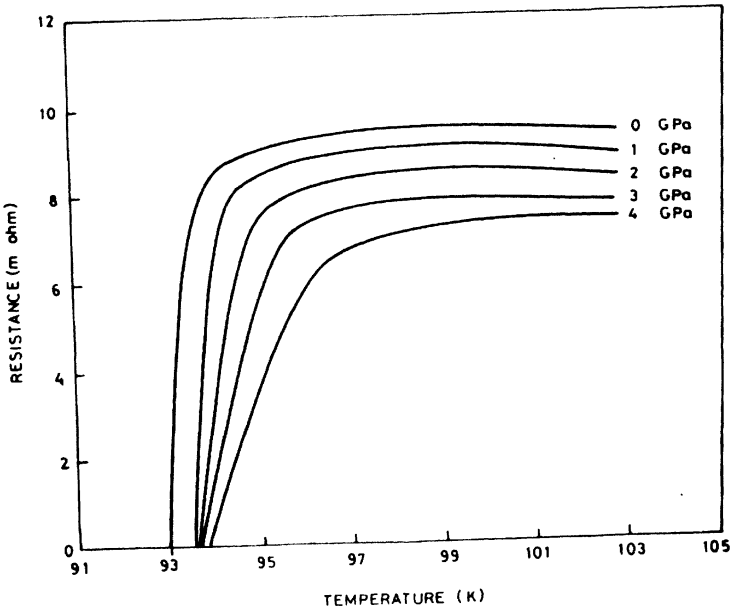

FIG 2·4 RESISTIVITY OF $Ba_2HoCu_3O_7$ VS TEMPERATURE

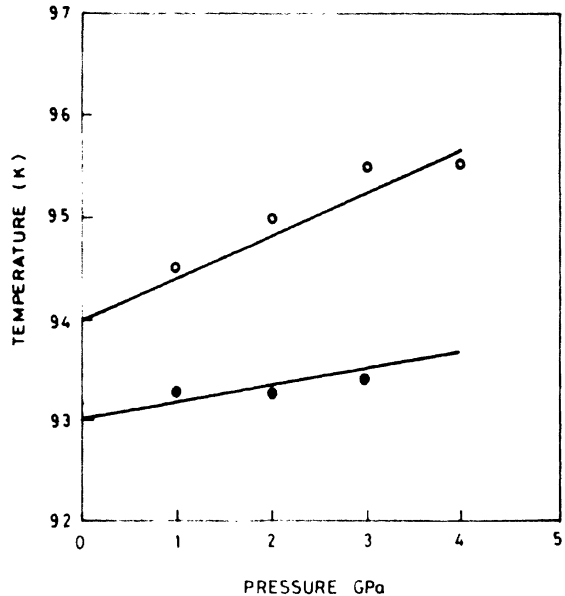

FIG 2·5 PRESSURE DEPENDENCE OF T_{co} AND T_{cf} FOR $Ba_2HoCu_3O_7$

and the normal state conductivity is controlled by electron-phonon scattering. However, T_{co} and T_{cf} shows maximum at 2,3 and 4 GPa. From the Figure 2.5,it is seen that both T_{co} and T_{cf} are apparently shifted up with the application of pressure. The rate of pressure of T_{cf} appears to be about two times larger than that of T_{co} and then, the transition temperature range is narrowed with pressure. This might be due to the pressure induced changes in stoichiometry and pressure effects due to vacancies.

The a.c susceptibility down to 5K was determined using the closed cycle refrigerator. The variation of χ_{ac} with temperatures is shown in Figure 2.6. The bulk sample exhibits a large diamagnetic signal at temperatures below 94K. When the sample is powdered, the diamagnetic signal is reduced almost to one third of the signal for the bulk sample at 5K. This implies that the sample possesses superconducting phase at T=94K only on the surface and/or given boundaries [9]. It is also interesting to note that even for a solid pellet, the diamagnetic susceptibility reaches a limiting value only at 55K, though the resistivity drops to zero at 93K.

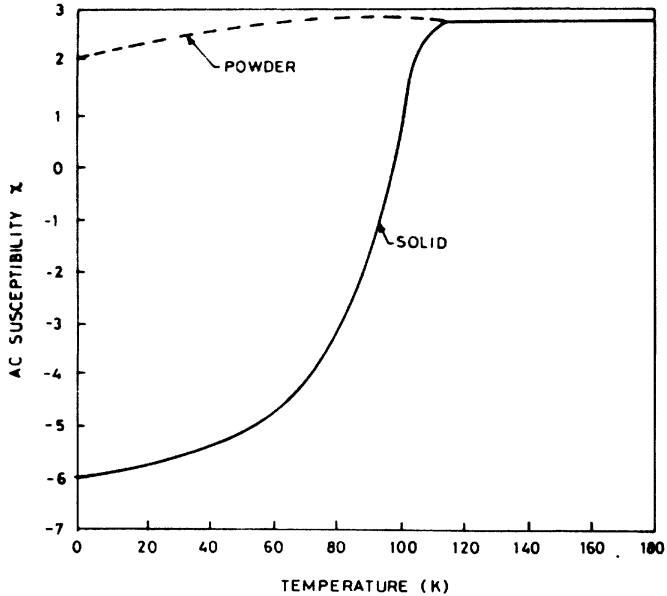

FIG 2·6 VARIATION OF MAGNETIC SUSCEPTIBILITY WITH TEMPERATURE FOR $Ba_2HoCu_3O_7$

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