CHAPTER II

METHOD OF THE EXPERIMENT

2.1 The Method for Measuring the Susceptibility

The magnetic susceptibility of many materials can be measured indirectly through the change in frequency of an oscillator, operating as a marginal vacuum tube oscillator with self-resonant parallel LC tank circuit. When speciman is removed from the coil of the oscillator a change, $\Delta\omega$, to the vacuum resonant frequency, ω_o will occur. A good approximation to the frequencies are[10]

$$\omega_o \tilde{=} \frac{1}{\sqrt{L_o C}} \quad \text{and} \quad \omega \tilde{=} \frac{1}{\sqrt{LC}} \tag{2.1}$$

where L_o, L are the inductance of the empty coil and the inductance when the sample is placed in the coil, respectively. The change $\Delta\omega$ is caused by the charge (i.e. small increase) in coil inductance ΔL, which is proportional to the real part x' of the complex magnetic susceptibility[10]

$$\chi_t = x' - ix'' \tag{2.2}$$

of the material being studied.

Since Leo Esaki [11] invented the tunnel diode, it has been used extensively as part of an oscillator. The use of tunnel diode oscillator to measure the susceptibility at low temperature was first described by R.B. Clover and W.P. Wolf[10]. The existence of

negative resistance in the characteristic curve of the tunnel diode made it useful for measuring paramagnetic susceptibility at r.f. frequency at low temperature. . This negative resistance allows for self-sustaining nearly sinusoidal oscillation. Since in the steady state condition, the power provided by the diode is equal the average value per cycle of the power dissipation in the rest of the circuit. To acheive the balance, the average value per cycle of the diode negative conductance, g_d, must be equal to the parallel conductance of the tank circuit. Experimentally, the tunnel diode oscillator (T.D.O) oscillates stably over the entire temperature range from 1 to 300 K[10]. It is found empirically that a good approximation to the T.D.O. frequency is the simple tank circuit frequency inspite of the non-linear behavior of T.D.O. Another interesting characteristic of the T.D.O. is that the frequency ω goes through a maximum as a function of bias voltage. This dependence of the frequency on bias voltage may be caused by a variation of the diode capacitance C_d as the bias voltage is varied. Experimentally, one does the measurements for a range of the bias voltage and then selects the value at which the frequency peaks. The average susceptibility are then more independent of the bias voltage. However, operating the T.D.O. closer to its frequency peak minimizes the frequency fluctuations that occur during the measurements. The accuracy of susceptibility estimated is thus maximized. Moreover, for this condition the frequency of the oscillator is least sensitive to losses introduced by any out of phase component χ'' of the susceptibility. Therefore the method can be used to measure χ' even when relaxation effects are significant.

Now, the relationship between ΔL and $\Delta\omega_m$ is given by

$$\frac{\Delta\omega_m}{\omega_o} = \frac{\omega-\omega_o}{\omega_o} = \sqrt{\frac{L_o}{L}} - 1 \qquad (2.3)$$

and where L is given by

$$L = L_o\mu = L_o(1+4\pi\chi_m) \qquad (2.4)$$

with μ being the permeability of the sample, Eq. (2.4) becomes

$$\frac{\Delta\omega_m}{\omega_o} = \frac{1}{\sqrt{1+4\pi\chi_m}} - 1 \qquad (2.5)$$

$$\chi_m = \frac{1}{4\pi}\left[\frac{1}{(1+\Delta\omega/\omega)^2} - 1\right] \qquad (2.6)$$

Thus, the susceptibility $\chi_m(\omega, H, T)$ of a magnetic compound may be found from measurements of $\Delta\omega_m$ for a suitable range of values of ω, H and T. If $\frac{\Delta\omega_m}{\omega_o} << 1$ or $\frac{\Delta L}{L_o} << 1$, the relation can be rewritten as

$$\chi_m = -\frac{1}{2\pi}\frac{\Delta\omega_m}{\omega_o} \qquad (2.7)$$

In direct measurement of $\frac{\Delta\omega_m}{\omega_o}$ at different temperature provides the temperature dependence of the susceptibility. In general, the self inductance of a coil is related to the total stored energy in it via

$$U = \frac{1}{2}LI^2 \qquad (2.8)$$

when I is a current flow in it. This energy is also equal to the total field energy

$$U = \frac{1}{8\pi}\int \vec{B}.\vec{H}\, d^3r \qquad (2.9)$$

Since the change in inductance is associated with the change in energy, we have

$$\Delta U = \frac{1}{8\pi}\int (\vec{B}\cdot\vec{H} - \vec{B_o}\cdot\vec{H_o})d^3r \qquad (2.10)$$

where $\vec{H_o}$ and $\vec{B_o}$ are the initial fields without any sample. If M is the magnetization in the sample, equation (2.10) can be written as

$$\Delta U = \frac{1}{2}\int_V \vec{M}\cdot\vec{B_o}d^3r \qquad (2.11)$$

The change in inductance is given by

$$(L-L_o)I^2 = \int_V \vec{M}.\vec{B_o}d^3r \qquad (2.12)$$

The value of integral on the RHS depends on the shape, volume and size of the sample inserted in the tank coil. For example, if the sample is ellipsoid[12] of revolution and is small enough to be in the uniform part of the coil field, then the magnetization is uniform and equal to

$$M = \frac{4\pi\chi}{1+\epsilon\chi} B_o \qquad (2.13)$$

where ϵ is the demagnetization factor and χ is the volume susceptibility, and so we get

$$\frac{L-L_o}{L_o} = \frac{-4\pi\chi}{1+\epsilon\chi}\frac{V}{V_o} \qquad (2.14)$$

where V is the sample volume, V_o the volume of the coil. Thus, by measuring the change in inductance, one does not measure directly χ but rather the factor $\frac{\chi}{1+\epsilon\chi}$ as χ_m. Depending on the shape of the sample (for instance cylindrical shape and nonferromagnetic samples where $\chi << 1$) we can ignore the term $\epsilon\chi$[13]. Then equation (2.14) depends only on the geometrical shape of the sample and coil, i.e.

$$\frac{L - L_o}{L_o} = -4\pi\chi F \tag{2.15}$$

where

$$F = \frac{\int_V B_o^2(r)d^3r}{\int_{V_o} B_o^2(\vec{r})d^3r} \tag{2.16}$$

is the geometrical filling factor for the sample. The basic equation then becomes

$$F\chi_m = -\frac{1}{2\pi}\frac{\Delta\omega_m}{\omega_o} \tag{2.17}$$

We now consider the difference which is due to the magnetization between the local and the applied field. The local field is the sum of the applied field H_o, a demagnetizing field H_D and an internal field H_{int} that arises from the magnetic interaction of the dipoles, i.e.

$$H = H_o - H_D + H_{int} \tag{2.18}$$

The interaction field can be due to a dipole-dipole field (Lorentz field) H_L or an exchange interaction field H_e, each of which is proportional to the magnetization: $H_L = \frac{4\pi}{3}M$[14],

$H_e = \gamma M$. Since the order of magnitude of the molecular field constant γ is 10^3,[12] the effect from the other two fields are small by comparison and so the local field simply becomes

$$H = H_o + \gamma M \tag{2.19}$$

The relation between the local and measured susceptibility is

$$\frac{1}{\chi} = \frac{1}{\chi_m} + \gamma \tag{2.20}$$

Since χ varies with T as $\chi = \frac{C}{T}$, we get by combining the equation (2.20) and (2.17)

$$T = -2\pi F\left(\frac{\omega_o}{\Delta\omega}\right)_m C + \gamma C \tag{2.21}$$

In the case of powder samples, we should include an additional filling factor to account for the difference in the density between that of powder samples and samples. Thus an single crystal,[12] (2.21) should be

$$T = -2\pi F\left(\frac{\omega_o}{\Delta\omega}\right)_m Cf + \gamma Cf \tag{2.22}$$

A plot of $-\frac{\omega_o}{\Delta\omega}_m$ versus T should be a straight line with slope $S = \frac{1}{2\pi FCf}$ and intercept $\Delta = \gamma Cf$. Once Δ and S are obtained, the constant C and $\theta = \gamma C$ can be determined.

In this experiment, an alternating field of frequency of about hundred kilohertz is present during the measurement. This alternating field affects the susceptibility measurements since the susceptibility

being measured is the r.f. susceptibility. When an applied field of high frequency acts on the material, the responce of the material (the induced magnetization) can not keep up with the changes of the field. Instead, the magnetization lags in phase with it. Suppose that the alternating field is

$$H_A = H_1 \cos\omega t \tag{2.23}$$

the magnetization would be given by

$$H_A = M_1 \cos(\omega t - \phi) \tag{2.24}$$

$$= M_1 \cos\omega t \cos\phi + M_1 \sin\omega t \sin\phi \tag{2.25}$$

where ϕ is the phase angle by which the magnetization lags the field H. Comparingly to the static susceptibility, or d.c. susceptibility, we can given with analogy to $\chi = \frac{M}{H}$ as the form;

$$\chi' = \frac{M_1 \cos\phi}{H_1}$$

$$\chi'' = \frac{M_1 \sin\phi}{H_1} \tag{2.27}$$

where χ' is the real part and χ'' is the imaginary part. Both χ' and χ'' depend on the frequency ω and the magnitude of the applied field. At low frequency, M and H are in phase, so $\chi'' = 0$ and $\chi' = \chi$ will be the static susceptibility. The two quantities, χ' and χ'' can be given in terms of the isothermal and adiabatic susceptibilities;[15] defined as

$$\chi_I = \left(\frac{\partial M}{\partial H}\right)_T \tag{2.28}$$

and

$$\chi_A = \left(\frac{\partial M}{\partial H}\right)_S \tag{2.29}$$

So we have

$$\chi' = \chi_A + \frac{\chi_I - \chi_A}{1+(\omega\tau_1)^2} \tag{2.30}$$

and

$$\chi'' = \frac{(\chi_I - \chi_A)}{1+(\omega\tau_1)^2}\,\omega\tau_1 \tag{2.31}$$

where τ_1 is the spin-lattice relaxation time. For low frequencies $\chi' = \chi_I$ and $\chi'' = 0$, where as for high frequencies $\chi' = \chi_A$ and $\chi'' = 0$, or are equal to combinations of two.

2.2 An Experiment for Measuring r.f. Susceptibility from 77 to 300 K

An experiment for measuring the susceptibility of antiferromagnetic material in the temperature range 77 to 300 K has been designed. It consists of a simple cryostat combinding with a set of a tunnel diode oscillator circuit.

2.2.1 The Simple Cryostat

The cryostat was similar to one constructed by F. Habbal, G.E. Watson and P.R. Elliston.[12] They were able to measure the paramagnetic susceptibility of various compounds in temperature range between 77 to 300 K. The cryostat was constructed mainly with glass tubes of three sizes both in diameters and lengths. The largest

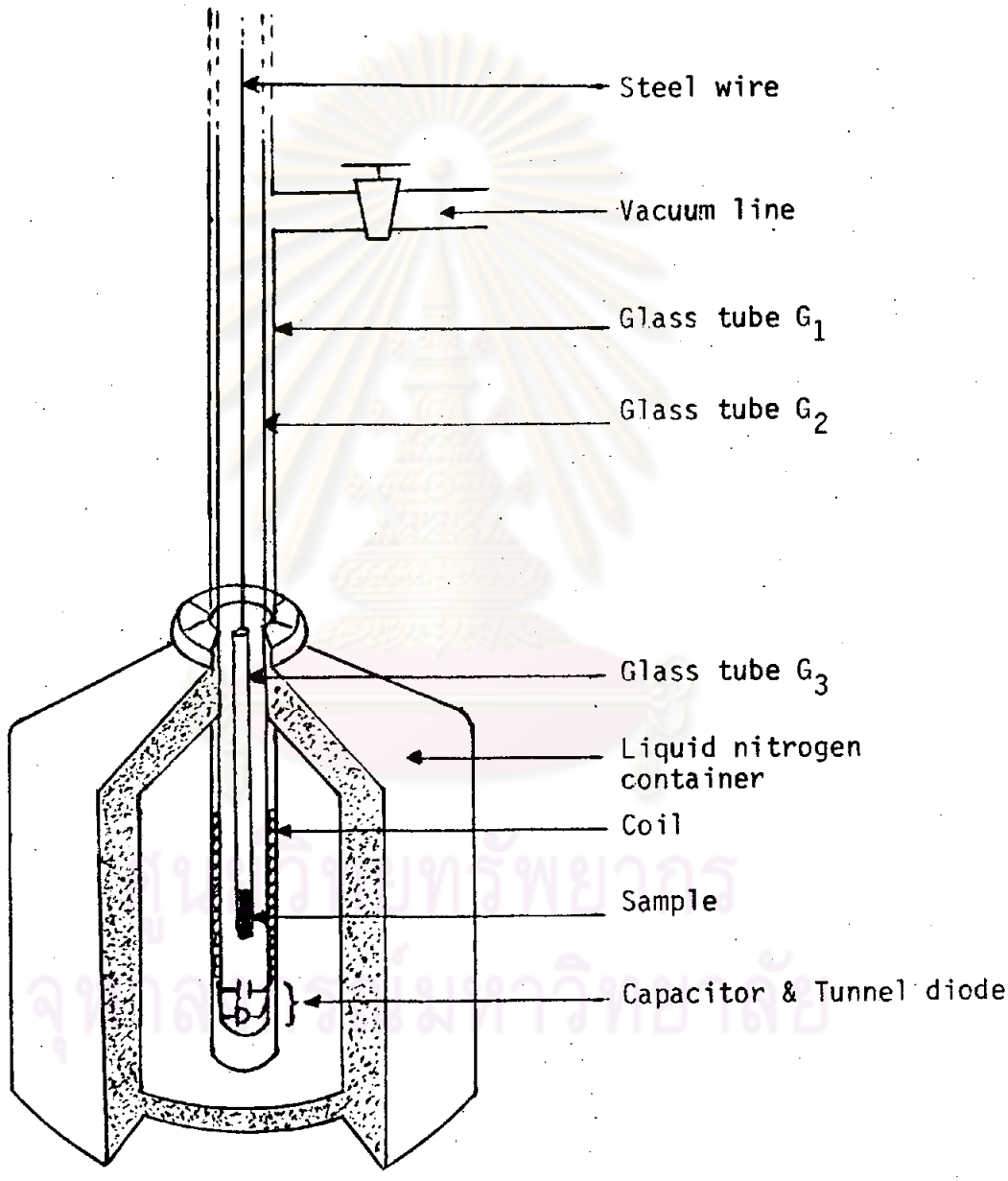

Figure 10 General view of cryostat and dewar

glass tube, G_1, was of 25.4 m.m. outer diameter(od) and 65 cm. long. This tube was connected to a vacuum line, and which therefore provided a way for use to isolated the sample from the surroundings. A second tube, G_2, of 8 m.m. od and 63 cm. long, was placed inside the G_1 the tank coil of the oscillator was tightly wound around G_2. The smallest glass tube, G_3, of 6 m.m. od and 15.5 cm. long was used to contain the sample. The powder samples were placed into G_3 and therefore were of a cylindrical shapes of 28 m.m. long. The sample tube, G_3, was lowered into the G_2 by a steel wire. This allowed the sample to be slid up and down inside the G_2 without disturbing the vacuum. All of these tubes were sealed by vacuum grease. The transparency of the glass tube allowed the position of the sample to be clearly visible. The sample was appliciably smaller in comparison to the coil, and so could approximately be considered to be an uniform field of the coil. The cryostat is finally placed into a dewar which surrounds the cryostat in constant temperature bath. The set up of the experiment is shown in Figure 10.

2.2.2 Tunnel Diode Oscillator

C.T. Van Degrift[16] has studied and designed a low-temperature tunnel diode oscillator in the past several years. The tunnel diode oscillator has been recognized as being a very useful measuring device. Several of its useful properties are its very small size,its simple construction, its sensitivity to extremely small changes in thermal expansion, surface impedence and electric and

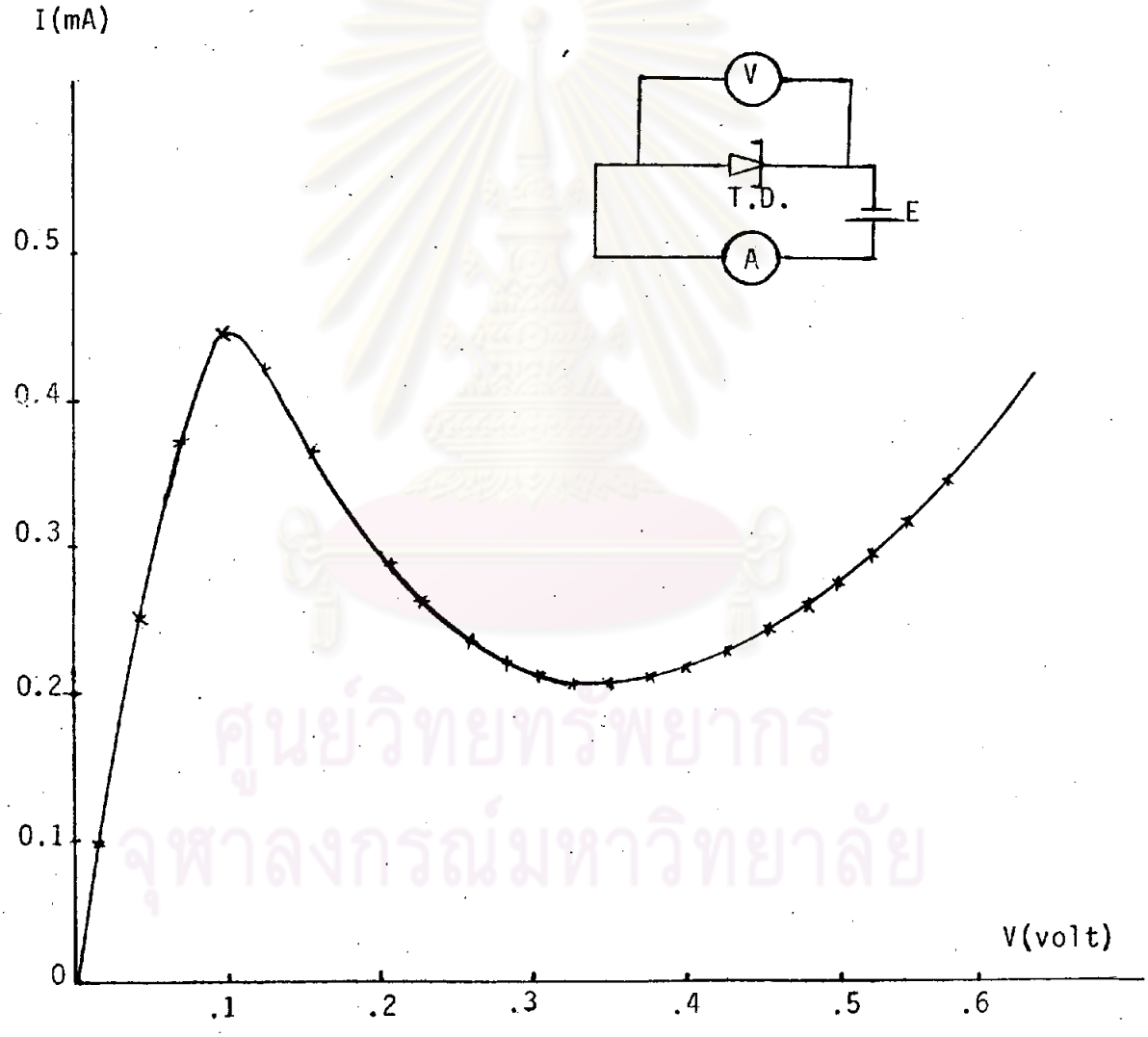

Figure 11 The I-V characteristic curve of tunnel diode #IN3712

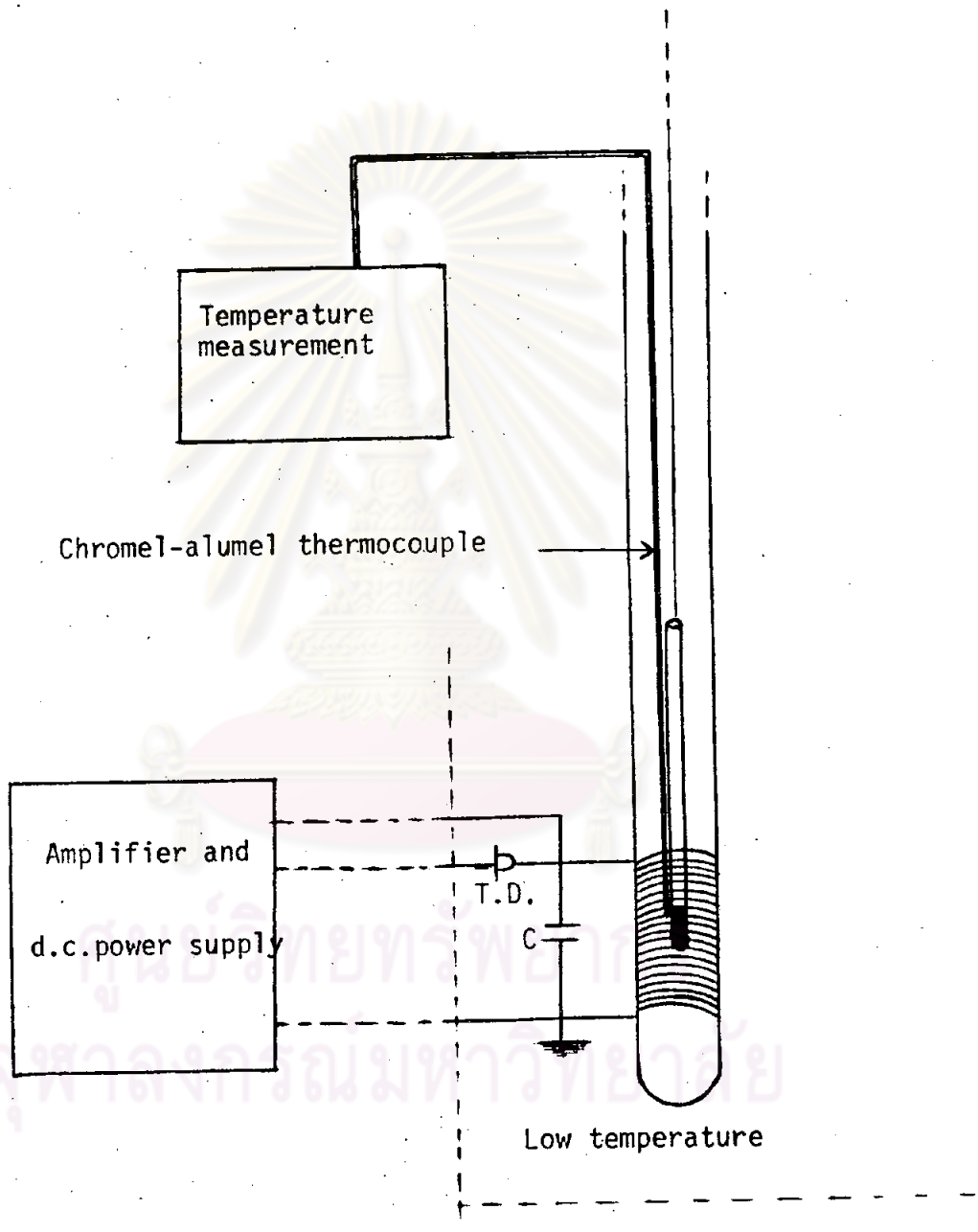

Figure 12 The generai view of oscillator

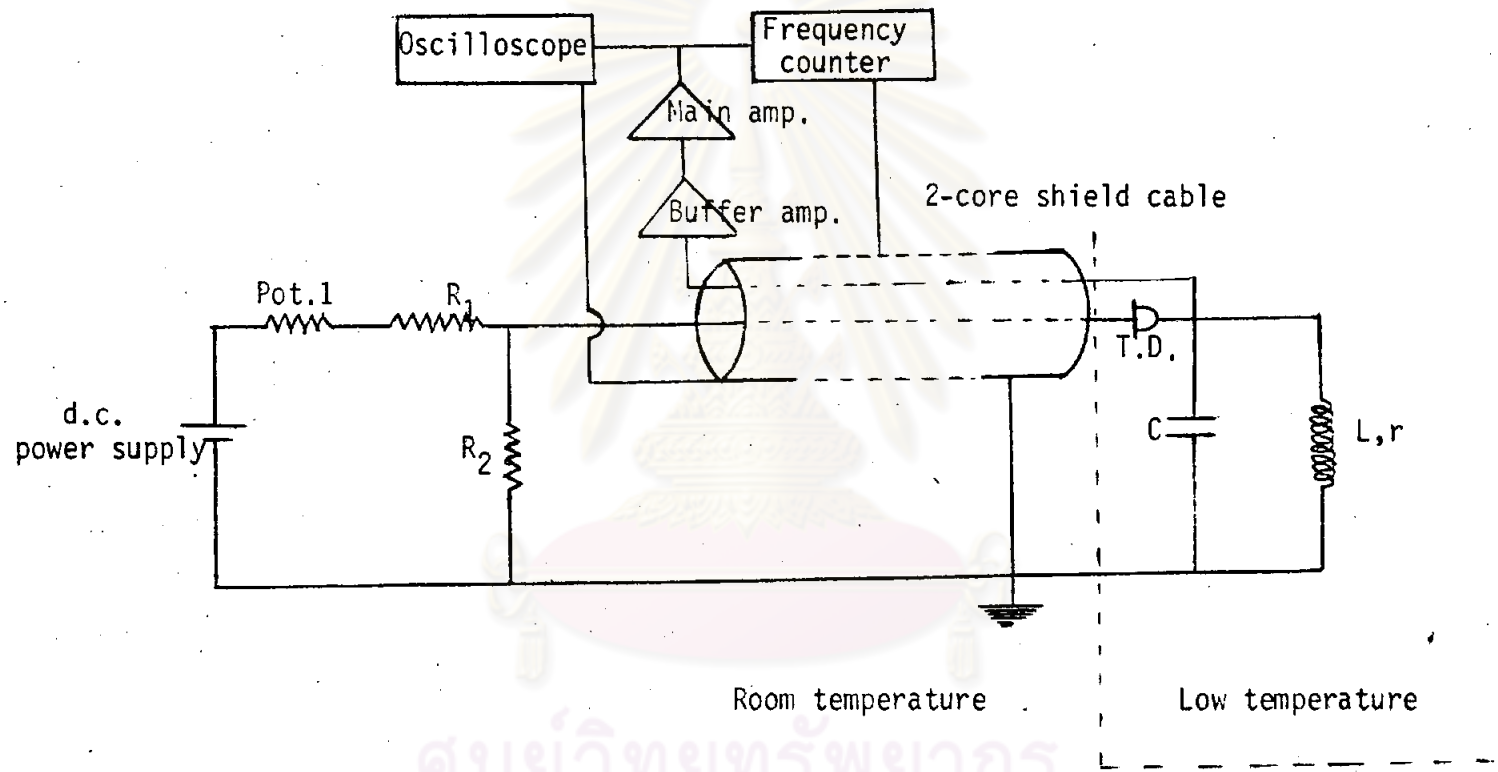

Figure 13 The resonant circuit

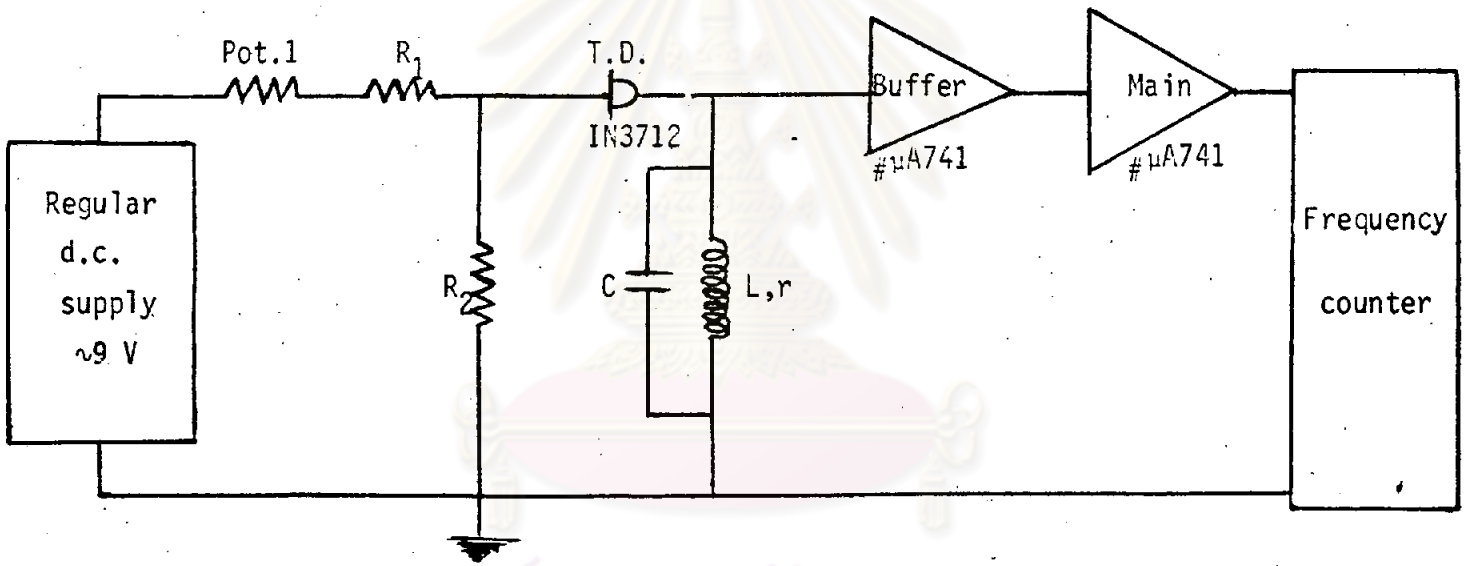

Figure 14 Schematic Diagram: Tunnel-diode oscillator, Buffer amplifier, Main amplifier

magnetic susceptibilities. Furthermore, the tunnel diode is temperature independent at low temperature and has very low frequency noise. Finally, the oscillator uses very little power and needs only very low voltages.

The tunnel diode oscillator used in our experiment designed is very similar to the one designed by R.B. Clover and W.P. Wolf[10] and Coraig T. Van Degrift.[16] The diode used in our circuit is a germanium IN 3712 which has the I-V characteristic curve at room temperature as shown in Fig. 11. The general oscillator circuit diagram is shown in Fig. 12. The coil consists of about 300 turns of 2 m.m. copper wire, which is wound around the glass tube G_2 of 10 cm. long, and is covered with a layer of epoxy. Two capacitor of 0.01 μF each is attached in parallel to the glass tube. A small 2-core shield cable runs from the tank circuit to room temperature. This carries the r.f. output signal to room temperature and bring down the d-c bias voltage for oscillator from room temperature through the same cable. The tunnel diode acts as a negative ac resistance, which cancels the losses of the tuned circuit. Since this negative resistance is temperature dependent, it is best to keep some it at room temperature for good frequency stability and for easy the d.c. bias adjustment. The tank circuit must be placed at low temperature throughout the experiment. The experimental set up is shown in fig. 13. The r.f. ac. signal is amplified by the buffer and main amplifiers before it enters the frequency counter and oscilloscope. The buffer amplifier is of the non-inverting, unity gain and high input

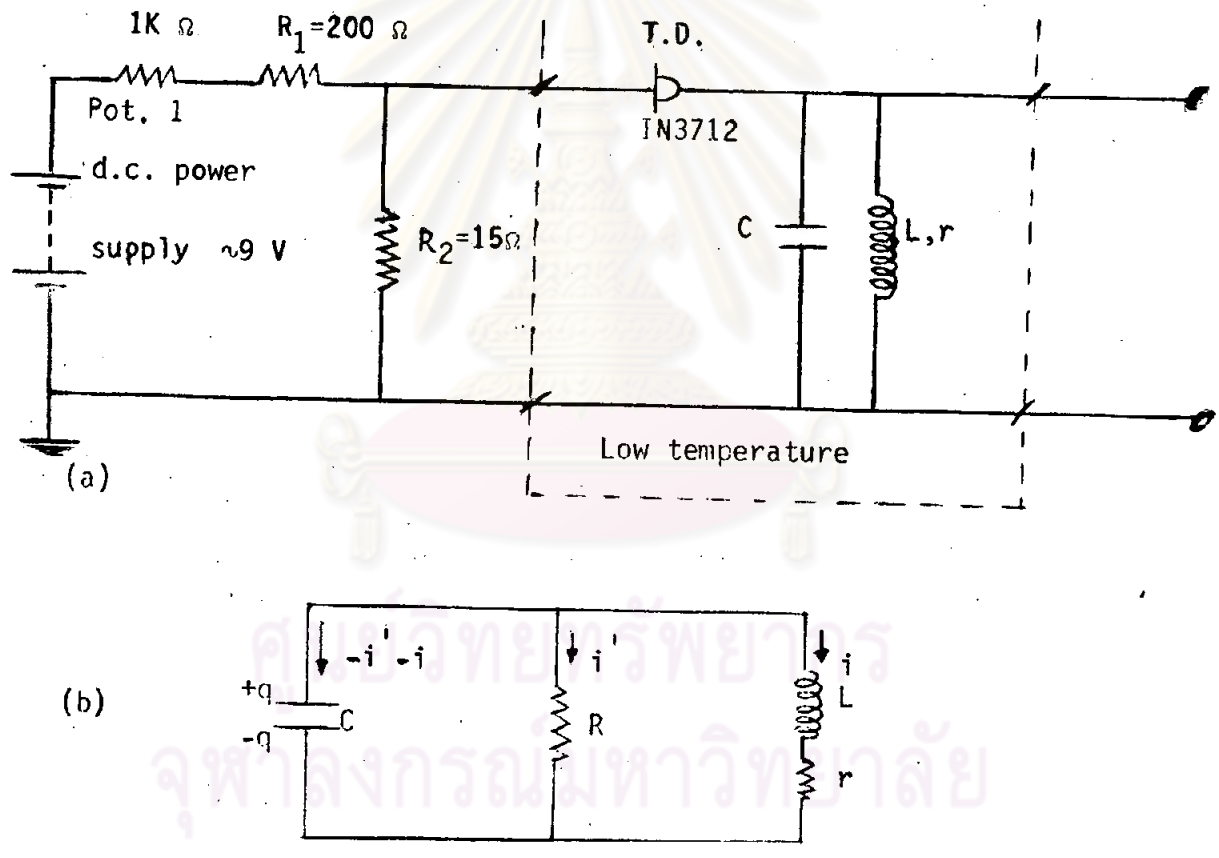

Figure 15 The tunnel diode oscillator

impedance type. The main amplifier is non-inverting amplifier type.

The general tunnel-diode oscillator circuit diagram is shown in Figure 15. For a simple oscillator, where R is the diode resistance C is the total capacitance, and L, r are the inductance and internal resistance of the inductor, circuit equations are

$$i' + i = -\frac{d}{dt} q \tag{2.32}$$

$$\frac{q}{C} = i'R = L\frac{d}{dt} i + ri \tag{2.33}$$

Taking the time derivative of (2.33), we get

$$\frac{d}{dt}\left(L \frac{d}{dt} i + ri\right) = \frac{d}{dt}\left(\frac{q}{C}\right) \tag{2.34}$$

$$= -\frac{1}{C}(i + i')$$

$$= -\frac{i}{C} + \frac{-1}{CR}\left[L \frac{d}{dt} i + ri\right] \tag{2.35}$$

$$L \frac{d^2}{dt^2} i + \left(r + \frac{L}{RC}\right) \frac{d}{dt} i + \frac{1}{C}\left(1 + \frac{r}{R}\right)i = 0$$

$$\frac{d^2}{dt^2} i + \left(\frac{r}{L} + \frac{1}{RC}\right) \frac{d}{dt} i + \frac{1}{LC}\left(1 + \frac{r}{R}\right)i = 0 \tag{2.36}$$

The solution to(2.36)is

$$i = Ae^{-\frac{1}{2}\left(\frac{r}{L} + \frac{1}{RC}\right)t} \sin\left[t\left\{\frac{1}{LC}\left(1 + \frac{r}{R}\right) - \frac{1}{4}\left(\frac{r}{L} + \frac{1}{RC}\right)^2\right\}^{\frac{1}{2}} + B\right] \tag{2.37}$$

For growing oscillation and steady state oscillation, we must choose

$$\frac{1}{2}\left(\frac{r}{L} + \frac{1}{RC}\right) \leq 0$$

For $\frac{1}{2}(\frac{r}{L} + \frac{1}{RC}) < 0$, we have $\frac{r}{L} < -\frac{1}{RC}$

and for $\frac{1}{2}(\frac{r}{L} + \frac{1}{RC}) = 0$, we have $R = -\frac{L}{rC}$

Thus we must take $|R| \leq + \frac{L}{rC}$, where R = negative resistance

For $|R| = \frac{L}{rC}$, we get

$$i = A \sin[\frac{t}{LC} + B] = A \sin[\omega t + B] \qquad (2.38)$$

where $\omega \equiv \frac{1}{LC}$ and $|R| = \frac{(L\omega)^2}{r}$ (2.39)

This last equation may be rewritten as

$$|R| = \frac{(L\omega)}{r}\omega = QL\omega \qquad (2.40)$$

where $Q \equiv \frac{L\omega}{r}$ is "Q-value of coil" (2.41)

Thus we need $Q \geq \frac{|R|}{L\omega} = |R|\frac{C}{L}$ (2.42)

To achieve this condition, the inductance should be large and C be small, in order that $|R| < \frac{L}{Cr}$. For the tunnel diode #IN3712, $|R| \simeq 500\Omega$ or $g_d = 0.002\Omega^{-1}$. Thus the inductor should be composed of 300 loops and C should be 0.02μF. To initiate the oscillation, the d.c. biasing circuit is adjusted until the d.c. load line no longer intersects the low voltage resistance region of the diode but intersects the negative region. For the experimental runs, the operation point is at 0.125 volts on the I-V curve at the negative region, the self sustained oscillation then begins. The r.f. resonant frequency of

about 112 kH_z at room temperature occurs when the coil is empty.

In Figure 16, the design of the buffer amplifier is shown. When we used # μA741 and other components in this amplifier, the non-inverting mode unity gain and high input impedance is obtained. To show that the gain is unity, we first write

$$e_o = -Av_i \tag{2.43}$$

$$e_i + v_i = e_o \tag{2.44}$$

$$v_i = -i\rho \tag{2.45}$$

From (2.43) and (2.44) we have

$$e_i - \frac{e_o}{A} = e_o \tag{2.46}$$

$$\frac{A+1}{A} e_o = e_i \tag{2.47}$$

$$\frac{e_o}{e_i} = \frac{A}{A+1} \simeq \frac{10^4}{10^4+1} \quad 1 \tag{2.48}$$

From (2.43) and (2.45) we get

$$e_o = -A[-i\rho] = +i\rho A \tag{2.49}$$

From (2.46) and (2.47) we have

$$\frac{i\rho A}{e_i} = 1 \tag{2.50}$$

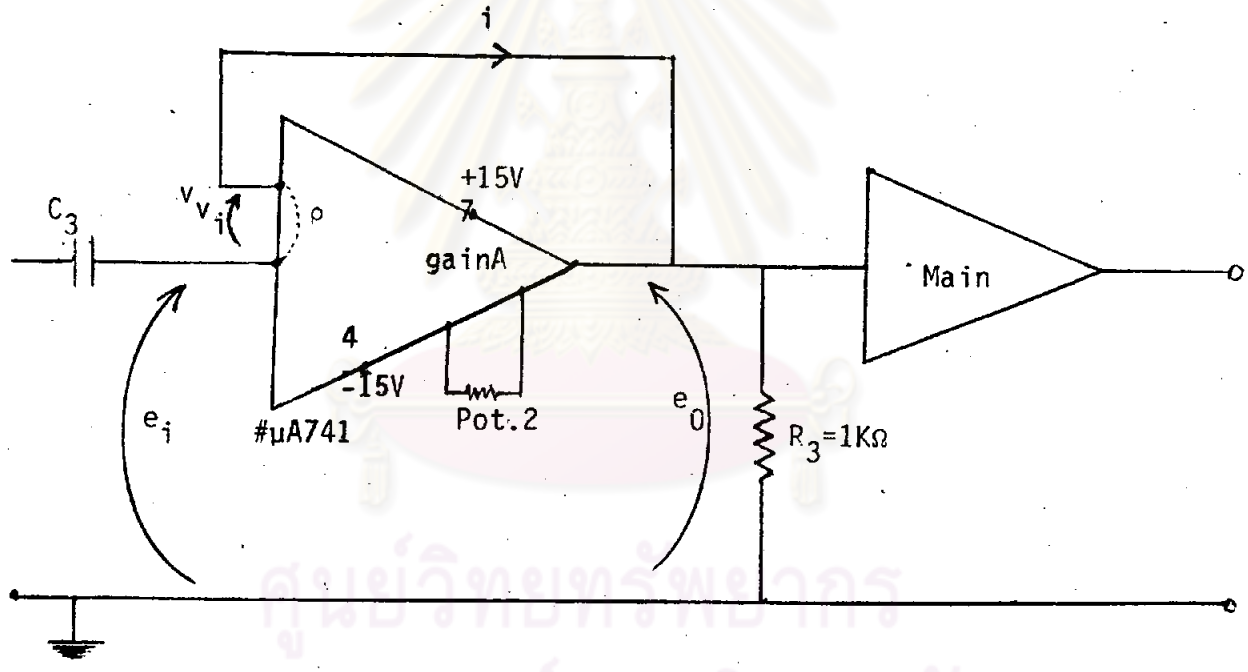

Figure 16 Buffer Amplifier

Impedance is calculated from

$$Z_i \equiv \frac{e_i}{i} = \rho_A \tag{2.51}$$

For # μA741 , ρ is 1 MΩ , so the high input impedance of the buffer amplifier is

$$Z_i \simeq 10^4 \text{ MΩ} \tag{2.52}$$

The main amplifier which we used in our measurement is shown in Figure 17. The gain of this amplifier is high enough so that the frequency counter can be recorded.

The governing characteristics of this amplifier are defined by the following equations

$$e_o = -Av_i \tag{2.53}$$

$$e_i - R_A i + v_i + R_3 i_o = e_o \tag{2.54}$$

$$e_i - R_A i + v_i = R_D(i + i_o) \tag{2.55}$$

$$v_i = -\rho i \tag{2.56}$$

From (2.53) and (2.56), we get

$$e_o = A\rho i \tag{2.57}$$

and (2.54) becomes

$$e_i - R_A i - \rho i + R_B i_o - A\rho i = 0 \tag{2.58}$$

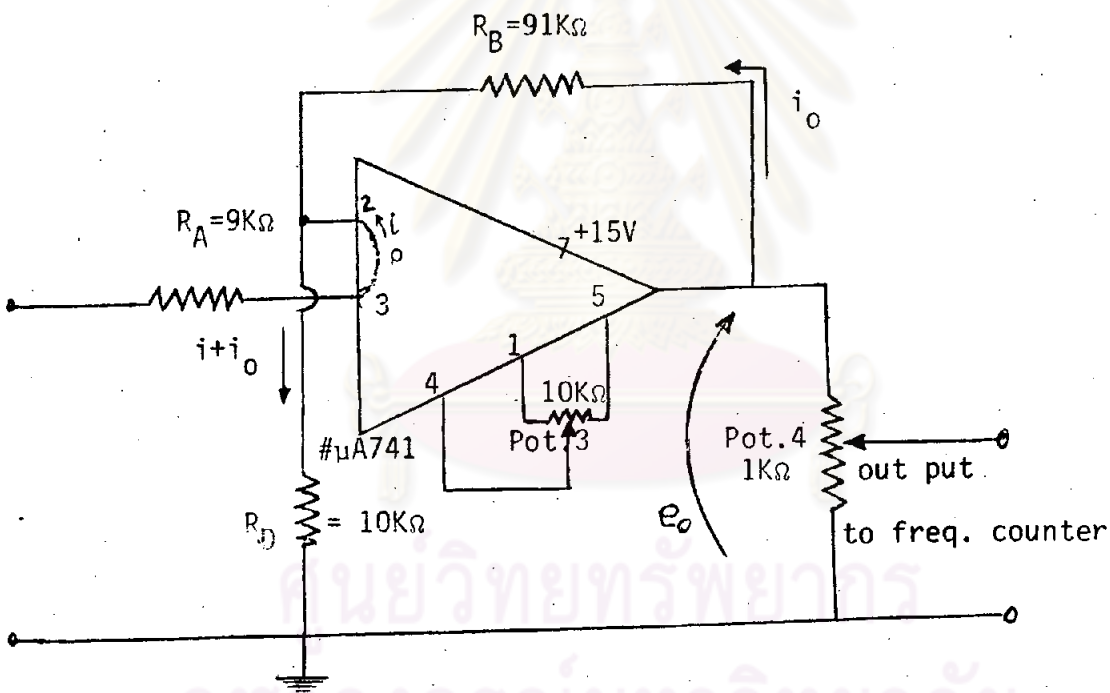

Figure 17 Main Amplifier

$$(A\rho + \rho + R_A)i - R_B\, i_o = +e_i \qquad (2.59)$$

(2.55), can be rewritten as

$$(R_D + \rho + R_A)i + R_D\, i_o = e_i \qquad (2.60)$$

and (2.58) - (2.59) combine to give

$$(A\rho - R_D)i - (R_B + R_D\, i_o) = 0 \qquad (2.61)$$

(2.58) now becomes

$$(A\rho + \rho + R_A)i - R_B\, i_o = e_i \qquad (2.62)$$

Therefore

$$i = \frac{\begin{vmatrix} 0 & -(R_B + R_D) \\ e_i & -R_B \end{vmatrix}}{\begin{vmatrix} (A\rho - R_D) & -(R_B + R_D) \\ (A\rho + \rho + R_A) & -R_B \end{vmatrix}} = \frac{(R_B + R_D)e_i}{(A\rho+\rho+R_A)(R_B+R_D)-(A\rho-R_D)R_B} \qquad (2.63)$$

and the input impedance is given by $Z_i \equiv \frac{e_i}{i}$

$$Z_i' = \frac{(A\rho + \rho + R_A)(R_B + R_D) - (A\rho - R_D)R_B}{(R_B + R_D)} \qquad (2.64)$$

$$Z_i' = \frac{A\rho(R_B + R_D) - A\rho R_B}{R_B + R_D} = A\rho \frac{R_D}{R_B + R_D}$$

for # μA741 , $\rho A = 10^4$ MΩ

$$Z_i' = 10^4 M\Omega \cdot \frac{10}{91 + 10} \approx 10^3\ M\Omega$$

The gain is given by $\frac{e_o}{e_i} = \frac{A\rho i}{e_i} = \frac{A\rho}{(e_{i/i})} = \frac{A\rho}{Z_i}$

With the components used, we find the gain to be

$$\text{gain} \simeq \frac{R_B + R_D}{R_D} \quad \text{for } \rho A \text{ very large}$$

$$\simeq \frac{91 + 10}{10} \Rightarrow 10$$

Therefore, the main amplifier is given the non-inverting and a gain of about ten was obtained.

A variable d.c. power supply of about 9 volts was placed in series with 1KΩ potentiometer and $R_1 = 200\Omega, R_2 = 15\Omega$.

2.2.3 Temperature Measurement

For the temperature measurement, we used a chromel-alumel thermocouple with a sensitive millivoltmeter as a detector for the temperature. One end of the thermocouple is placed closed to the tank coil which is enclosed the sample. The other end, it is connected to a sensitive millivoltmeter. The referent point is taken to be the triple point of water at 0^oC. We were able to measure the temperature of the sample from about 90K to room temperature.

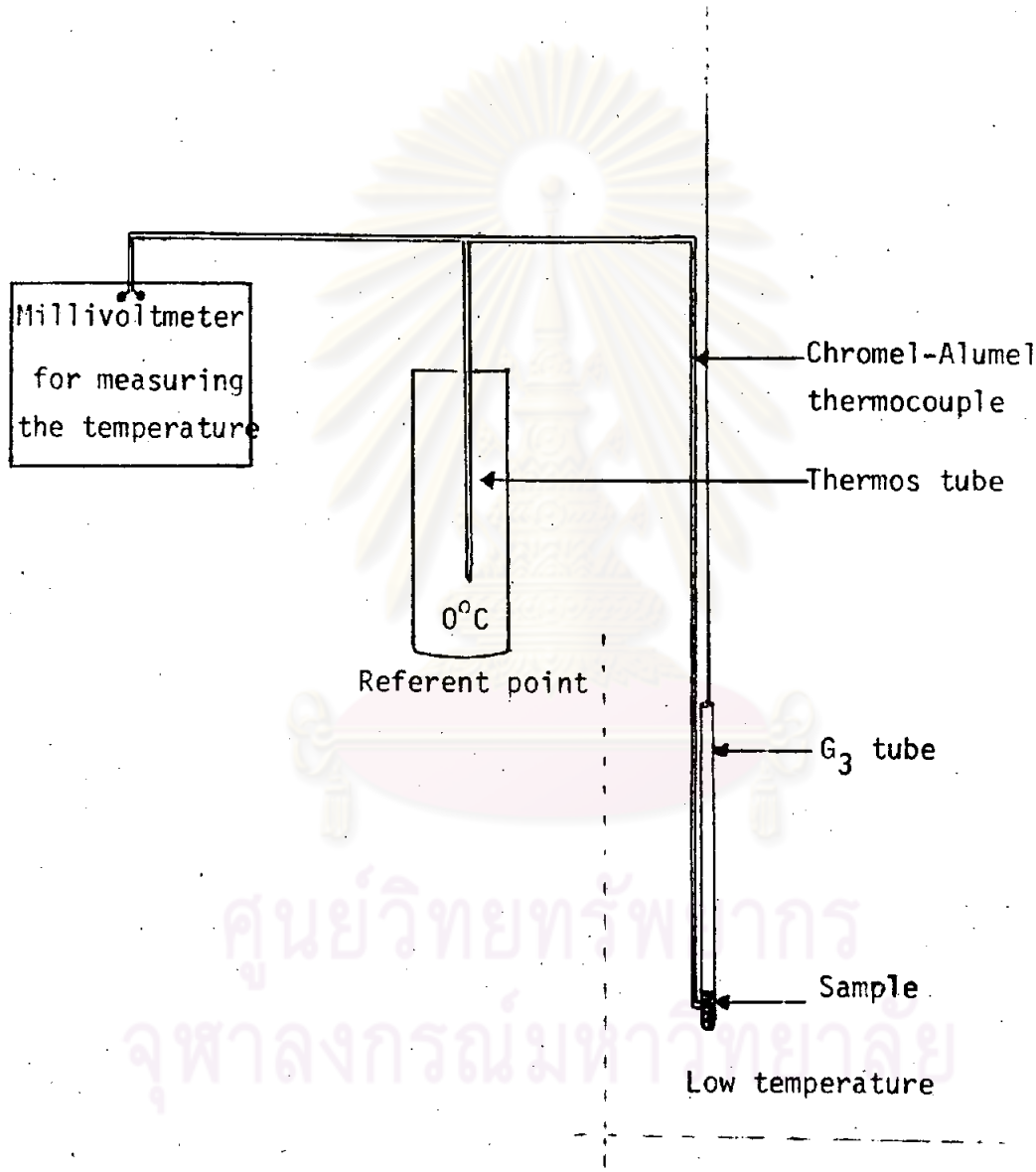

Figure 18 Temperature Measurement

2.2.4 The Experimental Procedure

The apparatus was first tested to make sure that every part of the apparatus work are available without the sample present. The stability of the oscillation was constantly checked.

Powder samples of cupric acetate monohydrate, $Cu(CH_3 . COO)_2 . H_2O$, which is transparent green or blue diamond-shaped plates,[17] were placed inside the G_3 tube. This tube was inserted into the tube, G_2. Both of tubes were then put into the G_1. The glass tubes were evacuated to a pressure of 10^{-5} m.m. Hg. Then they were placed into the dewar containing liquid nitrogen. The tank of the oscillator and the sample would eventually be in thermal equilibrium with liquid nitrogen. The whole apparatus was kept inside the dewar for two hours to be sure that all of them are constant temperature. Once we were sure that every thing was at 77K, we measured the frequencies when the sample was in placed and was out of the coil. The frequencies were recorded with a frequency counter. The temperature of the bath and of the coil was measured at the same time. The data are reliable only when the tunnel diode oscillator is at a fixed temperature. Similar procedure were repeated at 83K (vapour nitrogen temperature), 165K (dry ice and acetone temperature), 212K (dry ice temperature) 273K (the ice temperature) and 300K (at room temperature). At each temperature, the measurement were repeated several times.