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THE UNIVERSITY OF ALBERTA

HALL EFFECT MEASUREMENTS FOR  $\text{YBa}_2\text{Cu}_3\text{O}_{7-d}$

by



Brad Ingham

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND  
RESEARCH IN PARTIAL FULFILMENT OF THE REQUIREMENTS

FOR

THE DEGREE OF  
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IN

LOW TEMPERATURE PHYSICS

DEPARTMENT OF PHYSICS

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## DEDICATION

This thesis and all that is within in it is dedicated to both my Lord Jesus Christ who guided me to take this program, and to my wife Fiona who has encouraged me all along the way.

## ABSTRACT

Since the discovery of high temperature superconductors much experimentation has been performed in order to determine the mechanisms behind superconductivity at temperatures so far beyond the classical limits. The Hall effect is one of the experiments that has been used in this investigation.

In this project a simple experimental apparatus has been developed that allows highly accurate measurements of the Hall effect to be performed. A sample of the high temperature superconductor  $\text{YBa}_2\text{Cu}_3\text{O}_{7-d}$  has been analyzed with the apparatus. The Hall effect shows  $1/T$  behaviour around room temperature, and around the transition a sharp negative minimum in the Hall voltage is observed. At temperatures well above the transition temperature the data is discussed in terms of a simple phonon scattering mechanism while near the transition temperature the granular superconductor model can be used to explain these results.

## ACKNOWLEDGEMENTS

It is humbling to consider how much I have learned from day one of this project until now. While some of this learning has come through having to deal with problems myself, the bulk of it is due to all the devoted people who have helped me so much. Without these friends I doubt that I could have come this far.

Without the technical assistance of Mr. T. Valian, Mr. M. Mohamed and Mr. H. Zaleski, I can hardly imagine getting this experiment started little alone to the point where it practically runs itself.

I am deeply indebted to the people who have shared their ideas with me as well as listened to my own, often poorly informed, ideas. For this I would like to acknowledge Dr. Woods, M. Mohamed as well as Dr. J. Jung, W. Miner, and Dr. J. Franck.

I want to acknowledge foremost my friend and supervisor, Dr. S. B. Woods, who has helped keep this project headed in the right direction and who has been brave enough to let me learn many things through first hand experience. The conversations we have had are invaluable to me and are very much reflected in this thesis. His patience, understanding and thoroughness I have learned to admire greatly; I will do very well to take these characteristics into my own life and apply them as he has. Thank you Dr. Woods.

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## Chapter I. THE HALL EFFECT

**I.1 The Hall Effect:** The Hall effect was discovered in 1879 by E.H. Hall as he was investigating the effect of a magnetic field on electronic conduction. While investigating the effects of a transverse field on a current passing through a gold foil Hall observed that an electric field was set up in the foil that was perpendicular to both the applied field and the supplied current; the field was called the Hall field. Upon further investigation Hall also discovered that the field was proportional to the supplied current as well as the magnetic field strength.

Consider a sample of metal with a current  $I$  flowing through it, as well as a magnetic field  $H$  applied in a direction which is perpendicular to  $I$  and at right angles to the surface (see fig 1.1). In a metal the current will be carried by electrons with a charge  $-e$ , and these charge carriers will travel with an average drift velocity. This drift velocity  $V_d$  will be given by,

$$I = n_e dt e V_d$$

$$\text{or } e V_d = I / n_e dt \quad \text{eq. 1.1}$$

where the density of current carriers in the material is given by  $n_e$  (carriers per unit volume) and the sample has a cross sectional area of  $td$ . For a charged particle travelling in a magnetic field there will be

## Hall effect setup

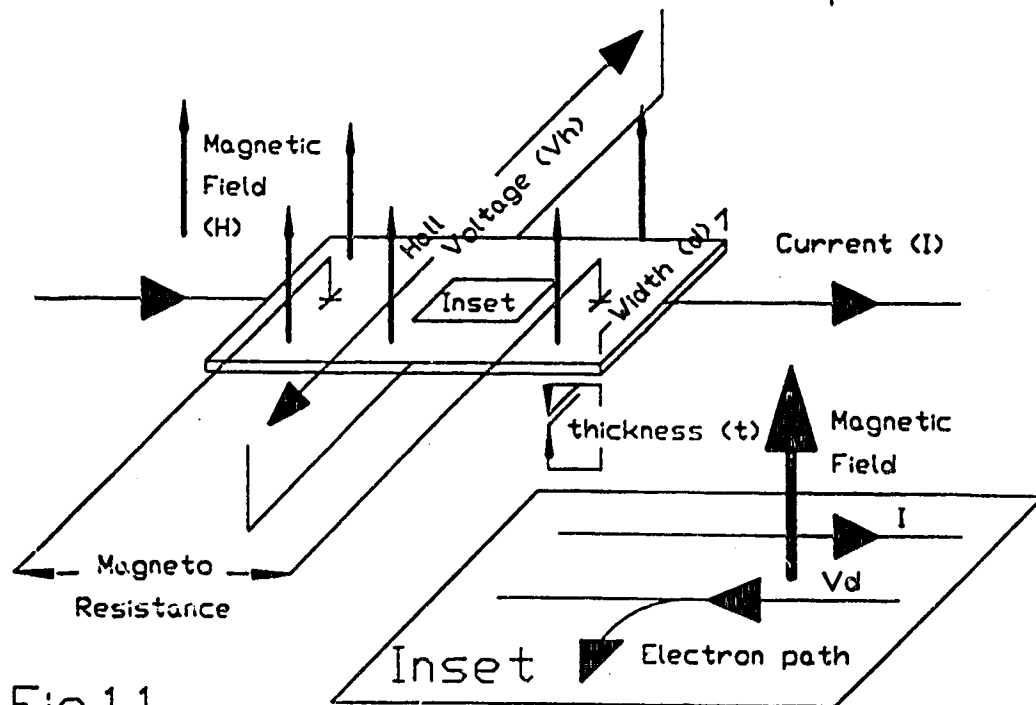


Fig.1.1

Fig 1.1: The standard method of measuring the Hall voltage and the magneto resistance for a rectangular specimen. The supplied sample current flows perpendicular to the applied magnetic field; this generates a Hall voltage across the sample and can be measured across the Hall leads shown in the diagram.

a Lorentz force associated with its motion; this force (in cgs units) will be given by,

$$\mathbf{F}_1 = -e\mathbf{V}_d \times \mathbf{H} \quad \text{eq. 1.2}$$

where  $\mathbf{F}_1$  is the Lorentz force on the electron,  $e$  is the charge of the electron, and  $\mathbf{H}$  is the magnetic field seen by the electron.

Substituting 1.2 into 1.1 we get,

$$\mathbf{F}_1 = I \times \mathbf{H} / n_0 d t \quad \text{eq. 1.3}$$

The electrons will be deflected toward the front surface of the material thus setting up a charge separation. This charge separation will create a transverse electric field  $\mathbf{E}_h$ , called the Hall field. When the charge separation satisfies

$$-e\mathbf{E}_h = \mathbf{F}_1 \quad \text{eq. 1.4}$$

then using eq.1.3 we get,

$$\mathbf{E}_h = I \times \mathbf{H} / t n_0 e d \quad \text{eq. 1.5}$$

At this point no further charge separation will occur and the electrons will flow undeflected through the material. Across the sample a Hall voltage ( $V_h$ ) can be measured where  $V_h = d |\mathbf{E}_h|$  where  $d$  is the distance over which  $\mathbf{E}_h$  (the Hall field) is measured. Therefore the Hall voltage is given by,

$$V_h = |I \times \mathbf{H}| / t n_0 e \quad \text{eq. 1.6}$$

We can see from this free electron case, that the Hall voltage will be proportional to both field strength and applied current. This is the simplest case of the Hall effect and from this the Hall coefficient ( $R_h$ ) can be defined by,

$$V_h = R_h |I \times H| / t \quad \text{eq. 1.7}$$

So in the free electron case the Hall coefficient will be given by,

$$R_h = 1/n_e e \quad \text{eq. 1.8}$$

In addition to the Hall coefficient it is common to define two other coefficients as well. The first is the Hall mobility  $\mu_h$  which is defined by,

$$\mu_h = R_h \sigma \quad \text{eq. 1.9}$$

where  $\sigma$  is the electrical conductivity. Another commonly defined quantity is the Hall resistivity ( $\rho_h$ ), which is given by,

$$\rho_h = R_h |H| \quad \text{or} \quad \rho_h = V_h / |I| \quad \text{eq. 1.10}$$

provided that  $I$  and  $H$  are orthogonal to one another. Because  $\rho_h$  does not assume a linear relationship of the Hall voltage with respect to the applied field it is common to use the coefficient  $\rho_h$  in cases where the Hall voltage is nonlinear with respect to the applied field.

The question is how can a nonlinear response of  $V_h$  as a function of applied magnetic field be explained? Here there are a few options. For a single band of carriers any effect that will influence the linearity of the Hall voltage will have to be an antisymmetric function of the applied field, ie. the application of a field will cause the current carriers to be scattered preferentially in one direction; any scattering that has a preferential direction of scatter is called skew scattering. This occurs frequently when magnetic ordering is present. Consequently, without any skew scattering the Hall coefficient has to be linear with respect to field. Antisymmetric (or skew) contributions

can originate in many different ways, spin-orbit coupling and other contributions to skew scattering are treated in an article by HURD [1].

**1.2 The Low Field Limit:** There are however many complications to consider in going to a real material from the ideal free electron model. For this reason it is important to look at a limiting case which should be the only limit we have to consider when working with High Temperature Superconductors (HTSC).

The low field limit is the limit where  $w_c$ , the cyclotron frequency of a current carrier in an applied magnetic field, and  $\tau$  the relaxation time of the current carriers satisfy the relation,

$$w_c \tau < 1. \quad \text{eq. 1.11}$$

In this limit the current carrier undergoes many collisions before it can complete one revolution of its cyclotronic orbit. This condition is generally satisfied in measurements done at high temperature (where the probability of undergoing phonon scattering is large) or in samples that have a large number of impurities or lattice imperfections.

The HTSC's are ceramics. The term ceramic itself refers to a material that has no long range crystal structure. At temperatures above 35K where all the HTSC's are superconducting the low field limit is satisfied in fields of a few kilogauss or less.

The low field limit can be theoretically determined (as done by HURD [2]) by starting with the Boltzmann equation. Under isothermal conditions with applied electric field ( $\mathbf{E}$ ) and magnetic field ( $\mathbf{H}$ ) the equation becomes,

$$(2\pi\hbar)\{\mathbf{E}+(\mathbf{v}\times\mathbf{H})/c\} \Delta_{\mathbf{k}}(f) = -(f(\mathbf{k}) - f_0(\mathbf{k}))/\tau(\mathbf{k}) \quad \text{eq. 1.12}$$

Where  $\mathbf{v}$  is the velocity of the charge carrier (ie. the Fermi velocity),  $c$  is the speed of light,  $f(\mathbf{k})$  is the number of carriers in the state defined by the wave vector  $\mathbf{k}$ , and  $\tau(\mathbf{k})$  is the relaxation time. Starting from this point one can solve for the various components of the current density  $\mathbf{J}$ . Assuming that the density of states is  $1/4\pi^3$ ,  $\mathbf{J}$  will be given by

$$\mathbf{J} = (e/4\pi^3) \int \mathbf{v}f(\mathbf{k})d\mathbf{k} = (e/2\pi^2\hbar) \int \Delta_{\mathbf{k}}\epsilon g(\mathbf{v})d\mathbf{k} \quad \text{eq. 1.13}$$

Given the various terms for  $g(\mathbf{v})$  and assuming that the material has cubic symmetry<sup>1</sup>, the terms for  $g(\mathbf{v})$  can be substituted into 1.11 to give

$$J_x = \sigma_0 E_x + \sigma_H (E_y H_z - E_z H_y) - TE_x H^2 + \rho H_x (\mathbf{E} \cdot \mathbf{H}) + \epsilon E_x E_y \quad \text{eq. 1.14}$$

Using the standard Hall configuration  $\mathbf{J} = (J_x, 0, 0)$ ,  $\mathbf{H} = (0, 0, H_z)$ ,  $\mathbf{E} = (E_x, E_y, 0)$  then Hurd [2] writes,

$$R_H = \sigma_H / \sigma_0^2$$

where  $\sigma_0 = -2e^2/\pi\hbar^2 \int \tau(\mathbf{k})(d\epsilon/dk_x) 2df_0/d\epsilon dk$  eq. 1.15

and  $\sigma_H = -4\pi e^3/\hbar^4 c \int \tau(\mathbf{k})(d\epsilon/dk_x) \Omega_z \tau(\mathbf{k})(d\epsilon/dk_y) df_0/d\epsilon dk$

where we have defined  $\Omega_{\mathbf{k}} = \Delta_{\mathbf{k}} \epsilon \Delta_{\mathbf{k}}$

---

<sup>1</sup>Although for the HTSC's this seems to be a poor assumption due to the large asymmetries in the lattice constants we will maintain this assumption for this discussion.

If the relaxation time  $\tau(\mathbf{k})$  is isotropic then we can write,

$$\sigma_0 = \frac{e^2}{6\pi^2\hbar} \int \tau v ds \quad \text{eq. 1.16}$$

If we define  $\Gamma$  to be the average curvature of the Fermi surface then it is possible to write  $R_h$  as,

$$R_h = (12\pi^3 / ce) \left\{ \int v^2 \Gamma ds \right\} / \left\{ \int v ds \right\}^2 \quad \text{eq. 1.17}$$

Upon inspection of eq. 1.17 it would seem that for a metal,  $R_h$  should be independent of the temperature. As shown later this is not the case and in order to explain a rapid temperature dependence we must introduce a more complicated model.

**The Two Band Model:** The next step in considering real materials is to no longer be limited to just one band of carriers but to expand this to two non-interacting bands of carriers. The two band model was originally intended for, and probably most accurately describes semiconductors; however in attempting to understand the Hall effect this model has been applied to many classes of material. A two band model has been used to qualitatively fit much of the experimental data on the HTSC's.

Details of the two band model are as follows.

- each band has its own characteristics; mobility, effective mass, etc.



-interband transitions are forbidden.

-no transitions between the bands are allowed so that their effects are simply additive<sup>2</sup>.

One of the major difficulties with this model is that it introduces enough arbitrary constants to describe almost any behaviour. This may account for its application to most materials. In the treatment done by Hurd [2] two spherical Fermi surfaces are treated. Sheet 1 is characterized by a carrier density of  $n_1$ , a charge  $e$ , effective mass  $m_1$ ; sheet 2 is defined similarly. For each sheet the magneto-conductivity can be completely described by a magneto-conductivity tensor given by

$$\sigma_{ij} = \frac{\sigma_0}{1 + \omega_c^2 \tau^2} \begin{bmatrix} 1 & \omega_c \tau & 0 \\ -\omega_c \tau & 1 & 0 \\ 0 & 0 & 1 + \omega_c^2 \tau^2 \end{bmatrix} \quad \text{eq. 1.16}$$

Intuitively with the rules for a two band model the full conductivity tensor for two bands is simply,

$$\sigma_{ij} = \frac{\sigma_1}{1 + \gamma_1^2} \begin{bmatrix} 1 & \gamma_1 & 0 \\ -\gamma_1 & 1 & 0 \\ 0 & 0 & 1 + \gamma_1^2 \end{bmatrix} + \frac{\sigma_2}{1 + \gamma_2^2} \begin{bmatrix} 1 & \gamma_2 & 0 \\ -\gamma_2 & 1 & 0 \\ 0 & 0 & 1 + \gamma_2^2 \end{bmatrix} \quad \text{eq. 1.17}$$

where  $\gamma_i = g_i = \omega_c \tau_i$ , and  $\sigma_i = n_i e_i^2 \tau_i / m_i$  is the conductivity for the  $i$ th band. If the conductivity tensor is inverted to give the resistivity tensor

---

<sup>2</sup>The details of the two band model are probably far from reality for all but a few materials. However, the model itself is a valuable tool in explaining many phenomena.

(p) then it can be shown that the Hall coefficient is given by [2],

$$R_h = \{\rho_{yx}(\mathbf{H}) - \rho_{xy}(\mathbf{H})\} / 2H \quad \text{eq. 1.18}$$

Inverting the conductivity tensor and solving for  $R_h$  gives,

$$R_h = (1/H) \{Ag_1 + Bg_2\} \{(A+B)^2 + (Ag_1 + Bg_2)^2\}^{-1} \quad \text{eq. 1.19}$$

where  $A = \sigma_1 / (1 + g_1^2)$  and  $B = \sigma_2 / (1 + g_2^2)$

It is most common to consider a band of holes and a band of electrons. If we also impose the low field limit and keep the leading terms we get only,

$$R_h = 1 / (\sigma_o^2 \theta) \{ \sigma_h^2 / n_h - \sigma_o^2 / n_o \} \quad \text{eq. 1.20}$$

Defining a new effective number of carriers  $N'$  so that when we write out  $R_h$  we get back to our free electron model.

If  $1/N' = 1/\sigma_o^2 \{ \sigma_h^2 / n_h - \sigma_o^2 / n_o \}$  then  $R_h = 1/N'e$  eq. 1.21

One thing to notice now is that the Hall coefficient depends on the conductivities of the two bands, so that if these have a temperature dependence we would expect the Hall voltage to also vary with temperature.

Before we can proceed there is another factor to consider. We have only considered single crystals, but the HTSC's we have analyzed in this experiment are polycrystalline and may be considered to be a random ordering of small crystallites. Most commonly this is accomplished by saying that the measured Hall coefficient is the average over all orientations of a crystal, yet it is important to examine this further.

**The Hall Effect In Polycrystal:** The Hall effect for a polycrystal can vary considerably from the average over all orientations of the single crystal. In an article by Xia and Stroud [3], a determination of the low field component of the Hall effect is suggested. The reader is referred to that article for a thorough treatment. Here we will consider only an outline of the treatment.

Starting with the conductivity tensor for the single crystal  $\sigma$  can be written as the sum of a symmetric ( $\sigma_s$ ) and an antisymmetric tensor ( $\sigma_a$ ).

$$\sigma = \sigma_s + \sigma_a \quad \text{eq. 1.22}$$

Defining a particular direction to be the reference, say the normal to one side of the sample, the most natural way to describe a grain which is oriented differently is to say that from the reference direction the grain has been rotated. This rotation can be described by a unitary transformation  $\mathbf{R}$ , so that the new symmetric and asymmetric tensors for that grain with respect to the reference direction are given by,

$$\sigma_s' = \mathbf{R}^{-1} \sigma_s \mathbf{R} \quad \text{and} \quad \sigma_a' = \mathbf{R}^{-1} \sigma_a \mathbf{R} \quad \text{eq. 1.23}$$

At this point we must assume that the  $\sigma_a$  and  $\sigma_s$  commute in order to solve the equation for  $\mathbf{R}$ . Xia *et al* gives no proof and states only that it is a good assumption. Assuming that the crystallites are

spherical in symmetry<sup>3</sup> one can sum all of the conductivity tensors over all orientations. Once the low field condition is imposed Xia [3] gets that for a single conduction band  $R_h$  is given by,

$$R_h = g_0 / \sigma_0^2 \quad \text{eq. 1.24}$$

where  $g_0$  and  $\sigma_0$  are approximated by,

$$\begin{aligned} \sigma_{ii} &= n_i q_i^2 \tau_i / m_i \\ \sigma_0 &\approx \sigma_x / 2 \\ g_0 &\approx \sigma_{xx} \sigma_{yy} / 5nq \end{aligned} \quad \text{eq. 1.25}$$

The authors then go on to treat the material for the two band model and get the following expression for the Hall coefficient,

$$R_h = 4 / (5n_h e c) \{ 1 - n_0 Q_x^2 / n_h \} / \{ 1 + n_0 Q_x / n_h \}^2 [ 1 + 4m_{hx} / m_{hz} \{ 1 - n_0 Q_x Q_z / n_h \} / \{ 1 - n_0 Q_x^2 / n_h \} ]$$

$$\text{where } Q_i = \mu_0 / \mu_{hi} \quad \text{eq. 1.26}$$

From equation 1.26 we see that the Hall coefficient depends on the ratios of the mobilities ( $Q_i$ ), the concentrations of carriers in the material ( $n_h$  and  $n_0$ ), as well as the effective masses of the carriers for the various crystal directions.

---

<sup>3</sup>This assumption is made to simplify the calculations. Even if this were far from true the result would not change considerably.

## Chapter II. THE 1-2-3 COMPOUND

**II.1 The Resistance:** Not only does a superconducting material show zero electrical resistance below  $T_c$ , its superconducting transition temperature, but it exhibits the Meissner effect as well. That is, in sufficiently small magnetic fields, it expels the magnetic flux completely. In this section we will take a brief look at the resistance for the HTSC's as well as the implications that this has for the Hall effect.

In general the resistance curve for a 1-2-3 superconductor is of the form shown in figure 2.1. In a metal the important collision processes experienced by the conduction electrons may be considered to act independently. The temperature independent scattering probability by impurities may be written as  $\tau_o^{-1}$  and that by phonons  $\tau_{ph}^{-1}$ .

Then when both are present,

$$\tau^{-1} = \tau_o^{-1} + \tau_{ph}^{-1} \quad \text{eq. 2.1}$$

and the resistance can be written as,

$$r = r_o + r_{ph} \quad \text{eq. 2.2}$$

if  $\tau_{ph}^{-1} = BT$  then the resistance will be described by,

$$r = r_o + BT \quad \text{eq. 2.3}$$

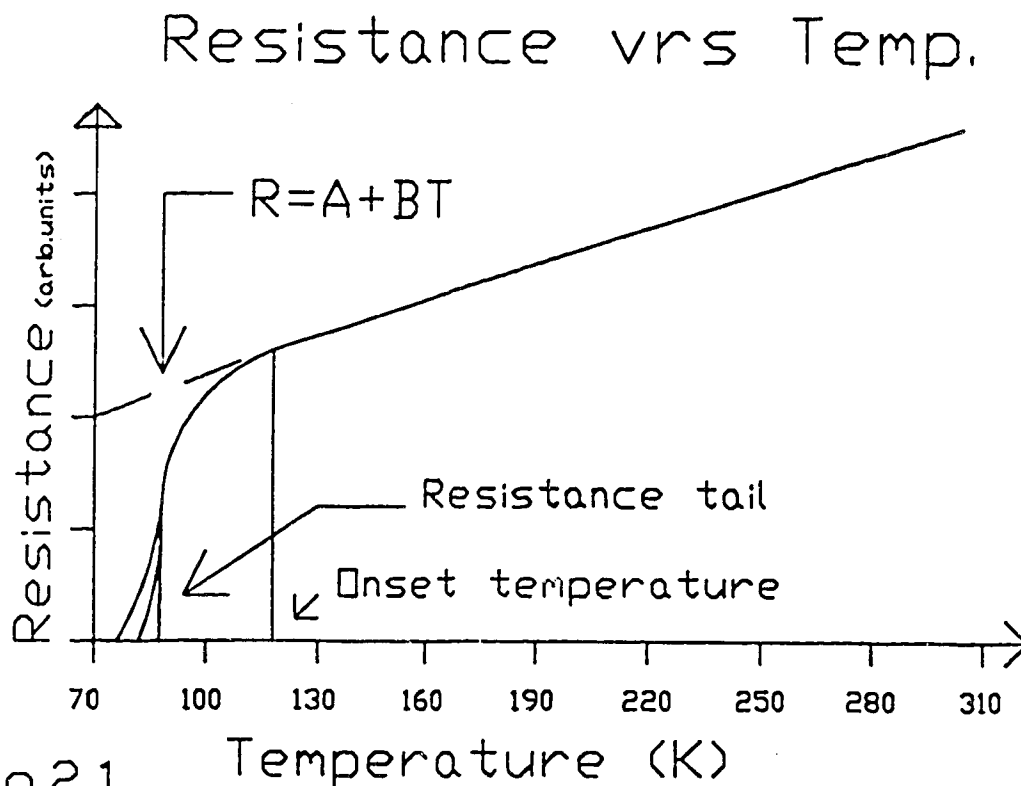


Fig.2.1

Fig 2.1: A typical resistance as a function of temperature curve for a sample of 1-2-3 compound is modelled<sup>4</sup> here.

---

<sup>4</sup>The figures shown in this chapter are not actual plots of data but only an artist's representation of actual data.

Since metals near room temperature are characterized by a linear dependence of resistance on temperature this separation of resistance ( $r$ ) into two parts is well established. The constant in the resistance  $R$  can occur from any temperature independent scattering, such as scattering by point defects (if the impurities have a strong magnetic moment then impurity scattering can show  $T$  dependence in certain temperature ranges). The  $1/T$  dependence in the conductivity is attributed to phonon scattering. Since the number of phonon modes at high temperatures (where  $hw/kT \ll 1$ ) in a metal is proportional to  $T$ , then the inverse of the scattering probability will be  $\propto T^{-1}$ . The fact that  $R=A+BT$  indicates that we do have a metal, or at least a metallic-like material.

What does the resistance tell us about the relaxation time  $\tau_e(\mathbf{k})$ <sup>5</sup>, which is very important in the interpretation of the Hall effect? If  $\tau_e(\mathbf{k})$  can be approximated as a well defined constant  $\tau_e$ , where  $\tau_e$  is the average of  $\tau_e(\mathbf{k})$  over all  $\mathbf{k}$  states, then using the macroscopic definition of the resistivity,  $\rho$ , we know that  $\rho$  is given by,

$$\rho^{-1} = \sigma = e^2 n_e \tau_e / m_e \quad \text{eq. 2.4}$$

where  $\sigma$  is the conductivity,  $e$  is the charge of the electron,  $n_e$  is the density of electrons per unit volume, and  $m_e$  is the effective mass of the electron. This is for a single band which can be expanded to two

---

<sup>5</sup>The  $e$  in  $\tau_e(\mathbf{k})$  indicates that we are referring to the electron relaxation time,  $h$  will be replaced when we are talking explicitly about holes and  $i$  will be used for cases that apply to either.

independent bands yielding,

$$\sigma = e^2 \left\{ n_e \tau_e / m_e^* + n_h \tau_h / m_h^* \right\} \quad \text{eq. 2.5}$$

Since  $m^*$  depends on the second derivative of  $E(k)$  with respect to the wave vector  $k$ , and we are dealing with a metallic like material in which  $n_i$  is not likely to be affected much by a change in temperature, we may consider  $n_i$  and  $m_i^*$  to contribute a negligible amount to the temperature dependence of  $\rho$ . So all the  $T$  dependence of the resistivity must come from  $\tau_e$  and  $\tau_h$ . Since both the electrons and the holes are in the same material we expect each to produce similar temperature behaviour. From an examination of eq. 2.1,  $\tau_e$  and  $\tau_h$  can be approximated by,

$$\tau_e^{-1} = \tau_{e0}^{-1} + B_e T \quad \text{and} \quad \tau_h^{-1} = \tau_{h0}^{-1} + B_h T \quad \text{eq. 2.6}$$

and we see that

$$\rho = a + bT \quad \text{eq. 2.7}$$

Where

$$a = e^2 \left\{ n_e a_e b / m_e^* + n_h a_h b / m_h^* \right\}$$

and

$$b = e^2 \left\{ n_e b_e / m_e^* + n_h b_h / m_h^* \right\}$$

Consider the relaxation times to be represented by a power law expansion in  $T^{-1}$  then we can write both  $\tau_e + \tau_h$  like eq 2.6. This is the simplest assumption we can make when neglecting terms of  $1/T^2$  and smaller. These contributions are negligible since the resistance shows no  $T^2$  behaviour.

---

<sup>9</sup>Here we have chosen to treat a band of holes along with a band of electrons, in a metal we would expect only to have to deal with electrons; however in the HTSCs the majority carriers at room temperature are holes.



It is simple to determine a and b empirically from the resistance data by noting that

$$\rho = a + bT = \rho_o + \rho_{ph}$$

and

$$\rho_o = a \text{ and } \rho_{ph} = bT$$

These will be important parameters when attempting to interpret any Hall effect data. The resistivity "tail" will be discussed in the section on Granular Superconductivity.

**II.2 The Hall Effect:** The Hall Effect in the pure 1-2-3 material has been measured by many groups [4-7]; from room temperature to about 100K. All the results are somewhat similar. The basic Hall Effect is as shown in fig. 2.2. From room temperature to about 100°K the Hall effect increases as 1/T. At about 100K the Hall voltage goes through a maximum and then begins to plunge. A few of the articles only display their data to temperatures just above the maximum in the Hall voltage.

Any experiments to date that have gone below the maximum in the Hall Voltage (to see if it goes to zero as it should) have measured a behaviour like that shown in fig. 2.3. Instead of going exponentially to zero, as BCS theory predicts, the measured Hall voltage goes through a negative minimum that has an absolute magnitude of 2 to 5

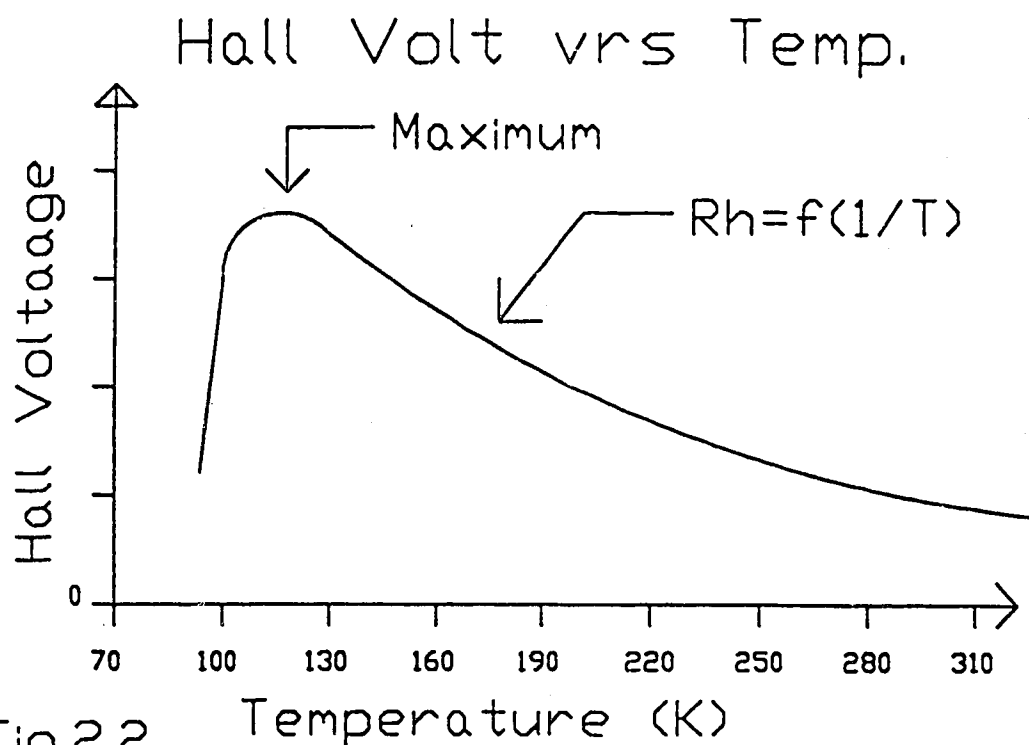


Fig.2.2

Fig 2.2: A model of the Hall voltage, as a function of temperature, above onset for the 1-2-3 compound is shown here. This curve has been measured by different groups [8,10,13,15] and is claimed by all to obey a Temperature<sup>-1</sup> relation.

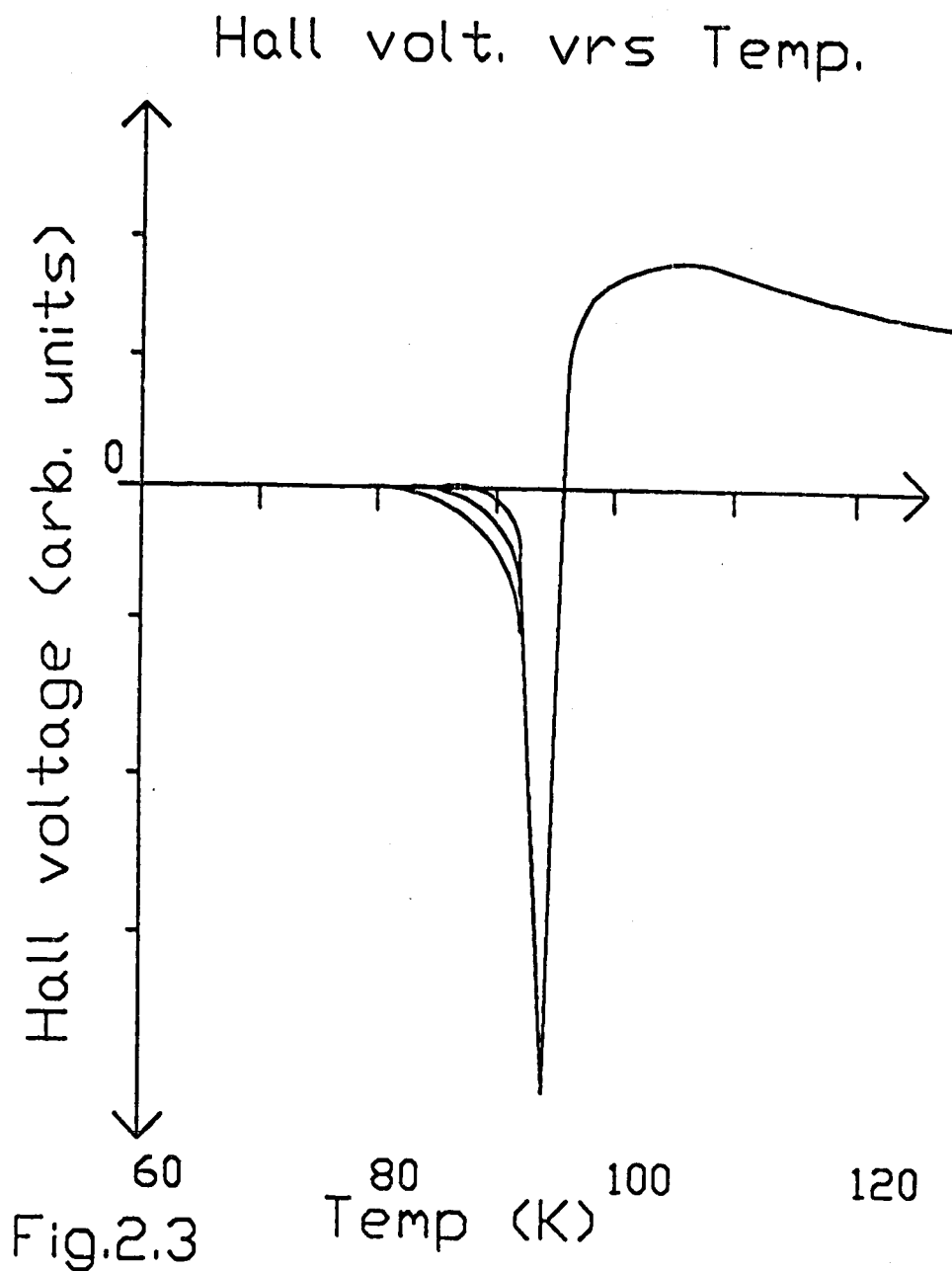


Fig 2.3: The Hall voltage below onset has only been measured by a few groups [10,13]. Some experimentalists have not seen such behaviour in their samples of 1-2-3 compound [15]. Our experiment has shown this to be the behaviour for our sample of 1-2-3 compound.

times the maximum in the Hall voltage. Until Galffy and Zirngiebl's article [7], nothing had really been done to investigate this phenomenon. From experiments, the Hall voltage at room temperature and at the trailing edge of the maximum in the Hall Voltage was found to be perfectly linear with the applied magnetic field and so a well defined Hall coefficient could be calculated.

The problem with measuring Hall Voltage just below the maximum is that the sample undergoes a normal to superconductive phase transition. This alone makes it very difficult to get good Hall data because complete isothermal conditions are necessary to minimize the thermal oscillations in the sample's resistance. On top of this the resistance in this region is very sensitive to the applied magnetic field; reversing the field could generate extraneous voltages. Later in the experiments it was found that below the maximum the Hall voltage is no longer linear in the applied magnetic field. These complications make the existence of a large negative spike, precisely located at the maximum rate of change or  $R(T)$  in some experiments, very questionable.

An early article that deals with an explanation of this "anomaly" was by Galffy and Zirngiebl [7]. Some of their results have been modelled in fig. 2.4. Using a 5 Tesla magnet, they measured the Hall Resistivity at different temperatures and as a function of magnetic field. They found that the Hall resistivity does include a notable negative contribution. From these results it is obvious that a large negative

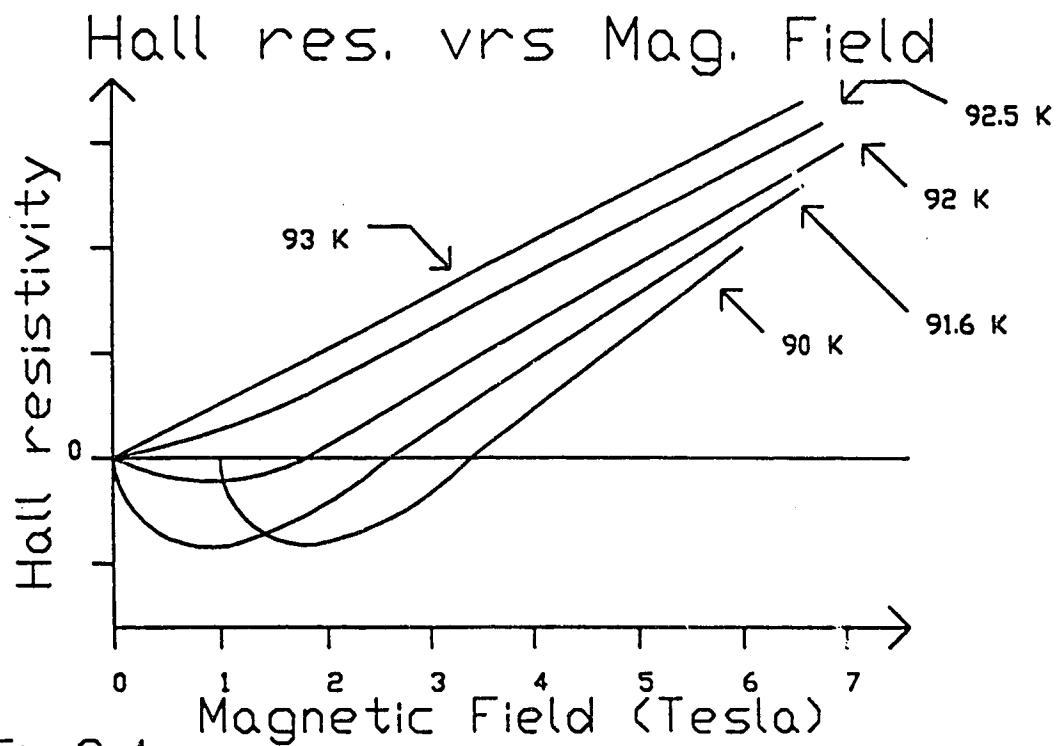


Fig.2.4

Fig 2.4: A model of the Hall resistivity that has been measured by Galffy and Zirngiebl in reference 13. It shows that the Hall voltage is non-linear with applied field and so a Hall coefficient can not be defined here.

spike (depending on the applied field) could be apparent in the Hall Voltage, and failing to check for linearity in the results could lead to a misinterpretation of the Hall Coefficient.

One article gives Hall coefficients which differ by a factor of 100 in magnitude from the usual values [4]. Several claim  $1/T$  dependence in Hall Voltage with few data points while by close inspection their data could be fitted to a linear temperature dependence [5] (modelled by A-BT).

**II.3 The Magneto-resistance:** The experimentalists have been unable to detect a magneto-resistance in magnetic fields up to 7 Tesla for all electrical currents and measuring to  $1 \times 10^{-9} \text{V}$  in the temperature range of 100K to 300K. The transverse component of the magneto resistance is given by the change in resistance along the direction of the current with a magnetic field directed perpendicular to the current. See fig. 1.1.

It is known that an applied field reduces the Critical Temperature by increasing the resistance, therefore the magneto-resistance should

be a positive function of the applied field<sup>7</sup>. In the experiment of Galffy *et al* [7] there appears to be a negative Hall Voltage generated in the sample. Sample inhomogeneity and the large magneto-resistance that is observed in the transition region [8] may account for these results. In these circumstances even a small change in magnetic field could produce a signal. No matter how the field is reversed, there is still the possibility of extraneous voltages, due to small field variations, which may mimic the Hall effect.

The solution would be to have a superconducting solenoid and after taking one set of Hall Voltage measurements, reverse the current in the magnet. This will reverse the direction but reproduce the magnitude of the field<sup>8</sup>. By taking data in the same way again magneto-resistant effects will remain the same, while the Hall effects will be reversed.

If there is a negative Hall Voltage, what does this mean? Simply it would guarantee that we have two active bands with charge carriers of opposite signs, and it would also indicate that the band of holes goes superconducting first! This would be important to know,

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<sup>7</sup>This is not true for several materials which become superconducting in an applied magnetic field, and are normal without the field applied. These special cases have been called re-entrant superconductors and are very rare.

<sup>8</sup>A superconducting solenoid would eliminate all the problems that occur because of hysteresis in a magnetic core.

but as yet it is only a conjecture.

**II.4 Granular Superconductivity:** It has been a challenge to produce a model that would explain some of the effects seen with High Temperature Superconductors (HTSC). The model must explain most of the phenomena discussed so far. The resistance tail and the onset temperature shown in fig 2.1 are characteristic of high  $T_c$  materials. A model with superconducting grains  $\sim 10^{-3}$  cm across and separated by intergranular material  $\sim 10^{-4}$  cm thick has been used successfully to account for this behaviour. Granular superconductors can be pictured in two dimensions as shown in fig. 2.5. The grains, because of the range in their size and possibly other characteristics, will have a small range (a few Kelvins) of  $T_c$ . The intergranular material {IGM} could be a semiconductor, or an insulator. If the IGM were an insulator the material could not have a linear resistance as a function of temperature as experiments indicate; therefore we only consider the alternative. Obviously, if the IGM is a semiconductor then for the resistivity to vary linearly with temperature the IGM must occupy a small portion of the sample volume.

Once the temperature is dropped below the onset temperature some of the grains will become superconducting, and the current



## A Granular Superconductor

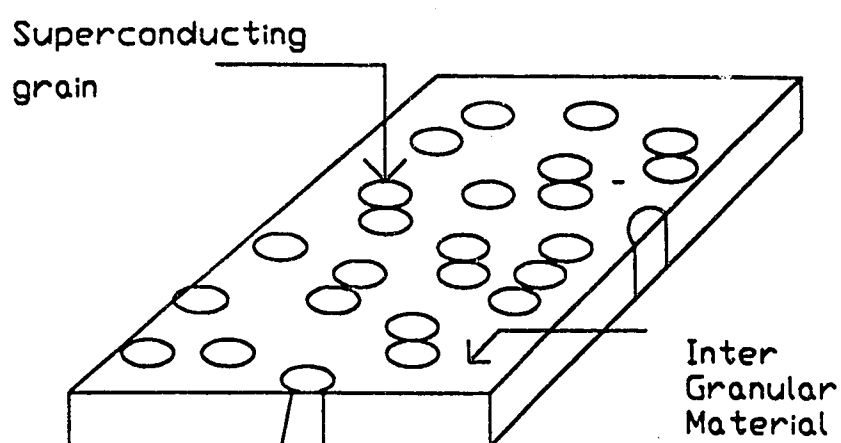


Fig.2.5

Fig 2.5: An artists rendition of a granular superconductor. For Josephson tunnelling between the superconducting grains to occur in these high  $T_c$  superconductors the gap between these superconducting grains must be of the order of  $10^{-5}$ cm and the inter granular material must be a semiconductor. carriers will trace the lowest resistive path

through the sample. Under mutual repulsion the carriers will spread throughout the material. The coherence length of the Cooper pairs will increase as the temperature is lowered, and when the temperature is reduced to the point where the resistance is zero then the coherence length ( $\Gamma$ ) is of the order of the width of the IGM barriers and so the pairs can then tunnel across the barrier without any net change in energy. As the sample current is increased, at some point the tunnelling mechanism will not be able to carry all the current carriers across the boundaries, and mutual repulsion will eventually make it energetically favourable for some carriers to travel within the IGM<sup>9</sup>.

Another way of looking at the critical current is to consider that for each pair there is a finite probability of completing one tunnelling event. If then we have a finite number of grains as well as a finite carrier density in these grains, there must be a maximum number of carriers per unit time that can be transported via tunnelling. Any number of carriers per unit time above this will be forced to become normal.

The resistivity "tail" can also be accounted for by supposing that some of the "weak" links (links between grains via the IGM) can be weaker than others. The largest boundaries will have a non-zero resistance until the temperature is low enough for the pairs to tunnel through. Evidence indicates that this "tail" is preparation dependant.

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<sup>9</sup>The current at which this occurs is known as the critical current for superconductivity.

The Granular Superconductor model may be used to help explain the Hall effect. With two phases of material in the High Temperature Superconductor, two distinct bands of carriers may be expected. The negative minimum in the Hall voltage below the onset temperature then could be explained because the two carriers need not go superconducting simultaneously. Once the holes disappear by becoming superconducting there could be a small number of electrons left over. When the current is increased beyond the critical current these leftover electrons should be recovered first, which would yield a negative Hall coefficient.

## Chapter III: The experiment

**III.1 Apparatus:** The Hall effect measurements were done using the standard four probe method (see figure 1.1). The sample current was regulated using a Lakeshore Instruments constant current supply. The regulation was found to be better than 0.1% for the currents used in the experiment (10-50 mA). This was determined by measuring the voltage drop across a standard resistor. The cryogenic apparatus consisted of a narrow tailed glass dewar (see figure 3.1) capable of containing LN<sub>2</sub> for a period of greater than twelve hours. The narrow tail was to allow pole separations as small as 10cm for the electromagnet in order to attain greater magnetic fields in the sample volume. The cryostat consisted of a two vacuum can system. The outer can was evacuated and the inner can was filled with helium gas to a pressure of one atmosphere. The sample could be rotated around the vertical axis, which permitted quick field reversals as well as eliminating the problems of hysteresis.

The magnetic field was applied using a ESI magnet powered by a Lambda LB-702 15 Volt 180 Amp DC regulated power supply. The magnet had an iron core that yielded a substantial field strength. This

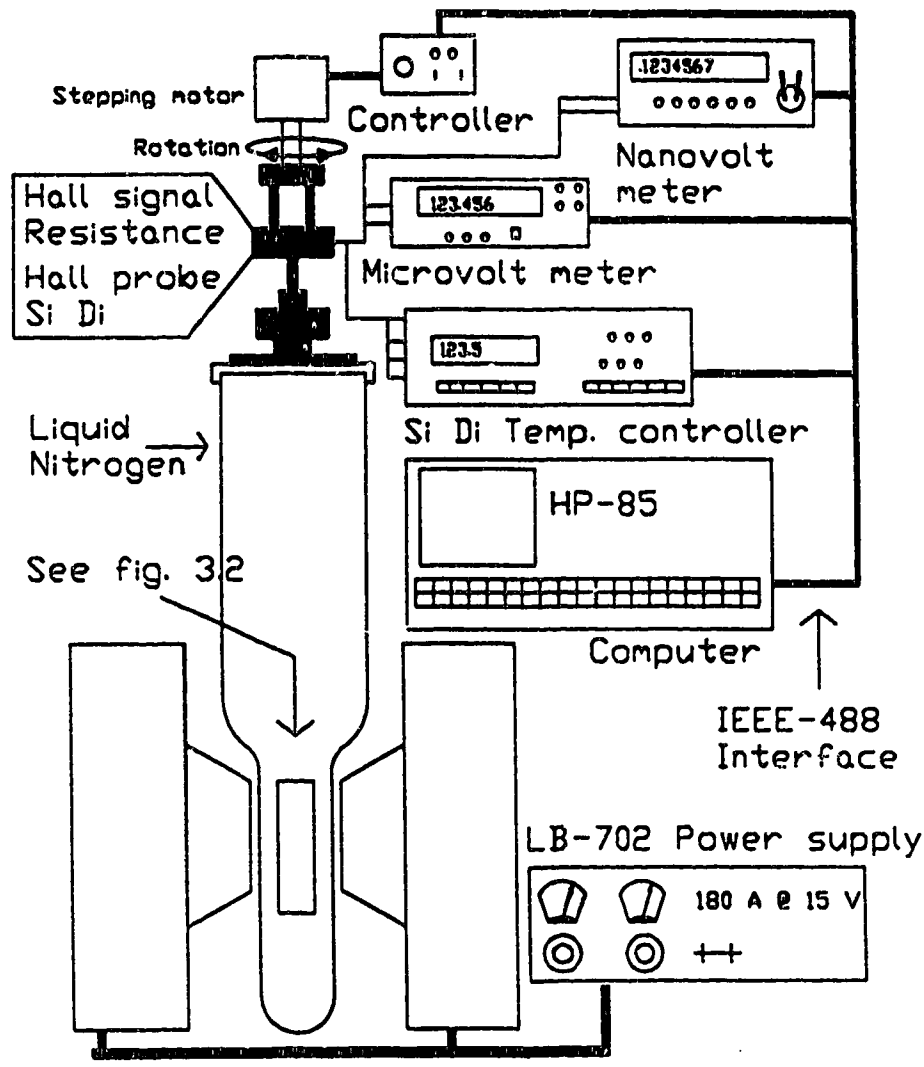


Fig 3.1: The Hall effect experiment as of December 1988.

lead to some significant problems as will be described later. The power supply was regulated to better than 0.1% and to insure that the variation in the magnetic field were as small as possible it was left on in the same direction at the same field for the duration of each experiment. The field at the sample (see figure 3.2) was monitored using an ATT hall probe located directly behind, and in the same orientation as, the sample. This consistently showed that the applied field did not change by more than 0.1%. Originally the magnetic field at the sample site was measured using a rotating coil gauss meter that had been calibrated with a 6 kilogauss magnet used for NMR experiments, the field was precisely 4.58 KG when the magnet voltage was at 15.00 volts. The temperature of the magnet coils was kept constant by flowing water through the coils themselves.

The temperature of the sample was controlled using a Lakeshore Instruments silicon diode temperature controller. The sample, Hall probe, and the thermometer were all in contact with the same copper sample block. Heat sink compound was also employed to maintain good thermal contact. Two heaters were used to control the temperature of the sample; one was located on the sample block while the other was attached to the inner can. These heaters were balanced by attempting to minimize the thermal time constant for changing the temperature of the sample. As a further precaution the inner can was pressurized to atmospheric pressure with He gas. The specimen would then come to thermal equilibrium at a new

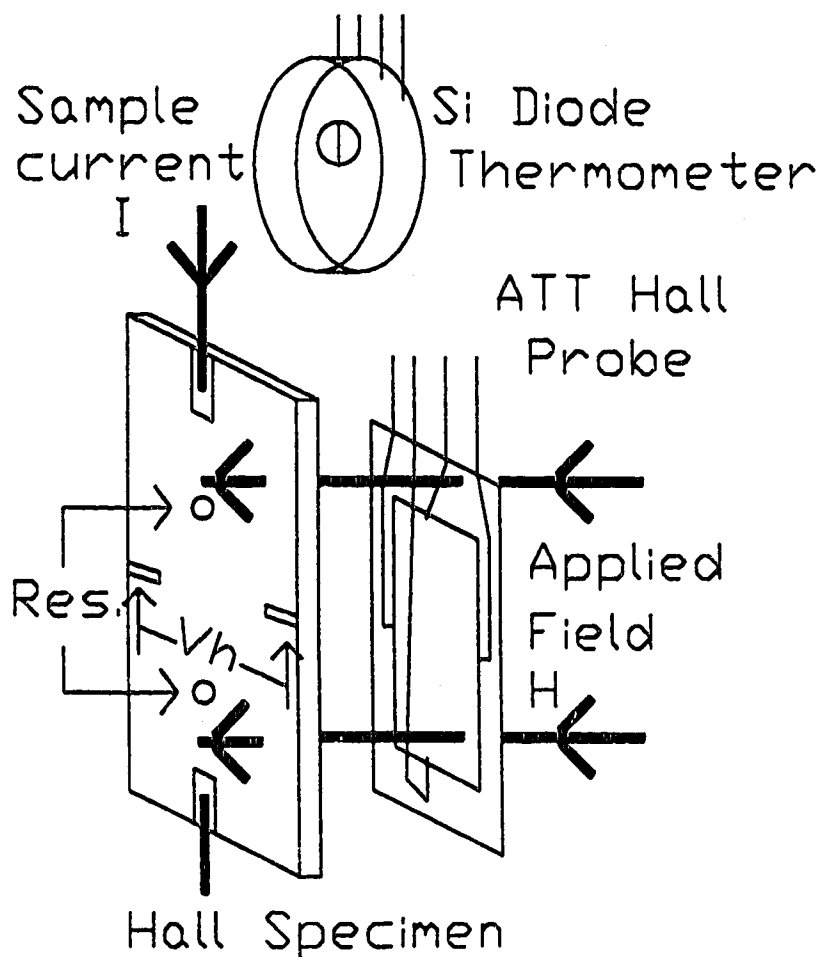


Fig. 3.2

Fig 3.2: The sample area showing the placement of the thermometer Hall probe sensor and the sample. To reverse the direction of the field during a measurement of the Hall voltage the sample is rotated through  $180^\circ$  along with the probe and thermometer.

temperature ( within 0.01 K) in a matter of minutes of changing the set temperature on the controller.

The Hall voltage was measured using a Keithley 181 nanovolt meter. An uncertainty of 20 nV was typical for one measurement of the Hall voltage. The resistance was measured using a Keithley 197 microvolt meter. The signals in this case were generally large enough that the uncertainty in the measurement was negligible. A relay was employed to allow the meter to also monitor the Hall probe that measured the field strength. To monitor the voltage across the magnet a 3.5 digit millivolt meter was used. As a result of spending 20 hours in the lab at a time a decision was made to computerize the entire experiment. This was done with an HP-85 computer equipped with an IEEE interface. The interface was compatible with the meters described, and with much help from my colleagues a parallel/serial port was built onto the IEEE bus. This permitted remote control of the motor and various relays used to perform the experiment. The program to run the experiment was optimized using an evolution approach. A detailed outline of the program and a diagram of the interface appears in appendix A.

**III.2 Sample preparation:** The samples were formed in a manner that is now standard. The basic oxide compounds were mixed in the



stoichiometrically correct proportions. The mixture was then pressed into pellets of an arbitrary thickness and a diameter which was usually 12mm. After the constituents were reacted in air at 925C for 24 hours, the pellets were crushed and again pressed into 12mm diameter pellets. These were annealed in flowing oxygen at 825C to form the superconducting (SC) tetragonal phase of the 1-2-3 compound. The SC disks were then cut to a thickness of between 0.2-0.4 mm and subsequently reannealed in O<sub>2</sub>. Using this same method samples with the chemical formula YBa<sub>2</sub>(Cu<sub>1-x</sub>Fe<sub>x</sub>)<sub>3</sub>O<sub>7-d</sub> where formed with x equal to 0.01.

The cutting was performed using an abrasive diamond wheel, which could be set to take off very thin slices of material while exerting a minimum of stress on the sample. Oxygen annealing was done to ensure that the cut surface was not oxygen-deficient.

Electrical contact with the sample was made by first evaporating pure gold contacts onto the specimens and then annealing them at 850C until the Au layer diffused into the surface of the specimen to form a strong bond. This process usually required between 8 and 12 hours of annealing. Indium could very gently be applied to these contacts for excellent electrical contact between the specimen and the copper lead wires. Several methods have been used by other groups [9-10] however I have found this method to be the most reliable.

**III.3 Measuring the Hall effect:** The signals from the Hall effect for the pure 1-2-3 material were of the order of 75-300 nV. With errors of at least 20 nV per measurement it was best to take more than one measurement and to use statistics to determine the most likely result. The voltage across the sample was measured and then the sample was rotated through 180° and the transverse voltage was again measured. If one can assume that the rotated specimen sees exactly the same field, or if the magneto-resistance due to field variation is small in comparison with the Hall voltage then the difference between these two measurements should be twice the Hall voltage of the specimen in that field. Measurement of the voltage drop across the specimen required the current be reversed. This must be taken into account when calculating the actual Hall voltage. A mathematical summary is given below.

For any single measurement of the transverse voltage, denoted  $V_h$  in fig 3.2, the measured voltage will have both a Hall contribution  $V_h(\mathbf{H},\mathbf{I})$  and a misalignment contribution  $V_m(R(\mathbf{H}),\mathbf{I})$ , and the measured voltage  $V(\mathbf{H},\mathbf{I})$  is given by,

$$V(\mathbf{H},\mathbf{I})=V_h(\mathbf{H},\mathbf{I})+V_m(R(\mathbf{H}),\mathbf{I})+V_o \quad \text{eq. 3.1}$$

$R(\mathbf{H})$  is the resistance and  $V_o$  is the voltage from any offset potentials in the system, such as a thermal voltage in the leads.  $R(\mathbf{H})$  assumes that there may be a non-zero magneto-resistance; this magneto-

resistance for a polycrystal is a function of the magnitude of the applied field only.

Reversing the current will enable us to eliminate  $V_o$  and we will get,

$$V(H,-I) = V_h(H,-I) + V_m(R(H),-I) + V_o \quad \text{eq. 3.2}$$

Assuming that both  $V_h$  and  $V_m$  are even functions of  $I$  and subtracting 3.2 from 3.1 gives,

$$V(H,I) - V(H,-I) = 2V_h(H,I) + 2V_m(R(H),I) \quad \text{eq. 3.3}$$

Repeating the same procedure with the field reversed,

$$V(-H,I) - V(-H,-I) = -2V_h(H,I) + 2V_m(R(H),I) \quad \text{eq. 3.4}$$

Subtracting 3.4 from 3.3 gives the result,

$$\{V(H,I) - V(H,-I)\} - \{V(-H,I) - V(-H,-I)\} = 4V_h(H,I) \quad \text{eq. 3.5}$$

Using these reversal methods it is possible to measure the Hall voltage accurately and reproducibly.

## Chapter IV. THE DATA

**IV.1 The Hall data for 1-2-3:** The measured Hall voltage, for the 1-2-3 compound, is plotted against the temperature in figures 4.1 and 4.2. The sample current was held at 30mA for the entire experiment and the field was reversed from +4.58 kGauss (kG) to -4.58 kG by reversing the orientation direction of the sample. Each data point is the weighted average of at least 10 independent measurements of the Hall voltage at a constant temperature.

A broad maximum in  $V_h$  appears at 100K followed by a sharp minimum at 93K. Above the onset temperature for the superconducting transition, the Hall voltage is positive indicating that the majority carriers are holes. The Hall voltage becomes negative around the minimum indicating that after the holes go superconducting there seems to be a remnant of normally conducting electrons that contribute to the Hall voltage.

### Hall voltage versus Temperature (high temperature)

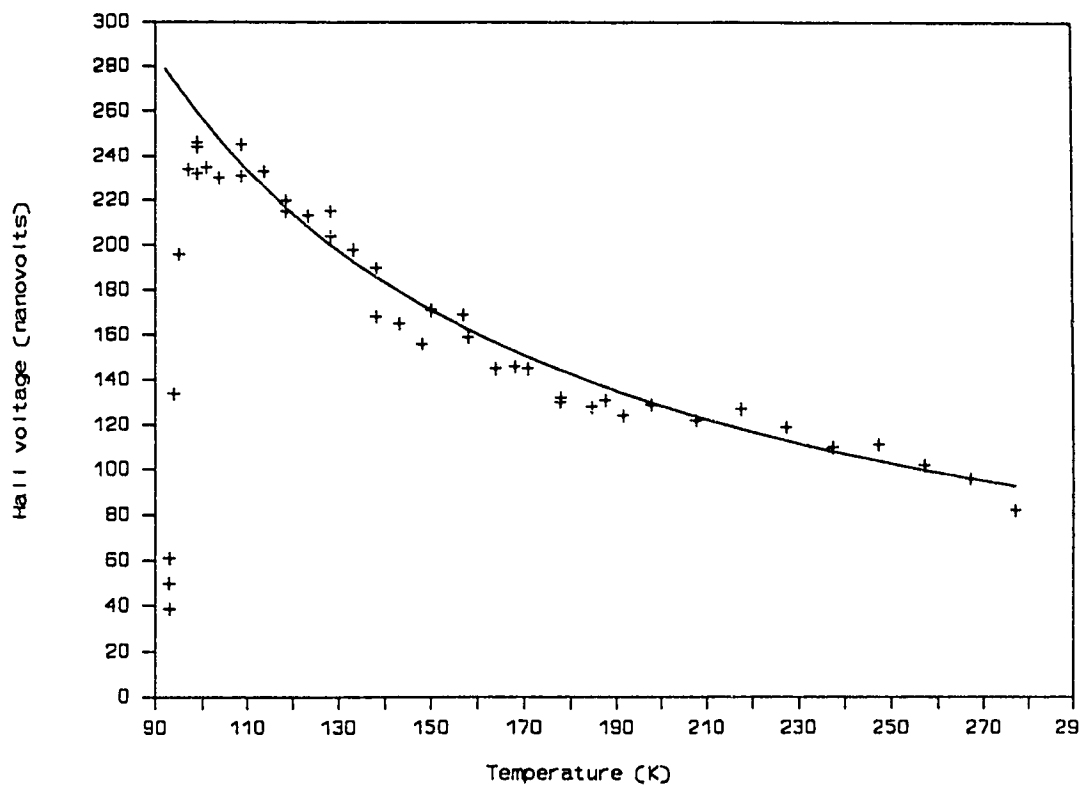


Fig 4.1: The Hall voltage for pure 1-2-3 compound is shown here, in the high temperature region, as a function of the sample temperature. The equation  $V_h = 25670/T$  (nV) is represented by the line. The applied magnetic field has a magnitude of 4.58 kgauss, the sample current is 0.030A and the sample thickness is 0.40mm.

### Hall voltage versus Temperature (low temperature)

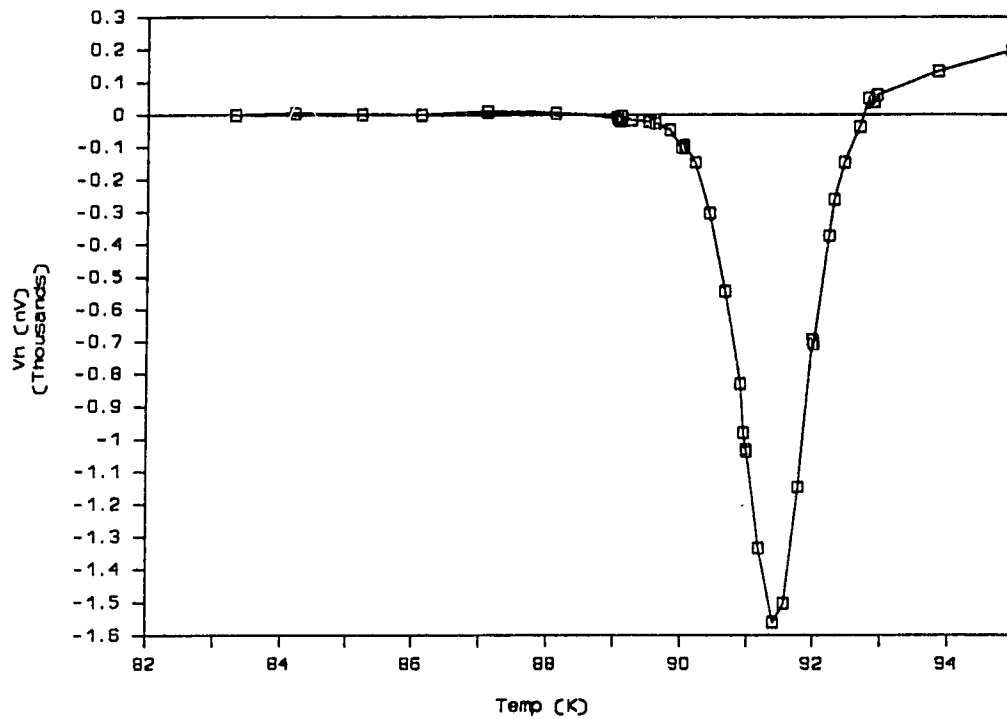


Fig 4.2: The Hall voltage for pure 1-2-3 compound is shown here, in the low temperature region, as a function of the sample temperature. The applied magnetic field has a magnitude of 4.58 kgauss, the sample current is 0.030A and the sample thickness is 0.40mm.

**The Hall data at high temperatures:** Neglecting the normal to superconducting transition for a moment, we notice that the Hall voltage above the onset temperature is positive. A plot of the Hall coefficient ( $R_h$ ) against the inverse temperature, for the temperatures above onset, is shown in figure 4.3. From this plot it is obvious that the Hall voltage depends very strongly on  $1/T$ .

From a least squares fit of  $V_h$  to  $1/T$  we find that the Hall voltage in this temperature region can be described empirically by the relation,

$$V_h = A/T + B \quad \text{eq. 4.1}$$

where  $A = 25670 \text{ nVK}$

and  $B = 0 \text{ nV}$

Preliminary results performed on the 1-2-3 compound showed that in this region of temperature the Hall voltage was proportional to the applied magnetic field. In this case we can define a Hall coefficient as in eq. 1.7 where,

$$R_h = V_h t / (I \times H) \quad \text{eq. 4.2}$$

**The Hall data at low temperatures:** When the temperature is lowered to a point where the sample begins to go through a normal to superconducting transition, the measured Hall voltage  $\{V_h\}$  advances

### Hall coefficient versus Temperature (high temperature)

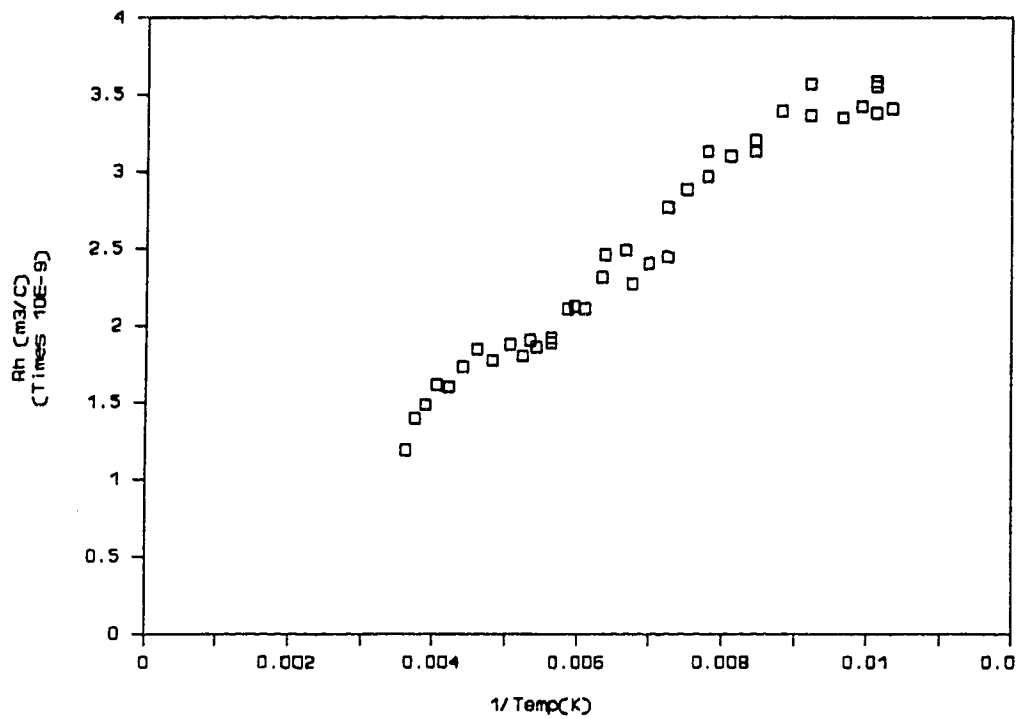


Fig 4.3: The Hall coefficient can be calculated for temperatures above 100K where the Hall voltage is a linear function of the applied field.



through a sharp negative minimum. This phenomenon is illustrated in fig 4.2. The Hall voltage in this region was also measured for several different applied magnetic fields; these data are shown in fig 4.4. From fig 4.4 it is obvious that the Hall voltage does not depend linearly on the applied field in this temperature range. For this reason it is impossible to define a Hall coefficient because  $R_H$  is only defined when the Hall voltage is linear with the applied field. Several authors have found the same behaviour in their samples of 1-2-3 material [13]. It should also be noted that still other experimentalists have not found this behaviour at all [10, 14]. Although there is no conclusion yet over this behaviour most of the recent experiments verify the kind of results obtained here.

**The resistance:** The resistance of the sample is shown in figures 4.5 and 4.6. At temperatures above onset the resistivity can be fitted to a straight line given by,

$$R=A+BT \quad \text{eq. 4.3}$$

where  $A=2.18$  mohm

and  $B=0.00775$  mohm/K

At low temperatures (see fig 4.6) at or just below onset it is

### Hall voltage versus Temperature for different magnetic field strengths

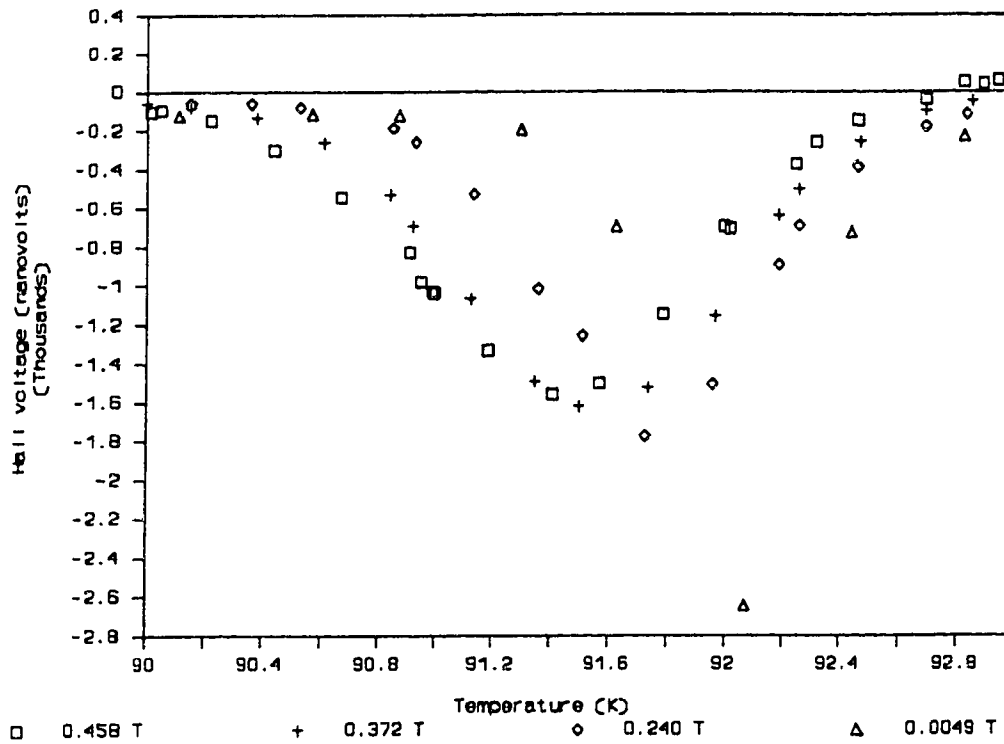
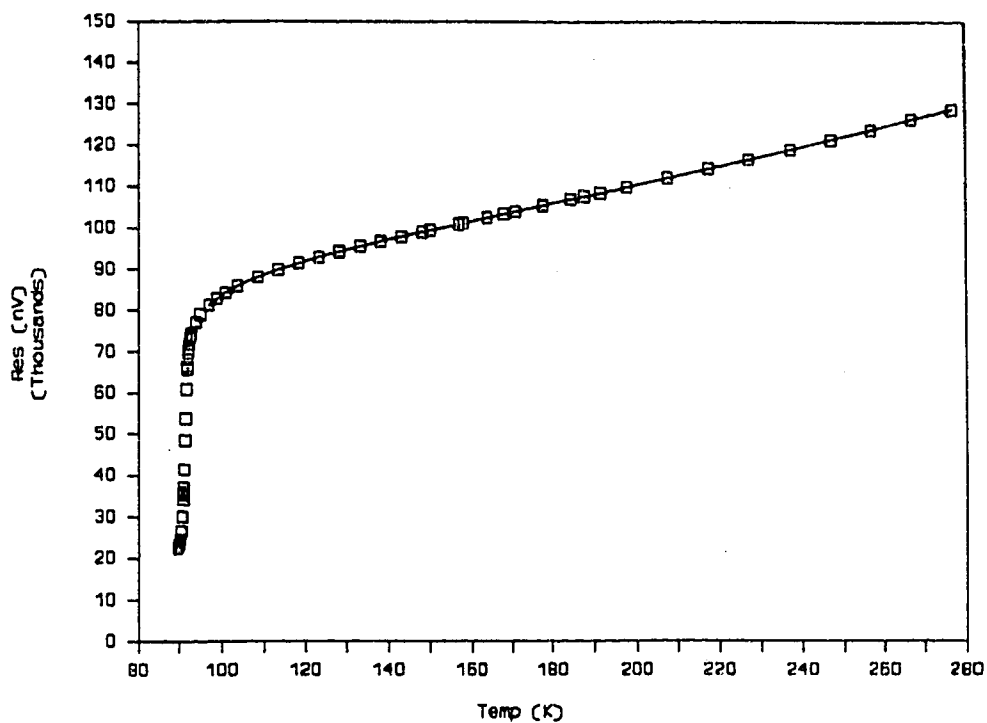


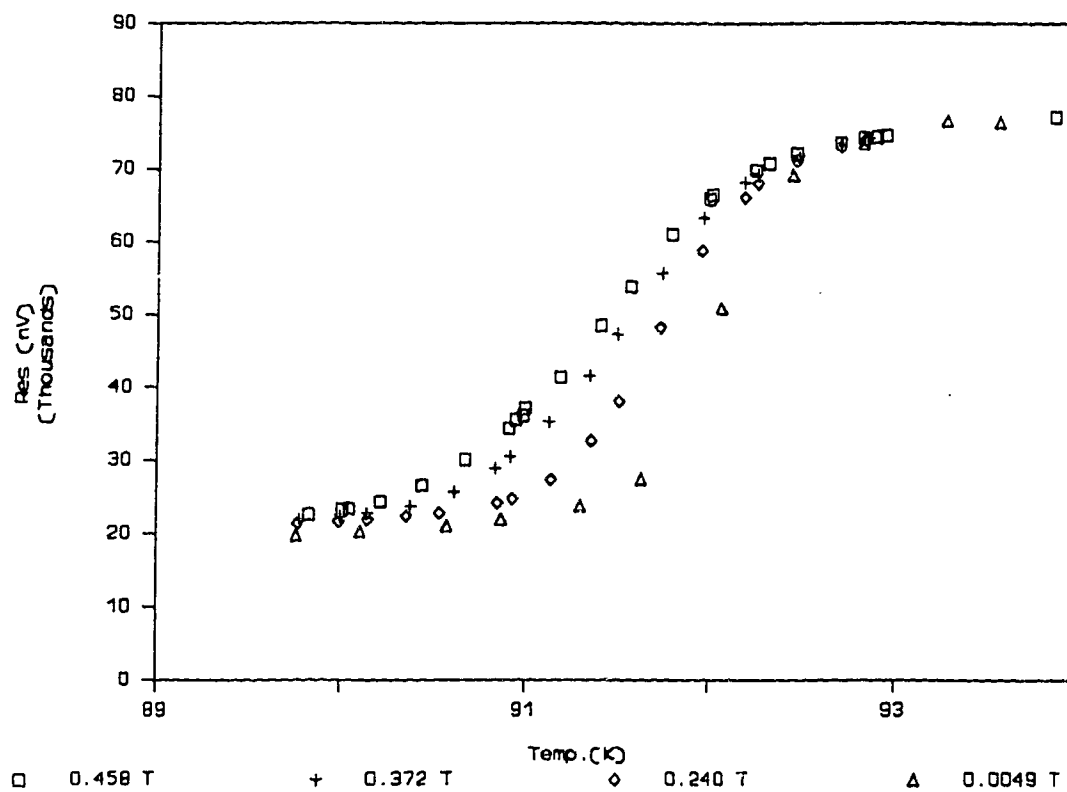
Fig 4.4: The minimum observed in the Hall voltage is shown here as a function of the temperature. The different magnetic field strengths applied show clearly that the Hall voltage in this region is not linear with the field strength.

Resistance versus Temperature  
(4.58 kgauss field applied)



Graph 4.5: The resistance of the 1-2-3 specimen is shown as a function of the temperature. This resistance was measured while the sample was in a 4.58 kgauss magnetic field. Application of a magnetic field only affects the tail as shown in graph 4.6.

### Resistance versus Temperature (for different applied fields)



Graph 4.6: From this plot it is clear that the resistance of the 1-2-3 compound is affected greatly by the application of a magnetic field in the temperature region between 90 and 93K.

obvious that the application of a field changes the sample resistance considerably. Magneto-resistance measurements, done during the preliminary stages of the experiment, illustrated a strong hysteresis with applied magnetic field. For this sample no detailed measurements were done concerning hysteresis, but detailed measurements have been done by S.Shifang [14] on another 1-2-3 sample.

## Chapter V: Analysis and Discussion

**The 1/T dependence of  $R_h$ :** The dependence of  $R_h$  on the inverse of temperature above  $T_{onset}$  is as yet unexplained. The author has found that it can be explained with the two band model. An article by Markewicz [15] also gives a simple explanation for this behaviour.

Bloch theory predicts that for a perfect metal at temperatures well above its Debye temperature, the lattice resistivity will be linear with respect to the temperature. This is a consequence of the electron-phonon interaction [Ziman ref#11 pp. 334-420]. Since the 1-2-3 compound does have a linear resistivity this is a good place to start.

Ziman [11 pg.365] tells us that the relaxation time  $\{\tau\}$  in a nearly perfect metal will be inversely proportional to the temperature, that is

$$\tau \propto T^{-1} \quad \text{eq. 5.1}$$

For a real metal we expect  $\tau$  to be finite at absolute zero due to lattice imperfections and material faults. In this case the average relaxation time can be approximately represented by,

$$\tau = (a + b T)^{-1} \quad \text{eq. 5.3}$$

Since the resistance of a metal is inversely proportional to the relaxation time we know that the resistivity,  $\rho$ , will be given by,

$$\rho \propto a + b T \quad \text{eq. 5.4}$$

$$\text{and } R=A+B T$$

where the resistance  $\{R\}$  should be linear in the temperature as we observe experimentally.

In chapter I a two band model has been treated. Here this material will be treated as a two band conductor, one of holes and one of electrons. For these two bands we consider two independent relaxation times. We can expect the two relaxation times to have the general form of the total relaxation time given by,

$$\tau_o=(a_o+b_o T)^{-1} \quad \text{eq. 5.5}$$

$$\text{and } \tau_h=(a_h+b_h T)^{-1}$$

In chapter IV the high temperature resistance is described by,

$$R=A+B T \quad A=2.18 \text{ mohm}$$

$$B=0.00775 \text{ mohm/Kelvin}$$

The total resistivity squared will be given by an expression of the form,

$$\rho^2=C(A^2+2ABT+B^2T^2) \quad \text{eq. 5.6}$$

$$\text{since, } R \propto T$$

The temperature range in which  $1/T$  behaviour has been observed in  $R_h$  is  $110K < T < 300K$ <sup>10</sup>. In this region for this sample  $B^2T^2$  turns out to be small when compared to either  $A^2$  or  $2ABT$ . In the other extreme if this were not so then the  $T^2$  behaviour would dominate in this temperature range and the Hall voltage would not

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<sup>10</sup>The  $1/T$  behaviour may persist at temperatures much higher than 300K.

follow  $1/T$  behaviour.

Substituting equations 5.5 into eq. 1.20 we get,

$$R_h \propto (A^2 + 2ABT) [n_h \{(a_h + b_h T)^2\}^{-1} - n_o \{(a_o + b_o T)^2\}^{-1}]$$

Since we observe  $1/T$  behaviour it is clear that the  $b_h T$  term must be significant in the temperature region of interest. In this model the Hall coefficient should become a constant at a low enough temperature. In fig 4.3, and in fig 4.1, it can be noted that before the drop in the Hall voltage due to the phase transition there is a short plateau. While the results are inconclusive in the 1-2-3 compound, experiments on compounds formed by substitutions into the pure 1-2-3 compound should give us more evidence to support this model.

It should also be noted that for this model if one were to have a compound with different qualities, such as 1-2-3 compound that is less dense due to greater porosity, this could lead to a linear dependence of  $R_h$  with respect to the temperature. Measurements shown in reference [6] are an example of this.

The equation derived as 1.26 describes the Hall effect in a polycrystal. The measurements would be even more difficult to interpret using this equation than for the simple, although poor, assumption that a crystal of 1-2-3 has little electrical anisotropy along its various crystal planes<sup>11</sup>.

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<sup>11</sup>. Single crystal Hall effect measurements have shown that the Hall coefficient varies greatly from a direction in the A-B plane to the C axis.



**The low temperature Hall effect:** The sudden drop of the Hall voltage when the sample begins to show signs of going through the normal to superconducting phase transition can be explained with the granular superconductor model. The Hall voltage will decrease when any amount of the material goes superconducting, because the current will follow the path of least resistance. The superconducting grains will short circuit some of the IGM and thus reduce the Hall voltage.

If the temperature is low enough for the current to be carried by Josephson tunnelling between many of the grains then we would expect the Hall voltage and resistance to be very sensitive to magnetic fields. This is the case for the Hall voltage as can be seen from Fig 4.4.

A possible explanation for the large negative signal found in the Hall effect is given at the end of chapter two where it is suggested that the IGM is the only material contributing to the Hall effect once the bulk material develops superconducting grains. From the data collected on the 1-2-3 compound it should be noted that this minimum increases in magnitude as the field is reduced<sup>12</sup>. This can be

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<sup>12</sup>. An attempt to zero the applied magnetic field on the sample was made, however the remnant magnetization in the iron core of the magnet made this impossible.

explained if we consider the IGM. We have shown that the majority carrier is negative in this material and the Hall coefficient is inversely proportional to the number of carriers in the conduction band for any material. Thus as the minimum gets smaller it indicates that there are more carriers in the conduction band. As a field is applied to the 1-2-3 specimen more charge carriers are introduced into the conduction band. If indeed the high  $T_c$  superconductors are based on Josephson tunnelling between superconducting grains we know that an applied field will reduce the probability for a Cooper pair to complete a tunnelling event undisturbed [see ref#12 pg.751]. The current must then flow along a resistive path through the non-superconducting IGM. In this case we would expect that the minimum should decrease in magnitude as the applied magnetic field is made stronger; this is observed (see Fig 4.4).

**The Resistance:** The change in the resistance around the transition temperature can also be explained in the same manner as for the low temperature Hall voltage. The larger the applied field the more difficult it will be for the Cooper pairs to Josephson tunnel across the IGM barriers. As the field is increased we see in fig 4.6 that the transition, as indicated by the electrical resistance, is broadened.

## Chapter VI: Conclusion

While quantitative explanations of the Hall effect are yet to be verified it is hard to draw any conclusions from the analysis of one single experiment done on one sample. What we have seen is that the granular superconducting model is able to account qualitatively for all the measurements done here on the 1-2-3 compound. Several authors have also used this model to explain other experiments performed on the 1-2-3 compound [13-14,16-17].

Explaining the  $1/T$  dependence of the Hall coefficient is possible by considering two independent bands of carriers and treating the Hall coefficient in a classical manner. The major drawback with this model is that our analysis is inconclusive due to the large number of unknown parameters.

The magnitude of the negative minimum found in the Hall voltage has been shown to be non-linear with applied magnetic field. This minimum is most likely due to the electrical character of the Inter Granular Material barriers that exist between the superconducting grains. The variation of the Hall voltage at the minimum can be explained by considering the effect the applied magnetic field would have on the Josephson tunnelling that occurs between the

superconducting grains. The resistance measured in a magnetic field around the superconducting transition temperature can be explained in the same manner.

For Josephson tunnelling to occur we know that the IGM must be a semi-conductor, or possibly an insulator, where the Cooper pairs occupy a forbidden energy level. The Hall voltage indicates that for temperatures close to the transition temperature of the 1-2-3 material, 94K, the majority carrier in the IGM must be electrons. This makes it inevitable that the superconducting portion of the sample must have holes as its majority carrier.

**Further experimentation:** Experimentation is now being done on samples of 1-2-3 compound that have small portions of the Cu replaced by Fe. With these samples further analysis of the magnetoresistance and Hall effect will be done around the transition temperature. Further investigation of the simple two band treatment of the Hall effect will be pursued in these materials.

## **Appendix A: The Program and Interface unit.**

Below the basic elements of the program used to measure the Hall voltage with the apparatus are outlined. Though effective this method is necessarily time consuming due to the very small signals; complicated by the presence of large misalignment voltages which are unavoidable because of the inhomogeneous nature of these ceramics.

### **Step 1: Taking a single Hall measurement**

#### **1.0-Set current to normal.**

-maximize the Hall probe sensor by rotating the sample holder and monitoring the sensors signal.

-Do Step 2.

-Reverse the Hall voltage by rotating sample through 180°.

-Do step 2.

-Calculate Hall voltage, average temperature and Hall probes signal.

-Rotate specimen back 180° to return to original position.

### **Step 2: Measure the Hall voltage**

**2.0-Measure the transverse voltage, temperature, resistance, and the Magnetic field with a Hall probe sensor.**

-Wait specified number of seconds (3s usually).

-Goto 2.0 until 10 Measurements have been done.

-Calculate average of transverse voltage and the deviation.

**2.1-If deviation is greater than specified number of nanovolts (usually**

10) then get another measurement of transverse voltage.

-Repeat step 2.1 until deviation of last 10 measurements meet requirements.

2.2-Reverse the sample current and Goto 2.0, then proceed.

Step 3:Measuring the Hall voltage for a range of temperatures

3.0-Repeat Step 1 10 times.

-Calculate average and deviation for temperature and Hall probe sensor.

-If  $\Delta T > 0.015\text{K}$  or  $\Delta H > .1\%$  then repeat Step 1 and keep only the ten most recent measurements.

-Once these criterion are met then calculate the Hall voltage,temperature,resistance and magnetic field for this temperature, print out results.

-Change the temperature and Goto Step 3.0.

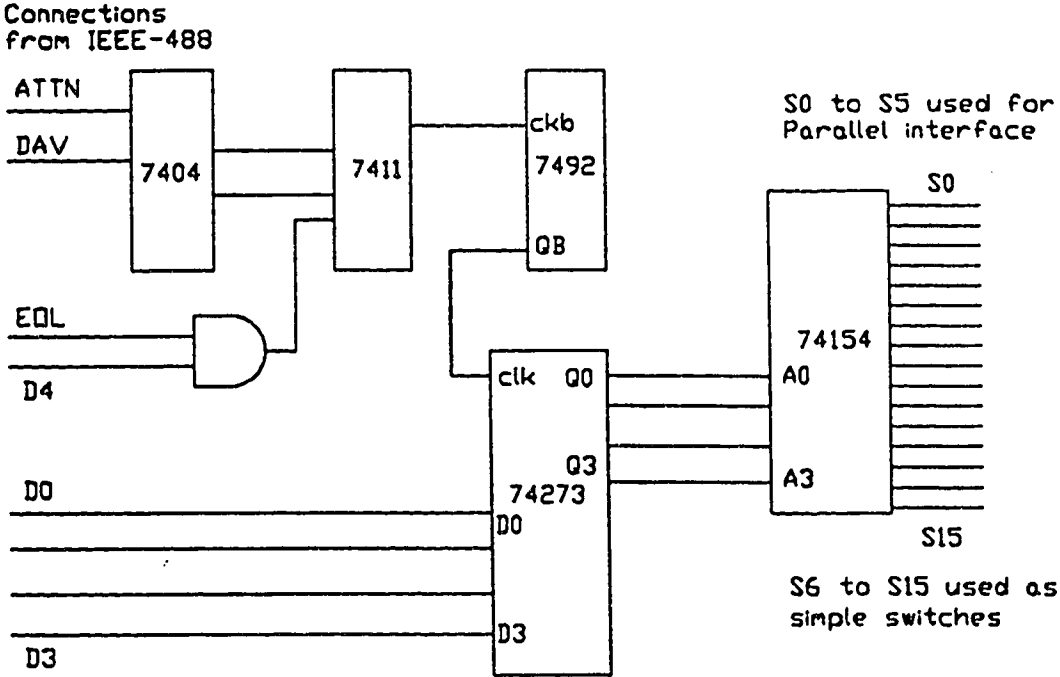


Fig A.1: The interface unit from the IEEE-488 interface bus to 16 switches of which any one can be set true and all the others are false.

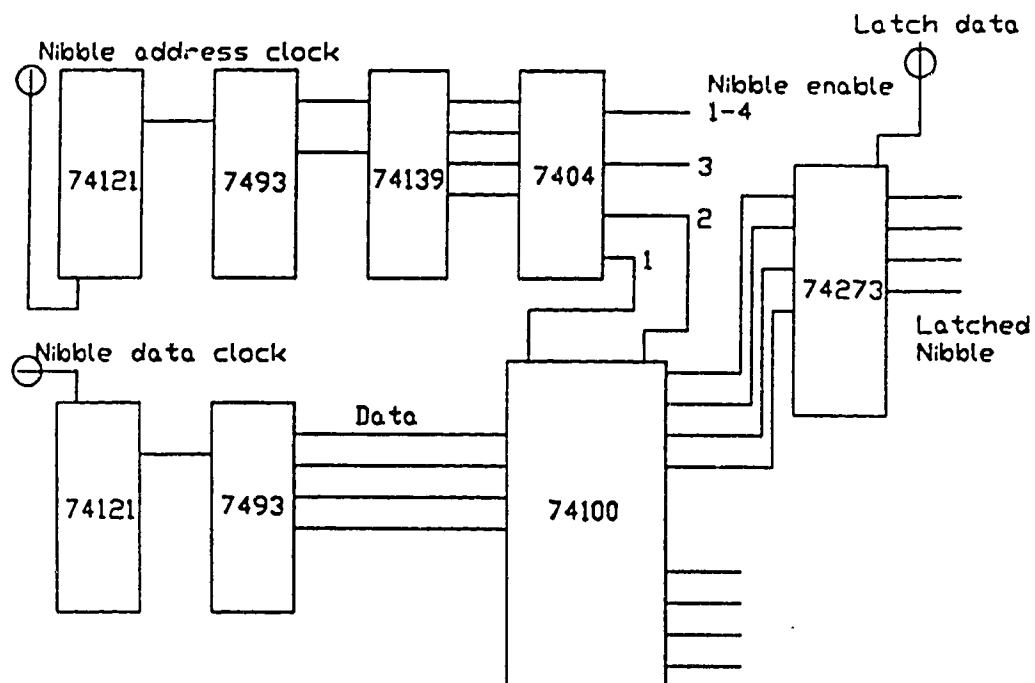


Fig A.2: The parallel interface that comes from 5 of the 16 switches as shown in fig A.1. This interface allows for 4 four bit buffers to be loaded and stored as switch settings.



## Appendix B: The data

Hall effect and magneto-resistance  
 1-2-3 compound  
 $t=0.40$  mm       $I=0.030$  A  
 $H=\pm 4.58$  KG

Temp (K)	V <sub>h</sub> (nV)	Res (nV)	R (mohm)	R <sub>n</sub> (m <sup>3</sup> /C)
277.04	82	128720	5.97E-10	4.2907
267.15	96	126225	6.99E-10	4.2075
257.19	102	123734	7.42E-10	4.1245
247.29	111	121298	8.08E-10	4.0433
237.45	110	118888	8.01E-10	3.9629
227.29	119	116463	8.66E-10	3.8821
217.60	127	114228	9.24E-10	3.8076
207.76	122	112003	8.88E-10	3.7334
197.88	129	109803	9.39E-10	3.6601
191.65	124	108393	9.02E-10	3.6131
187.70	131	107597	9.53E-10	3.5866
184.72	128	106904	9.32E-10	3.5635
177.97	132	105511	9.61E-10	3.5170
177.88	130	105433	9.46E-10	3.5144
170.93	145	103946	1.06E-09	3.4649
168.06	146	103364	1.06E-09	3.4455
164.01	145	102447	1.06E-09	3.4149
158.08	159	101222	1.16E-09	3.3741
156.97	169	100926	1.23E-09	3.3642
150.13	171	99417	1.24E-09	3.3139
148.13	156	99016	1.14E-09	3.3005
143.22	165	97848	1.20E-09	3.2616
138.24	168	96719	1.22E-09	3.2240
138.20	190	96665	1.38E-09	3.2222
133.22	198	95469	1.44E-09	3.1823
128.34	204	94265	1.48E-09	3.1422
128.32	215	94230	1.56E-09	3.1410
123.36	213	92887	1.55E-09	3.0962
118.49	220	91470	1.60E-09	3.0490
118.48	215	91446	1.56E-09	3.0482
113.51	233	89834	1.70E-09	2.9945
108.65	231	88065	1.68E-09	2.9355
108.65	245	88093	1.78E-09	2.9364
103.69	230	85865	1.67E-09	2.8622

100.84	235	84289	1.71E-09	2.8096
98.87	244	82951	1.78E-09	2.7650
98.84	232	82915	1.69E-09	2.7638
98.83	246	82887	1.79E-09	2.7629
96.92	234	81316	1.70E-09	2.7105
94.95	196	79036	1.43E-09	2.6345
93.87	134	77166	9.75E-10	2.5722
92.95	61	74615	4.44E-10	2.4872
92.90	39	74449	2.84E-10	2.4816
92.83	50	74278	3.64E-10	2.4759
92.70	-37	73582	undefined	2.4527
92.47	-146	72150	undefined	2.4050
92.32	-261	70779	undefined	2.3593
92.25	-374	69875	undefined	2.3292
92.02	-705	66385	undefined	2.2128
92.00	-695	65859	undefined	2.1953
91.79	-1147	60934	undefined	2.0311
91.57	-1503	53780	undefined	1.7927
91.41	-1560	48444	undefined	1.6148
91.19	-1334	41424	undefined	1.3808
91.00	-1036	37038	undefined	1.2346
90.99	-1032	36091	undefined	1.2030
90.95	-980	35570	undefined	1.1857
90.91	-830	34310	undefined	1.1437
90.67	-545	30090	undefined	1.0030
90.44	-303	26636	undefined	0.8879
90.22	-147	24438	undefined	0.8146
90.05	-94	23483	undefined	0.7828
90.01	-101	23353	undefined	0.7784
89.83	-47	22655	undefined	0.7552
89.61	-24	22146	undefined	0.7382
89.51	-20	22000	undefined	0.7333
89.26	-16	21655	undefined	0.7218
89.11	-4	21422	undefined	0.7141
89.07	-16	21120	undefined	0.7040
89.04	-8	21327	undefined	0.7109
88.13	5	20478	undefined	0.6826
87.11	9	19772	undefined	0.6591
86.13	-1	19185	undefined	0.6395
85.22	1	18696	undefined	0.6232
84.20	5	18146	undefined	0.6049
83.30	-1	17662	undefined	0.5887

Hall effect and magneto-resistance  
 1-2-3 compound  
 $t=0.40$  mm  $I=0.030$  A  
 $H=\pm 3.72$  KG

Temp (K)	Vh (nV)	Res (nV)	R (mohm)
92.86	-47	74220	2.4740
92.70	-97	73423	2.4474
92.48	-253	71761	2.3920
92.26	-504	69429	2.3143
92.19	-637	68092	2.2697
91.97	-1158	63236	2.1079
91.74	-1528	55678	1.8559
91.50	-1621	47298	1.5766
91.35	-1493	41561	1.3854
91.13	-1069	35231	1.1744
90.92	-694	30519	1.0173
90.84	-532	28867	0.9622
90.61	-263	25725	0.8575
90.38	-134	23806	0.7935
90.15	-80	22833	0.7611
90.00	-60	22430	0.7477
89.78	-54	21996	0.7332
89.55	-26	21657	0.7219
89.47	-25	21537	0.7179
89.24	-34	21267	0.7089
89.05	-31	21068	0.7023

Hall effect and magneto-resistance  
1-2-3 compound  
t=0.40 mm      I=0.030 A  
H=+/- 2.40 KG

Temp (K)	Vh (nV)	Res (nV)	R (mohm)
92.84	-118	74090	2.4697
92.70	-179	73188	2.4396
92.47	-385	71185	2.3728
92.26	-691	68042	2.2681
92.19	-892	66062	2.2021
91.96	-1509	58709	1.9570
91.73	-1775	48232	1.6077
91.51	-1259	38015	1.2672
91.36	-1017	32638	1.0879
91.14	-530	27427	0.9142
90.93	-261	24835	0.8278
90.85	-187	24186	0.8062
90.53	-81	22876	0.7625
90.36	-60	22445	0.7482
90.15	-59	22014	0.7338
89.99	-42	21748	0.7249
89.77	-28	21435	0.7145
89.55	-24	21173	0.7058
89.48	-18	21070	0.7023
89.25	-27	20830	0.6943
89.06	-8	20671	0.6890

Hall effect and magneto-resistance  
1-2-3 compound  
 $t=0.40$  mm  $I=0.030$  A  
 $H=\pm 0.049$  KG

Temp (K)	Vh (nV)	Res (nV)	R (mohm)
96.79	-23	81180	2.7060
96.44	-20	80822	2.6941
96.00	-27	80353	2.6784
95.73	-31	80028	2.6676
95.29	-37	79475	2.6492
94.85	-40	78864	2.6288
94.48	-44	78301	2.6100
94.02	-56	77492	2.5831
93.57	-80	76505	2.5502
93.28	-105	76686	2.5562
92.83	-231	73595	2.4532
92.45	-724	69107	2.3036
92.07	-2646	50860	1.6953
91.63	-695	27441	0.9147
91.30	-195	23834	0.7945
90.87	-122	21920	0.7307
90.57	-114	21141	0.7047
90.11	-124	20322	0.6774
89.76	-140	19810	0.6603
89.47	-111	19472	0.6491
89.04	-104	19048	0.6349

## List of references

1. Hurd C. M., 1975, ASSYMETRIC SCATTERING OF ELECTRONS IN METALS, Contemp. Phys. **16** (6), pp.517-532 (1975).
2. Hurd C. M., 1972, THE HALL EFFECT IN METALS AND ALLOYS. (Plenum Press, New York)
3. Xia T. and Stroud D., THEORY OF THE HALL COEFFICIENT OF POLYCRYSTALS, Phys. Rev B, **37** (1), pp.118-122 (1988).
4. Yong Z., *et Al*, HALL EFFECT IN SINGLE PHASE Ba<sub>2</sub>YCu<sub>3</sub>O<sub>7-d</sub>, Sol. Stat. Comm., **64** (6), pp.885-888 (1987).
5. Duan H., Lu L., Wang X., Lin S., and Zhang D., HALL EFFECT OF HIGH T<sub>c</sub> SUPERCONDUCTOR Y-Ba-Cu-O COMPOUND, Sol. Stat. Comm., **64** (4), pp.489-491 (1987).
6. Ricketts B., *et Al*, HALL EFFECT MEASUREMENTS ON A BULK 1-2-3 SAMPLE, Sol. Stat. Comm., **64** (10), pp.1287-1289 (1987).
7. Galffy M. and Zirngiebl E., HALL EFFECT OF BULK YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-d</sub>, Sol. Stat. Comm., **68** (10), pp.929-933 (1988).
8. Sun Shifang, *et Al*, THE BEHAVIOUR OF NEGATIVE MAGNETORESISTANCE AND HYSTERESIS IN YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-d</sub>, Europhys. Lett., **6** (4), pp.359-362 (1988).
9. Yasuhiro I., Tsuyoshi T., Hiroyuki T., and Humihiko T., A SIMPLE METHOD FOR ATTACHING ELECTRICAL LEADS TO SMALL SAMPLES OF HIGH T<sub>c</sub> OXIDES, Jap. Jour. of App. Phys., **27** (4), pp.L658-L660 (1988).
10. Wieck A., VANISHING CONTACT RESISTANCE ON POLYCRYSTALLINE YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-d</sub>, Appl. Phys. Lett, **52** (12), pp. 1017-1019 (1988)
11. Ziman J. M., 1967, ELECTRONS AND PHONONS. (Oxford Press)

12. Ashcroft N. W. and N. D. Mermin, 1976, SOLID STATE PHYSICS. (Holt, Rinehart and Winston, Philadelphia)
13. Cia X., Joynt R., and Larbalestier D., EXPERIMENTAL EVIDENCE FOR GRANULAR SUPERCONDUCTIVITY IN Y-Ba-Cu-O AT 100 TO 160 K, Phys. Rev. Lett., **58** (26), pp.2798-2801 (1987).
14. Lu L., Duan H., Zhang D., COOPERATIVE WEAK LINKS IN SINTERED Y-Ba-Cu-O SUPERCONDUCTOR, Phys. Rev. B, **37** (7), pp.3681-3684 (1988)
15. Markiewicz R., SIMPLE MODEL FOR THE HALL EFFECT IN  $\text{YBa}_2\text{Cu}_3\text{O}_{7-d}$ , Phys. Rev. B, **38** (7), pp. 5010-5011 (1988)
16. Marcon R., Fastampa R., Guira M., EVIDENCE OF JOSEPHSON JUNCTIONS IN SINTERED  $\text{YBa}_2\text{Cu}_3\text{O}_7$  SAMPLE BY MEANS OF MICROWAVE ABSORPTION IN A LOW MAGNETIC FIELD, Phys. Rev. B, **39** (4), pp. 2796-2799 (1989)
17. Brocklesby W. *et Al*, TUNNELLING CHARACTERISTICS OF INTERNAL JOSEPHSON JUNCTIONS IN  $\text{YBa}_2\text{Cu}_3\text{O}_{7-d}$  THIN FILMS, Phys. Rev. B, **38** (16), pp. 11805-11808 (1988)