TEMPERATURE DEPENDENCE OF NUCLEAR QUADRUPOLE RESONANCE IN $KClO_3$

by

Jacques Vanier

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The Eaton Electronics Research Laboratory,
Department of Physics,
McGill University,
Montreal, Quebec.

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ABSTRACT

The resonant frequency of the Cl^{35} Nuclear Quadrupole in $KClO_3$ has been measured as a function of temperature in the range 16.5°K to 273.2°K. Comparison has been made with Bayer's theory based on lattice vibrations, and agreement is excellent below 80°K. It has been found that the result obtained by Kushida, using an equation of state of the solid, is not exact. The possibility of using this temperature dependence as the basis of a sensitive thermometer also has been studied.

INTRODUCTION

Long before the discovery of Pure Nuclear Quadrupole Resonance in solids by H. G. Dehmelt and H. Krüger (1) in 1951, many nuclei were known to possess a quadrupole moment. Nuclear quadrupole effects were observed in optical spectra by H. Schuler and T. Schmidt (2) as early as 1935. Kellogg and his co-workers (3), in the years 1939, 1940, observed also the effects for free molecules in molecular beam resonance experiments. Later, in 1946, D. K. Coles and W. E. Good (4) reported quadrupole interactions in rotational absorption spectra in the microwave region.

These interactions were subsequently observed in nuclear magnetic resonance. The nuclear quadrupole moments introduced a splitting of the nuclear magnetic energy levels and led to a fine structure of the resonance lines. By investigation of the spectra, useful information was obtained concerning nuclear spins and molecular structures.

R. V. Pound (5), in 1950, announced that it should be possible to excite transitions between the nuclear quadrupole energy levels existing in certain types of molecules in the solid state, without any applied external field. He gave the essential feature of the theory and of the experimental difficulties that could be met. For technical reasons he did not observe any resonances experimentally. At about the same time, H. G. Dehmelt and H. Krüger (1) observed the phenomena in the solid state in trans-dichloroethylene using a super-regenerative oscillator.

Since that time, pure N.Q.R. has been observed for many nuclei in different types of molecules. From the observed spectra, valuable information can be obtained concerning crystal structures, the symmetry of molecules and the ratio of quadrupole moments. In some cases, where the electric field can be calculated from approximate wave functions, the absolute value of the nuclear quadrupole moments can be determined. When the nuclear quadrupole moment is known from another experiment, the principal value of the field gradient tensor can be obtained.

While workers were investigating the characteristics of the new type of resonance, a strong temperature dependence of the resonance frequency was observed. H. Bayer (6) gave a theoretical explanation of this temperature effect. The theory, based on lattice vibrations, was later generalized by Kushida (7). It failed, however, to give detailed agreement with experiment (8, 9). Kushida, Benedek and Bloembergen (8) have shown that the disagreement was mainly due to a shortcoming in the theory, to account for the thermal expansion of the lattice as temperature increases. The theory should agree with experiment below a given temperature where lattice expansion can be neglected.

Considering the phenomena, C. Dean and R. V. Pound suggested the idea that N.Q.R. could be used as a sensitive thermometer. A first investigation of this possibility has been made by Benedek and Kushida; their measurements extended from 350°K to 77°K. The range below this last temperature is important in physics. It is also a difficult range as long as accurate temperature measurements are concerned, since very few types of thermometers are available at these low temperatures; a gas thermometer or a special thermocouple is used in most cases.

The purpose of this thesis is primarily an experimental investigation of the nuclear quadrupole resonance frequency as a function of temperature below 80°K. A review of the theory of N.Q.R. is also given as well as a generalized Bayer's theory of the temperature dependence of the resonance frequency.

Finally, the data obtained in the present experiment is compared with this last theory, and the possibility of using the phenomena as the basis for a sensitive thermometer is investigated.

1. PURE N. Q. R. Theory

Nuclear Quadrupole Resonance, henceforth abbreviated N.Q.R. is very similar to nuclear magnetic resonance, because both are concerned with the detection of radio frequency magnetic absorption. In nuclear magnetic resonance, however, transitions are excited between levels corresponding to different orientations of the nuclear magnetic moments against an applied external field. No such field is needed in N.Q.R.; the energy levels are created by the interaction of a non-spherical nucleus with a non-homogeneous, axially symmetric, electric field existing in certain types of molecules. In that way, the N.Q.R. frequency is a fundamental property of matter.

Starting with the electrostatic interaction between the nucleus and the neighbouring, electric, field, a theory can be developed, giving the energy levels of the quadrupole system. The theory given below will follow very closely that given by H. G. Dehmelt in a recent review article (12).

(a) Electrostatic Interaction.

Consider a nucleus of total charge Ze and charge density ρ'_n represented on figure 1.1 by an enlarged ellipsoid. A system of coordinates (x', y', z') is attached to it; the z' axis coincides with the nuclear axis. Another system (x, y, z), fixed in space, is introduced; an angle θ exists between z and z'. The z axis coincides with the symmetry axis of the molecular electric field produced by the neighbouring ions or electrons. Both origins as well as x and x' axis coincide also. In the following classical treatment the nucleus is assumed to be an ellipsoid of revolution around the nuclear spin. The electrostatic energy of interaction W of such a system can be written as:

$$W = \int \rho'_n \; V(x', y', z') \, dv' \qquad (1)$$

where V(x', y', z') is the potential at the position (x', y', z') and dv' is an element of volume. The integral must be taken over the whole nuclear charge distribution. Expanding V (x', y', z') in a McLaurin's series near the origin, the energy of interaction takes the form:

$$\begin{aligned} W = & \int \rho'_n \; V(o) \, dv' \\ & + \int \rho'_n \left\{ x' V_{x'}(o) + y' V_{y'}(o) + z' V_{z'}(o) \right\} dv' \\ & + \frac{1}{2} \int \rho'_n \Big\{ x'^2 V_{x'x'}(o) + y'^2 V_{y'y'}(o) + z'^2 V_{z'z'}(o) \\ & \qquad + 2x'y' V_{x'y'}(o) + 2x'z' V_{x'z'}(o) + 2y'z' V_{y'z'}(o) \Big\} dv' \qquad (2) \end{aligned}$$

where V(o) is the potential at the origin and where V, followed by a subscript, must be understood as the partial derivative of V in respect to that subscript.

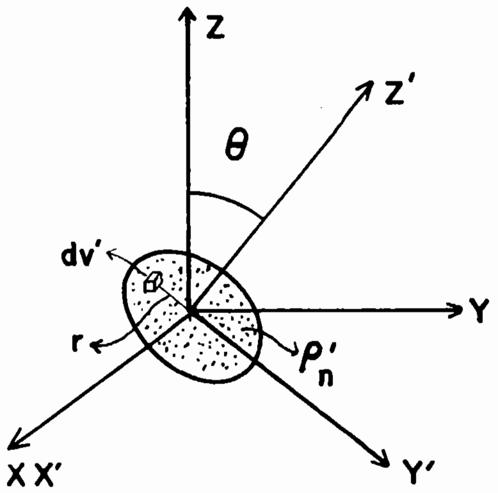


FIG. 1·1 SYSTEMS OF AXIS

$$V_{x'} = \frac{\partial V}{\partial x'} \quad \cdots \qquad V_{x'x'} = \frac{\partial^2 V}{\partial x'^2} \quad \cdots$$

The first integral gives a constant value $Z e V_o$ which is of no interest, since it does not depend on the relative orientation of the two axis (z, z') neither on the size and shape of the nucleus. For the assumed symmetry of the nucleus it can be shown that each term of the second integral vanishes. Each term forms the components of an electric dipole moment and calculation shows that no dipole moment can be associated with an ellipsoidal distribution of charges. This statement is verified experimentally, since no dipole moment has been observed for any nucleus. We are left with the third integral and terms of higher order which are neglected here. It will be shown later that these terms are well negligible. The energy is thus reduced to

$$W = \sum_{i'j'} V_{i'j'} \; e \; Q^{+}_{i'j'} \qquad (3)$$

where i' and j' hold for any x', y', z' and $e\,Q^{+}_{i'j'}$ forms the components of a symmetrical tensor called the "electric quadrupole moment tensor." By tensor analysis, it is seen that, for the case where the principal axis of the quadric representing the tensor coincide with the axis of the chosen system of co-ordinates, all mixed terms (those where $i' \neq j'$) vanish. It could also be shown by direct integration that all mixed integrals

$$\int x' y' \, dv' \; ; \qquad \int x' z' \, dv' \; ; \qquad \int y' z' \, dv'$$

vanish for the assumed symmetry of the nucleus. The expression for the energy is again simplified to

$$W = \sum_{i'i'} V_{i'i'} \quad e \; Q^{+}_{i'i'} \qquad (4)$$

The asterisk on top of Q is to remind us that it is evaluated in respect to the figure axis of the nucleus.

The other terms $V_{i'j'}$ are also the components of a tensor called the "electric field gradient tensor". In the system of axis chosen, this tensor is symmetrical, since the order of differentiation is meaningless, and is not diagonal. Evidently, from equation (4) one needs only consider the diagonal terms. In its principal axis system (x, y, z) this tensor will be diagonal.

We now make use of Laplace equation, which holds at the site of the nucleus since the field is produced by external charges,

$$V_{x'x'} + V_{y'y'} + V_{z'z'} = 0 \tag{5}$$

and of the fact that

$$Q^{+}_{x'x'} = Q^{+}_{y'y'} \tag{6}$$

because of the assumed symmetry (ellipsoid of revolution), to transform equation (4) to

$$W = \frac{1}{2} e\, V_{z'z'} \left\{ Q^{+}_{z'z'} - Q^{+}_{x'x'} \right\} \tag{7}$$

We want now to express $\left\{ Q^{+}_{z'z'} - Q^{+}_{x'x'} \right\}$ as a function of only one quantity. Using

$$r^2 = x'^2 + y'^2 + z'^2 \;; \qquad e\, Q^{+}_{z'z'} = \iint \rho'_n\, z'^2\, dv'$$

we obtain

$$\iint \rho'_n\, x'^2\, dv' = \iint \rho'_n\, (r^2 - y'^2 - z'^2)\, dv'$$

or

$$e\, Q^{+}_{x'x'} = \iint \rho'_n\, (r^2 - z'^2)\, dv' - e\, Q^{+}_{y'y'} \,.$$

From equation (6) we can write

$$e\, Q^{+}_{x'x'} = \frac{1}{2} \iint \rho'_n\, (r^2 - z'^2)\, dv'$$

and replacing the last expression in equation (7) we finally obtain

$$W = \frac{1}{4} V_{z'z'} \int \rho_n' (3 z'^2 - r^2) \, dv' \qquad (8)$$

The integral defines an inherent property of the nucleus and is called e Q^+, the "nuclear quadrupole moment". It measures the departure from spherical symmetry. An ellipsoidal distribution of charges elongated in respect to its symmetry axis has a positive quadrupole moment. If the ellipsoid is flattened, its quadrupole moment is negative. This last case applies to the chlorine nucleus.

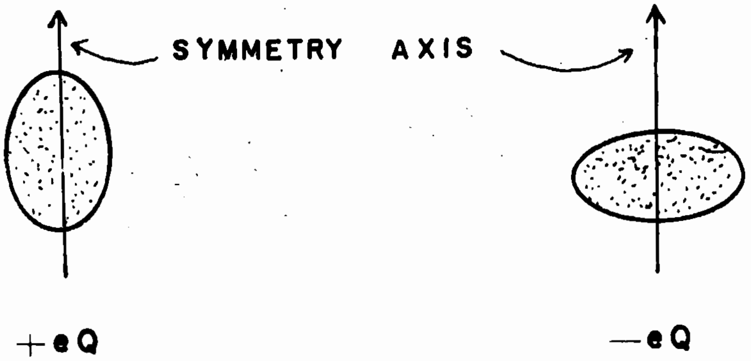


FIG. 1.2 Q.MOMENT SIGN OF SPECIAL DISTRIBUTION OF CHARGES

We can then write:

$$W = \frac{1}{4} e \, Q^+ \frac{\partial^2 V}{\partial z'^2} \qquad (9)$$

We see that the quadrupole moment interacts only with the gradient of an electric field.

Before going any further with the discussion, it is worthwhile making a few comments about the order of magnitude of the successive terms appearing in the expansion (2). The ratio of the hexadecapole term, the next non-vanishing term, to the quadrupole term is of the order of

$$\frac{e^2\, r_n^2/r_e^3}{e^2\, r_n^4/r_e^5} = \left(\frac{r_n}{r_e}\right)^2 \simeq 10^{-8}$$

where r_n, the nuclear radius, has been taken to be of the order of 10^{-12} cm and r_e, an atomic dimension, of the order of 10^{-8} cm. Hence, we are well justified in the neglect of terms following the quadrupole interaction.

The second derivative of the potential in equation (9) has now to be expressed in terms of the co-ordinates of the fixed system which is identical to the system of axis fixed with the molecule. $V_{z'z'}$ is the component of a tensor and a transformation from one system to another must follow all the rules of tensor analysis. This is done in Appendix 1 and the result obtained is

$$V_{z'z'} = \frac{1}{2} V_{zz} (3 \cos^2 \theta - 1). \tag{10}$$

Replacing in equation (9), one obtains:

$$W = \frac{1}{4} V_{zz} \left(\frac{3}{2} \cos^2 \theta - \frac{1}{2}\right) e\, Q^+. \tag{11}$$

This is entirely different from Zeeman effect in which the rate of precession of the nuclear magnetic moment is independent of the angle θ between the applied magnetic field and the nuclear axis:

$$\omega_L = \gamma H_z \,.$$

where ω_L is the Larmor angular frequency and γ is the magnetogyric ratio. In the quadrupole system, the interaction gives rise to a torque that tends to align the nuclear and the molecular axis. The angular momentum

$\sqrt{I\ (I+1)}\ \hbar$ of the nucleus, where I is the spin, will respond to the torque by a precession, the rate of which will depend on θ in the following way. The rate of change of the angular momentum p of the precessing nucleus is given by the two following fundamental equations:

$$\frac{\partial p}{\partial t} = \omega \times p$$

$$\frac{\partial p}{\partial t} = \Gamma = \frac{\partial W}{\partial \theta} = -\frac{9}{4} V_{zz}\, e\, Q^{+} \cos\theta \sin\theta$$

where Γ is the torque. Combining these two equations one obtains:

$$\omega = -\frac{9}{4} \frac{e\, Q^{+}}{p} V_{zz} \cos\theta.$$

Since p is a constant not depending on θ, we see that the precession is a maximum at $\theta = 0$ slows down as θ increases, comes to a standstill at $\theta = \pi/2$ and reverses its sign to increase between $\theta = \pi/2$ and $\theta = \pi$. Quantum mechanically this is reflected by different spacings between the energy levels.

It can be seen from figure 1.3, that the nuclear magnetic moment $\vec{\mu}$ associated with the nucleus is precessing at the same rate than the quadrupole moment. In making an absorption experiment, it is obvious that appreciable coupling with a rotating magnetic field will take place only with the magnetic moment; while the quadrupole moment will not be subject to any appreciable interaction.

(b) Hamiltonian Operator and Quantum Mechanical Energy Eigenvalues.

The hamiltonian of the quadrupole system is formed by replacing in equation (11) cos θ by its quantum mechanical operator I_z/I obtained from figure 1.3. Then

$$H_{op} = \frac{1}{8}\, e\, Q^{+} V_{zz} \left(\frac{3\, I_z^{2} - I^{2}}{I^{2}} \right) \qquad (12)$$

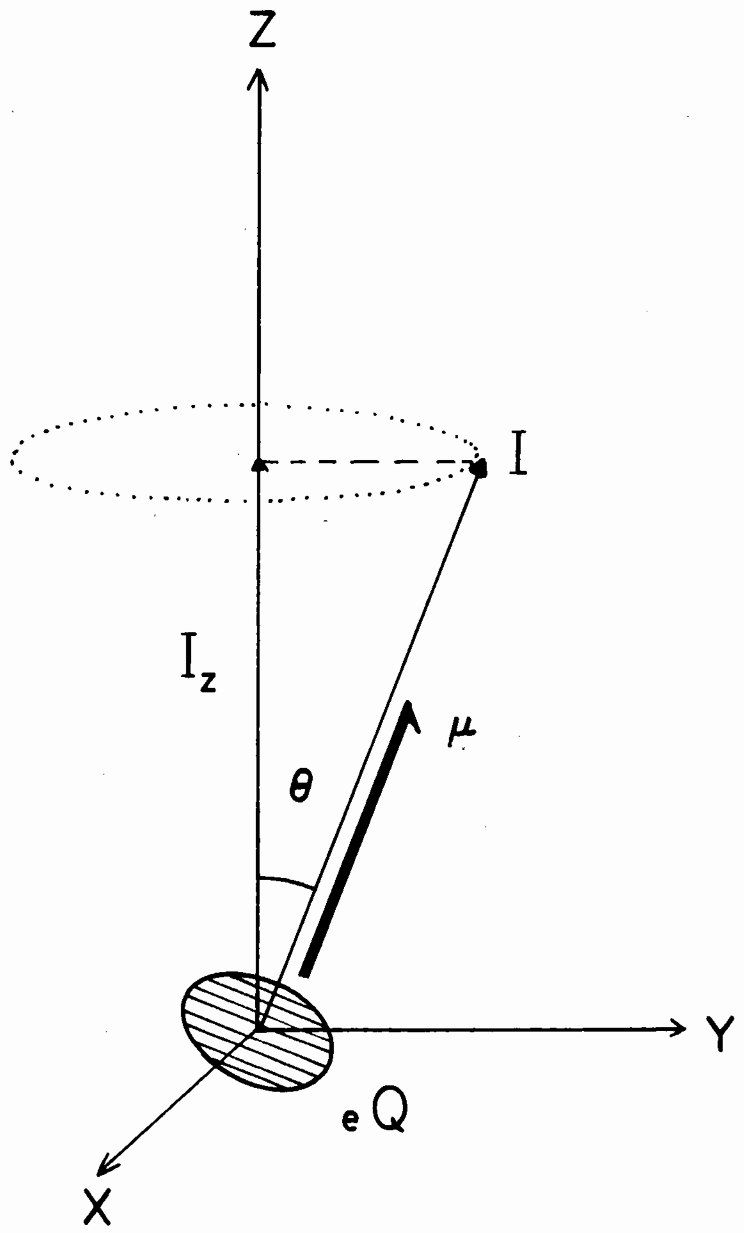


FIG. 1·3 PRECESSION OF I, μ AND eQ.

Since the projection of the angular momentum on an axis of quantisation is a constant of motion, and since its square is also a constant of motion, we can substitute directly the eigenvalues m_z and $I(I + 1)$ for the operators I_z and I^2 in equation (12). The energy eigenvalues are thus

$$E_m = \frac{1}{8} \, e \, Q^+ \, V_{z\,z} \left(\frac{3m_z^2 - I(I + 1)}{I(I + 1)} \right) \qquad (13)$$

In this equation, as said previously, $e \, Q^+$ has been evaluated in respect to the figure axis of the nucleus. That differs from the usual definition of $e \, Q$ which is to be taken for the aligned state $m = I$, even if quantum mechanical complete alignment is not possible. In that state $(\rho_{m = I})$ is axially symmetric in respect to the axis of symmetry z of the electric field. For $\theta = o$, z' coincides with z and equation (8) becomes:

$$E_{m = I} = \frac{1}{4} V_{z\,z} \int \rho_n \, (3z^2 - r^2) \, dv = \frac{1}{4} \, V_{z\,z} \, e \, Q. \qquad (14)$$

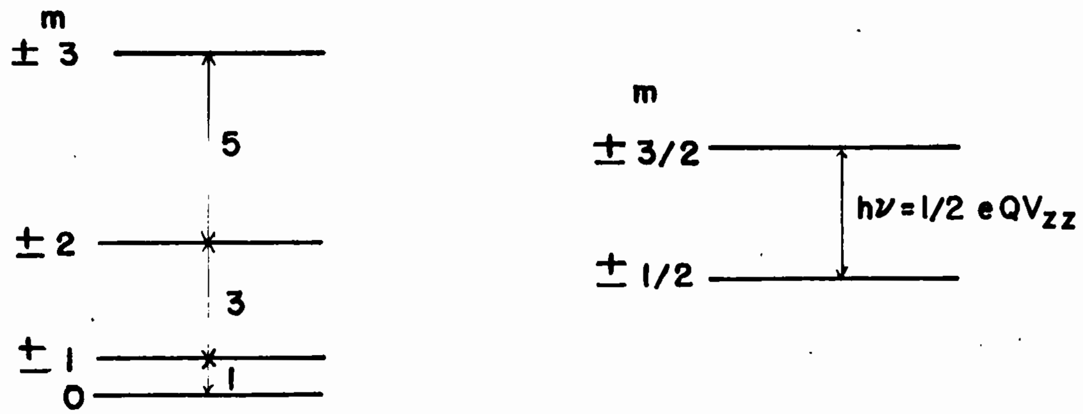
Equating this with the energy eigenvalue for the state $m = I$ given by (13), one obtains:

$$Q^+ = 2Q \; \frac{(I + 1)}{(2I - 1)} \qquad (15)$$

Finally, the energy levels are:

$$E_m = \frac{1}{4} \, e \, Q \, V_{z\,z} \left(\frac{3m^2 - I(I + 1)}{I(2I - 1)} \right) \qquad (16)$$

For $I = 0$ the charge distribution is spherically symmetric and from equations (14) and (15) the quadrupole moment vanishes. For $I = \frac{1}{2}$ equation (16) vanishes. For $I \geqslant 1$ we have energy levels which are degenerate in respect to the sign of m. The energy levels are shown in figure (4) for $I = 3$ (integer) and for the special case of the chlorine nucleus where $I = \frac{3}{2}$.



I·INTEGER

I = 3/2 (Cl. NUCLEUS)

FIG. 1.4 N.Q. ENERGY LEVELS

In this figure, for I integer, the spacings are multiples of the unit of energy $3\,e\,Q\,V_{z\,z}/4\,I(2I - 1)$. From the known experimental absorption frequency it is seen that, from a knowledge of Q, the gradient of the electric field, $V_{z\,z}$, can be evaluated. For the case where the symmetry of the electric field is only approximate an asymmetry parameter may be defined:

$$\eta = \frac{V_{x\,x} - V_{y\,y}}{V_{z\,z}}\,.$$

The asymmetry can be determined from the observed zero field (magnetic) spectrum except for $I = \frac{3}{2}$. Since this is the case of interest here, and since η is rather small in potassium chlorate which is the studied sample, the effect will not be considered further.

(c) Zeeman Splitting.

If the quadrupole system is subjected to a small magnetic field, a Zeeman splitting of the energy levels is obtained and the ± m degeneracy is affected. Two cases must be considered.

1. Single Crystal

If the magnetic field is parallel to the electric field axis, the magnetic contribution to the energy levels can be written down at once since I_z is still diagonal. Hence

$$E_m = E_Q - \frac{\mu_I H_z}{I} m_z \qquad (17)$$

The ± m degeneracy is thus removed (see figure 1.5).

When the magnetic field makes an angle θ with the electric field axis a perturbation calculation (13) shows that the field mixes both states $m = \pm \frac{1}{2}$ creating two new states 1, 2, given by

$$E_{1,\,2} = \pm \frac{1}{2} \frac{\mu_I}{I} H \sqrt{(I + \frac{1}{2})^2 \sin^2 \theta + \cos^2\theta} \qquad (18)$$

For θ = 90°, the new contribution is reduced to

$$E_{1,\,2} = \pm \frac{1}{2} \frac{\mu_I}{I} H (I + \frac{1}{2}). \qquad (19)$$

Figure 1.6 represents this other extreme case where θ is the angle between the magnetic field and the molecular axis.

2. Powder

If the sample is in the form of a powder, the relative orientation of the electric field axis and the magnetic field will be random, and a band of closely spaced energy levels will be obtained. The resonance frequency will then be spread out over a wide range. This spread, as it will be seen later, is found to be very convenient. It provides a means of modulating the absorption line by the application of a square-wave, magnetic, field (on-off) on a sample composed of a great quantity of small crystals.

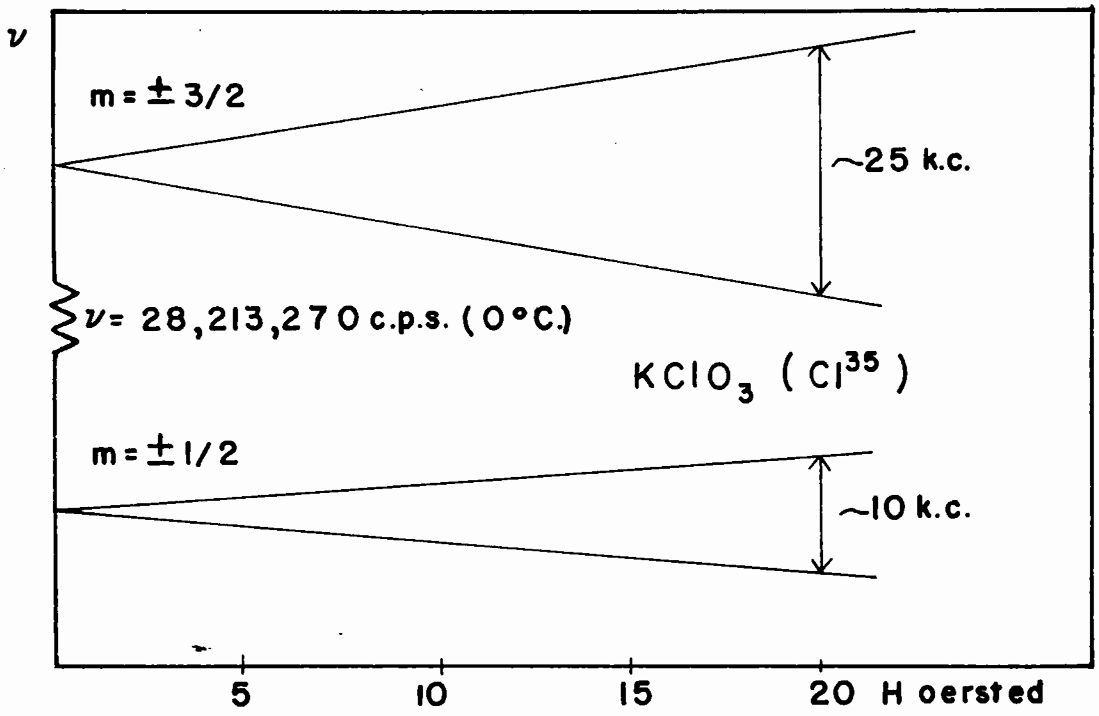


FIG. 1·5 Q.S. ENERGY LEVELS $\theta = 0°$

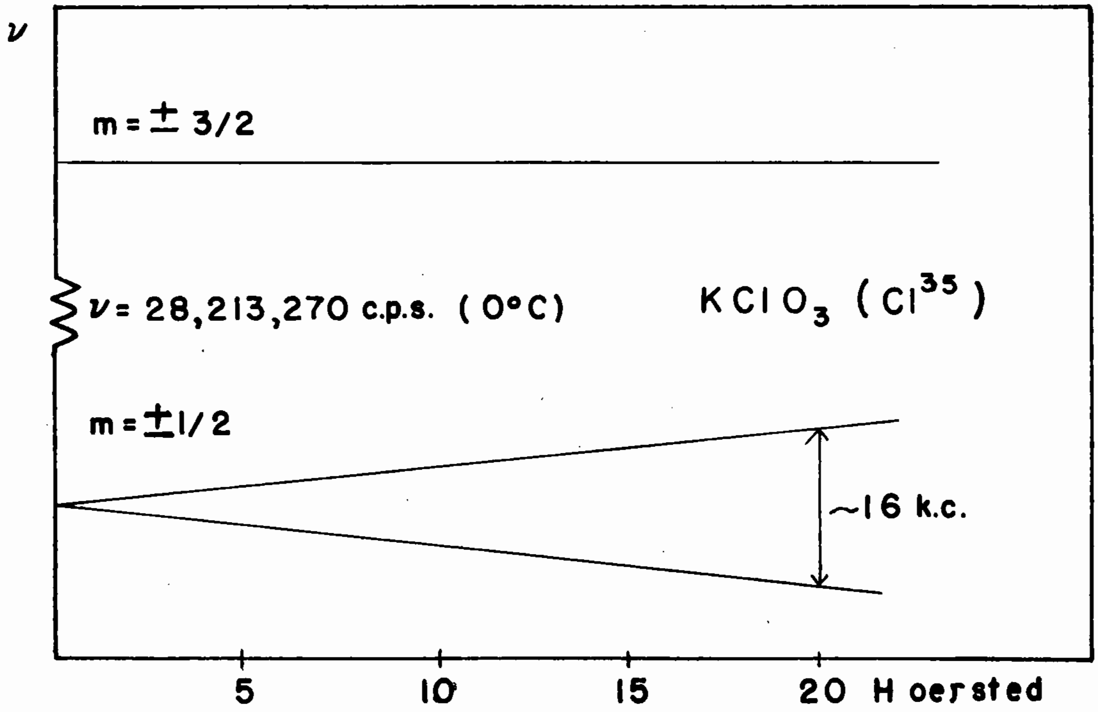


FIG. 1.6 Q.S. ENERGY LEVELS $\theta = 90°$

2. N. Q. R. TEMPERATURE DEPENDENCE THEORY

Soon after N.Q.R. has been discovered in solids (1), a strong temperature dependence of the resonance frequency was observed. A theory whose objective would be an accurate explanation of the phenomena, would have to consider many factors, because a change in temperature will be accompanied by the following effects:

(i) The amplitude of the lattice vibrations increases with increasing temperature, decreasing subsequently the average value of the maximum principal axis of the field gradient tensor.

(ii) The accompanying increase in volume affects the lattice dimensions, changing the field at the nucleus.

(iii) Due to the precedent change in the lattice dimensions, the constants of the lattice, like the restoring forces on each molecule, are modified. The frequency spectrum of the lattice vibrations is then changed and the first effect is altered.

The effect (i) investigated first by Bayer (6) for a special mode of vibration and later generalized by Kushida (7) for all lattice and molecular modes, answers for the general form of the temperature dependence. The increase in volume which accompanies an increase in temperature is mostly effective only at intermediate and high temperatures, as will be seen from the results of the present experiment. This seems reasonable since the thermal expansion is not expected to be constant at all temperatures, but should decrease in the same manner as specific heat at low temperatures (14, 23). The effect has been studied by Kushida Benedek and Bloembergen for $K\,C\ell\,O_3$ and similar substances, at temperatures above 77°K (liquid nitrogen). Since from their data the effects (ii) and (iii) seem to decrease quite rapidly with temperature, and since the present experiment has been done, mostly below 80°K, only the first effect will be considered. The theory given here will follow closely the one given by Kushida (7), except that no approximation for high temperatures will be made.

In this theory it is assumed that the field gradient tensor is caused to fluctuate by the vibrations of the lattice. These vibrations, as given by Raman spectroscopy, are of the order of 10^{12} $\sec^{-1}$; the N.Q.R. frequency being of the order of 10^6 $\sec^{-1}$, we are allowed to consider only their average over time. Let us consider a general mode of oscillation of the molecules, say ω_i. The principal axis of the field gradient along the z direction, which is the only one effective on the energy levels, when the asymmetry parameter is zero, will then vibrate at that frequency. In $K\,C\ell\,O_3$, the asymmetry parameter is not zero, but is small and its variation will be neglected here. Let us call V_{oo}, the maximum value of the principal axis of the field gradient tensor. A (x'y'z') system of axis is fixed to the principal axis of the tensor, and follows it in its motion due to thermal vibrations. Another system called (x, y, z) is also fixed with the principal axis of the tensor at its equilibrium value. It is clear that V_{oo} is always equal to $V_{z'z'}$ if this last one is not affected in length by the vibrations. We can then use equation (10), transforming it for these two new systems (see Appendix 2).

$$V_{zz} = \left\langle V_{z'z'} \right\rangle \left(\frac{3}{2} \left\langle \cos^2 \theta \right\rangle - \frac{1}{2} \right) \tag{20}$$

where θ is the angle between z and z' and the brackets mean that we must average over time. $V_{z'z'}$ is also put into brackets, since it is fairly obvious that a distortion of the molecule due to the lattice vibrations will also be effective on its magnitude. For small amplitude

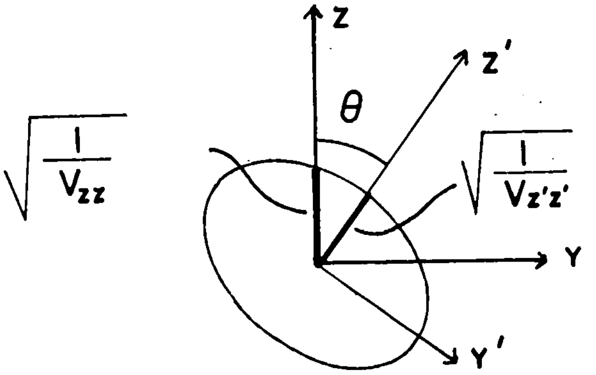


FIG. 2.1 FIELD GRADIENT TENSOR ELLIPSOID

$\cos\theta \simeq 1 - \frac{\theta^2}{2}$ and equation (20) becomes:

$$V_{z\,z} = \left\langle V_{z'z'} \right\rangle \left(1 - \tfrac{3}{2}\left\langle \theta^2 \right\rangle\right).$$

Replacing in equation (16)

$$E_m = e\,Q\,\frac{3m^2 - I(I+1)}{4(2I-1)\,I}\left\langle V_{z'z'}\right\rangle\left(1 - \tfrac{3}{2}\left\langle\theta^2\right\rangle\right)$$

Assuming $\Delta m = \pm 1$ and $I = \frac{3}{2}$ for the chlorine nucleus,

$$\nu = \frac{e\,Q\left\langle V_{z'z'}\right\rangle}{2h}\left(1 - \tfrac{3}{2}\left\langle\theta^2\right\rangle\right) \qquad (21)$$

We can now expand θ and $V_{z'z'}$ in terms of the normal co-ordinates of the lattice vibrations ξ_i

$$\theta = \sum_i \left(\frac{\partial\theta}{\partial\xi_i}\right)_0 \xi_i + \frac{1}{2}\sum_{i\,j}\left(\frac{\partial^2\theta}{\partial\xi_i\,\partial\xi_j}\right)_0 \xi_i\xi_j + - - -$$

$$V_{z\,z} = V_{oo}\left(1 + \sum_i\left(\frac{\partial V}{\partial\xi_i}\right)_{V_{oo}} \xi_i + \frac{1}{2}\sum_{i\,j}\left(\frac{\partial^2 V}{\partial\xi_i\,\partial\xi_j}\right)_{V_{oo}} \xi_i\xi_j + - - -\right)$$

Assuming harmonic lattice vibrations, we can write

$$\xi_i = \xi_i^{o} \sin(\omega_i t + \phi_i)$$

where ϕ_i is a phase angle; the averages of θ^2 and $V_{z'z'}$ are then easily calculated:

$$\left\langle \theta^2 \right\rangle = \sum_{i\,j} \left\langle \alpha_i \, \alpha_j \, \xi_i \xi_j \right\rangle$$

where α_k stands for $\left(\frac{\partial \theta}{\partial \xi_k}\right)_{V_{oo}}$ and higher terms are neglected, being consistant with the approximation that θ is small. Hence

$$\left\langle \theta^2 \right\rangle = \sum_i \frac{1}{2} \, \alpha_i^{\,2} \, \xi_i^{o2} + \text{cross terms} \qquad (22)$$

For non-degenerate modes $(\omega_i \neq \omega_j)$ the cross terms vanish, when they are averaged over time. For degenerate modes $(\omega_i = \omega_j)$ the cross terms are of the form

$$\alpha_i \, \alpha_j \, \xi_i^{o} \, \xi_j^{o} \left\langle \sin(\omega_i t + \phi_i) \sin(\omega_i t + \phi_j) \right\rangle$$

$$= \frac{1}{2} \, \alpha_i \, \alpha_j \, \xi_i^{o} \xi_j^{o} \left\langle \cos(\phi_i - \phi_j) \right\rangle$$

Owing to random fluctuations (lifetime of a mode being 10^{-11} sec) (7) $(\phi_i - \phi_j)$ will be completely averaged out over a Larmor frequency of the nucleus, and we can put:

$$\left\langle \cos(\phi_i - \phi_j) \right\rangle = 0.$$

With similar considerations on $\left\langle V_{z'z'} \right\rangle$, one obtains

$$\left\langle V_{z'z'} \right\rangle = V_{oo} \sum_i \frac{1}{2} \quad \delta_{ii} \; \xi_i^{o2} \qquad (23)$$

where δ_{ii} stands for $\left(\frac{\partial^2 V}{\partial \xi_i^{2}}\right)_{V_{oo}}$. The resonance frequency is then, replacing equations (22) and (23) in equation (21):

$$\nu = \nu_o \left(1 - \frac{3}{4} \sum_i \xi_i^{o2} \, A_i\right) \qquad (24)$$

where

$$A_i = \alpha_i^2 - \frac{2}{3}\delta_{ii}$$

and $\nu_o = e\,Q\,V_{oo}/2h$ is the resonant frequency at zero amplitude lattice vibrations. The amplitude ρ_i^{o2} is then obtained by assuming that the mean energy of each normal mode is equal to the mean energy of the corresponding Planck's oscillator:

$$\frac{1}{2}\omega_i^2\,\rho_i^{o2} = \hbar\,\omega_i\left(\frac{1}{2} + \frac{1}{\exp\frac{\hbar\omega_i}{kT} - 1}\right) \tag{25}$$

Replacing ρ_i^{o2} in (24)

$$\nu = \nu_o\left(1 - \frac{3}{2}\sum_i \frac{\hbar A_i}{\omega_i}\left(\frac{1}{2} + \frac{1}{\exp\frac{\hbar\omega_i}{kT} - 1}\right)\right) \tag{26}$$

The physical meaning of A_i is not simple in the general case of molecular vibrations. But for special modes, like a torsion of the molecule around an axis perpendicular to the z axis we can write (see Appendix 3)

$$A_i = \Theta_i^{-1}$$

where Θ_i^{-1} represents (moment of inertia)$^{-1}$. In $K\,Cl\,O_3$ the field gradient at the position of the nucleus is produced primarily by ionic and covalency bonding in the $Cl\,O_3^-$ group with a few percent ionic contribution from the K^+ ion (8). The K^+ vibrations should then contribute very little to the temperature dependence of the resonance frequency.

The $K\,Cl\,O_3$ Raman spectrum can be divided into a high and a low frequency group. The former corresponds to internal vibrations of the $Cl\,O_3^-$ ion. Kushida (7) has shown that these internal oscillations do not contribute much to the change in the resonance frequency. Furthermore, owing to the appearance of ω_i in the denominator and the exponential term of equation (26), the contribution from the high frequency vibrations is much smaller than that from low frequency.

We can then reduce the summation to one over modes corresponding to a torsion or a tilting of the $C\ell\, O_3^-$ group as a whole, and write Θ_i^{-1} the moment of inertia associated with these types of motion instead of A_i. Thus, we have:

$$\nu = \nu_o \left(1 - \frac{3}{2} \sum_i \frac{h}{\omega_i \Theta_i} \left(\frac{1}{2} + \frac{1}{e^{\frac{\hbar\omega_i}{kT}} - 1}\right)\right) \tag{27}$$

The rate of variation of ν with T can be obtained directly by differentiation of (27)

$$\left(\frac{d\nu}{dT}\right)_T = -\frac{3}{2} \nu_o \sum_i \frac{h}{k\,\Theta_i} \frac{1}{T^2} \frac{e^{\frac{\hbar\omega_i}{kT}}}{\left(e^{\frac{\hbar\omega_i}{kT}} - 1\right)^2} \tag{28}$$

From this, we see that, at low temperatures, the important term is $e^{-\hbar\omega_i/kT}$. So, the rate of change of ν with temperature should decrease in the same manner as that given by Einstein for the specific heat of a solid. If an experiment could be worked out at sufficiently low temperatures, it would be possible to verify this last equation, and by the same fact the consistency of the whole theory. Unfortunately, as will be explained later, resonances are difficult to obtain below 15°K, and equation (28) cannot be verified accurately.

From these lattice vibration effects one can see also the possibility of determining with what type of motion of the molecule, one mode, observed in Raman spectroscopy, can be associated. This is due to the fact that, as will be seen later, only two normal modes out of three of the $C\ell\, O_3^-$ group vibrations, are effective in modifying the N.Q.R. frequency. These normal modes are approximately of the same frequency; the same moment of inertia can be associated with them. From an analysis of the experimental data one can find the ω_m that gives the best fit and compare it to the closer value in the Raman spectrum; then, in the case of $K\,Cl\,O_3$, $Na\,Cl\,O_3$ or similar substances, this frequency can be associated to a tilting motion of the $Cl\,O_3^-$ group as a whole.

3. APPARATUS

(a) General Considerations.

Among the various ways of detection of nuclear resonance in solids, the simplest is the marginal oscillator method described here and used in the experiment. In that type of detector the sample is made the core of a radio-frequency coil which is paralleled by a variable air capacitor. The combination forms a resonant circuit to which energy is supplied by a vacuum tube circuit incorporating positive feedback. The amplitude of oscillation is maintained at a very low level. The purpose of this is twofold: first, a small field applied to the sample will not lead to an equalization of the population of the energy levels, i.e. saturation, with a subsequent decrease in signal strength; secondly, any small change in the Q of the coil, due to nuclear absorption, will be reflected by a relatively great change in the level of oscillation.

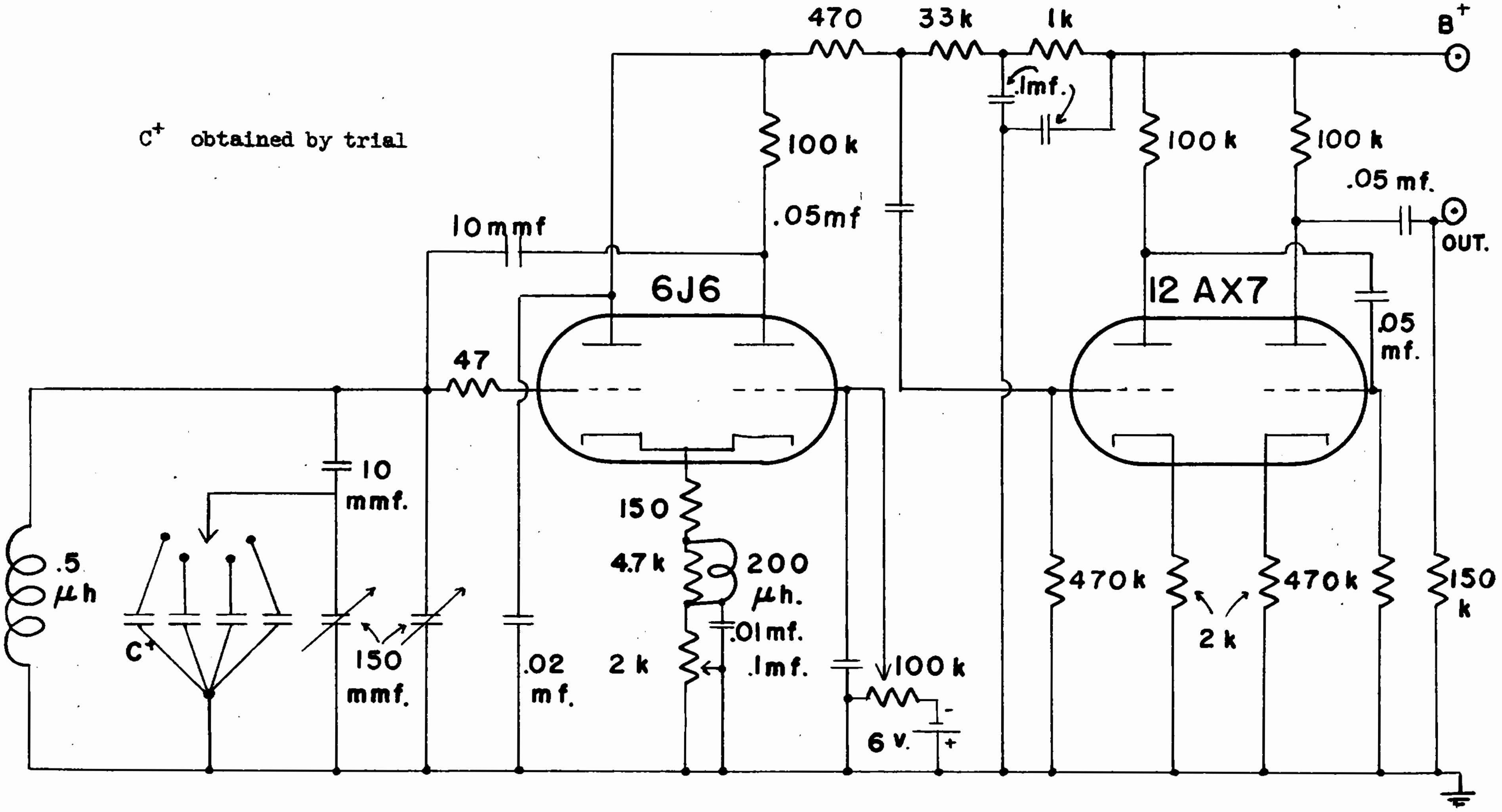
The absorption line is obtained by either frequency or magnetic field modulation of several times its width, and is observed on an oscillograph. It can be displayed, also, by recording techniques like that used here.

Although the marginal oscillator method is one of the most sensitive in nuclear magnetic resonance, the same statement is not true for nuclear quadrupole resonance. In this last experiment, short relaxation times permit the use of a rather large sample and a large amount of power. It is found that noise increases with the r.f. level in a marginal oscillator; in practice most workers use a super-regenerative oscillator which can operate at high r.f. level without a proportional increase in noise. The marginal oscillator was used here because of its greater frequency stability, even if poorer signal to noise ratios were obtained.

(b) The Oscillator.

The oscillator employed in this experiment was a version of the Pound-Knight-Watkins, marginal oscillator (15, 16) suggested by Cowen and Tantilla (18). In this circuit, the oscillator made use of a 6-J-6 double triode, and the signal was detected directly at the plate by an appropriate bias on the cathode. The r.f. was by-passed at the same point. The audio signal was then amplified by a double triode (12 AX7). The level of oscillation was controlled by the application of a negative d.c. voltage on the second grid of the 6-J-6 oscillator tube. Some modifications were made in the suggested circuit. First, the capacitors of the audio amplifier were found to be too small and introduced phase lags. Since phase detection was used in a later stage, these had to be avoided, and the coupling capacitors were increased. Furthermore, a motor-driven condenser with different sweep rates was introduced. This last device permitted a very convenient way of sweeping the oscillator frequency through the resonance line at different speeds.

In building such an oscillator one must take care of many factors. One of its qualities is a good frequency stability, as was said previously. This is very important in the experiment, since great accuracy is needed in the determination of the frequency of the line centre. The stability was further improved by using a chassis made of 3/8" brass plate, and by keeping all leads as short as possible. The filament current was taken from a 6 volts d.c. accumulator, and a charger was always clipped across its terminals. For the B^+ a λ regulated power supply preceeded by a Sorensen line voltage regulator was used. The frequency stability obtained with this arrangement and the probe described below was better than 1 part in 10^6 when frequency was swept at a rate of 3 kc per minute. The present system has been preferred to



C+ obtained by trial

FIG.3·1 N.Q.R. OSCILLATOR DETECTOR

the usual detector incorporating an r.f. amplifier for its simplicity. The signals observed were strong enough, and good determination of the frequency of the line centre could be made.

(c) The Probe.

The purpose of the present experiment being a study of the N.Q.R. frequency at low temperatures, the design of a probe must take care of many technical details. The most important of these are as follows:

(1) In order to avoid heat conduction to the refrigerant, the coaxial cable connecting the coil to the chassis must be of low thermal conductivity.

(2) At temperatures below 77°K air liquefaction may take place between the inner and outer conductors of the coaxial cable. Due to the air condensation, changes in the dielectric constant may occur between the two conductors with subsequent change in the oscillator frequency. Hence, the space between the two conductors must be filled with an insulating material.

(3) For reason of frequency stability the cable must be rigid.

(4) Finally, the r.f. coil must be shielded from external effects and still have a high Q for greatest sensitivity. This part should also form a big mass, so that variations in temperature for relatively long periods of time would be small.

A probe which fulfils in great part the preceeding requirements has been built. The outer conductor of the coaxial cable was made of a monel tube, which has small thermal conductivity and relatively good electrical conductivity. The inner conductor consisted of a small capillary copper tube; the space between them was filled almost entirely with a glass

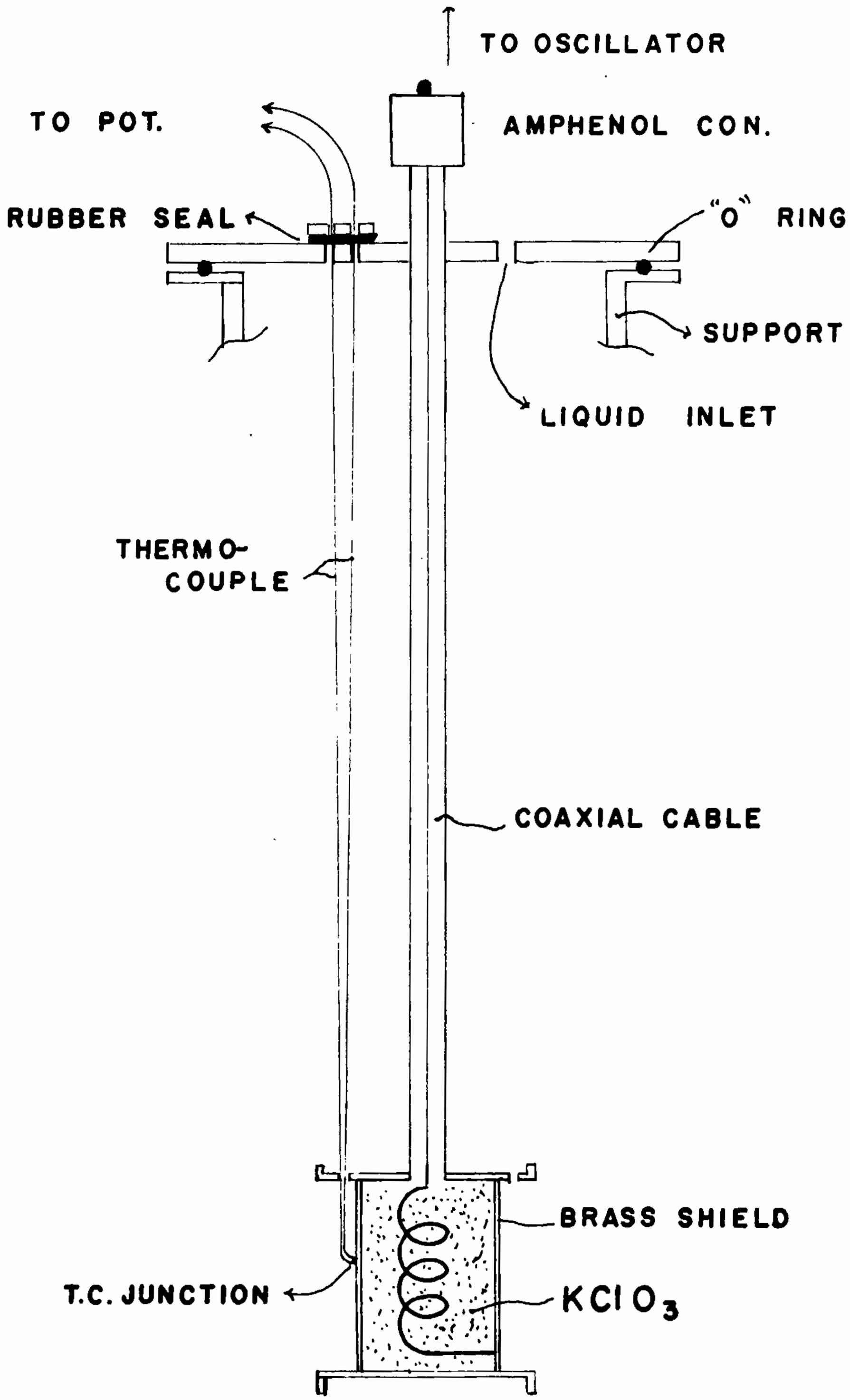

TO OSCILLATOR
TO POT.
AMPHENOL CON.
RUBBER SEAL
"O" RING
SUPPORT
LIQUID INLET
THERMO-COUPLE
COAXIAL CABLE
BRASS SHIELD
T.C. JUNCTION
KClO3

FIG. 3.2 PROBE

cylinder, and both ends were sealed with plastic. The r.f. coil was soldered at the end of the coaxial cable, and was shielded by a 1 mm thick, 4 cm long brass tube, forming the potassium chlorate container, and giving a filling factor near unity. As seen in (b), the probe gave good result with respect to frequency stability. The thermal conduction was very small. Nevertheless, the Q of the coil was not found to be very high, but the signals were strong enough to make accurate measurements. The reduction of the Q was mainly due to a loss of energy to the brass shield.

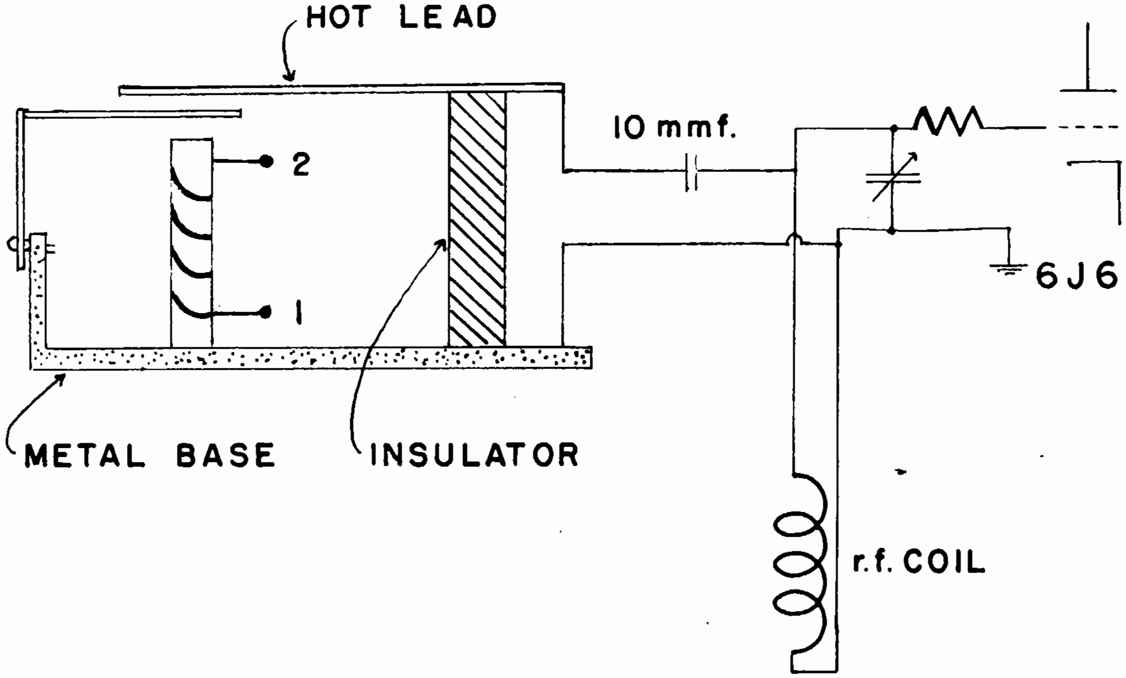
(d) Modulation.

The onset of nuclear resonance causes the oscillation level to decrease by reason that energy is absorbed from the r.f. coil. A d.c. technique could be used to detect the change of the oscillation amplitude. Nevertheless, it has a serious inconvenience since d.c. amplifiers are not stable and drift. The nuclear signals are small and could be masked by these drifts. In N.M.R., where a magnetic field of several thousands of oersteds is applied, the absorption signal is easily observable: an a.c. component of several oersteds is superimposed on the steady magnetic field. The nuclear absorption then appears as a modulation of the radio frequency kept fixed, while the Larmor frequency of the nuclei is swept by the a.c. component of the magnetic field. After detection, the signal can be amplified by an a.c. technique and observed on a scope. The magnetic field modulation is easily done in practice: a pair of Helmotz coils are wound around the two poles of the magnet. The necessary current is small, and no serious problems are encountered.

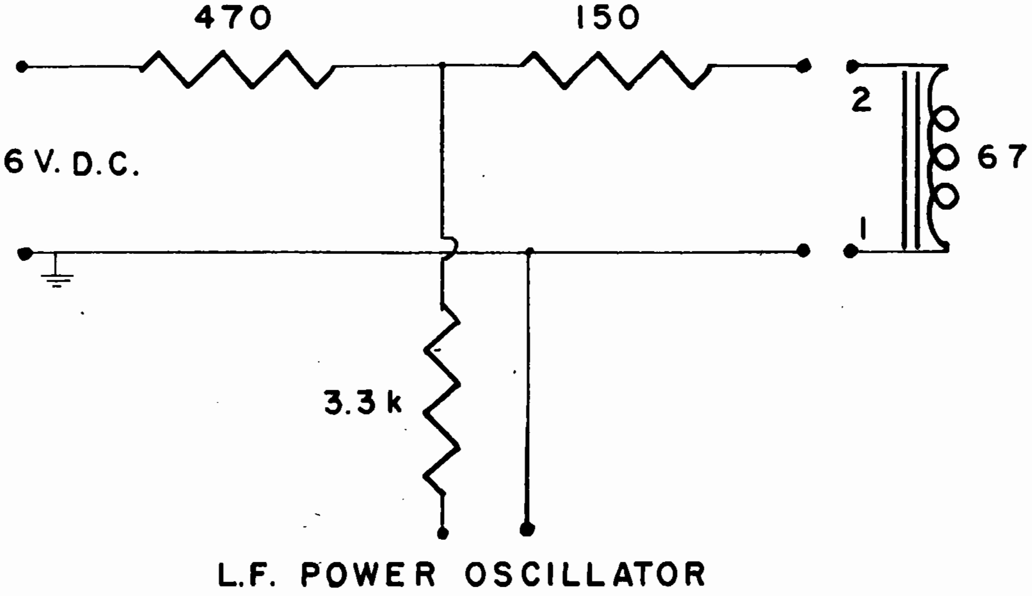
In N.Q.R. a magnetic field is not applied except in the special case where Zeeman splitting of the energy levels is observed in a single crystal. A special technique had to be employed in the experiment since a powder was used.

A simple method to detect the N.Q.R. signal is a frequency modulation less than the line width. The derivative of the absorption line is observed on the recorder chart. That method has a serious drawback: it is rather difficult to determine the centre frequency at any instant since the r.f. is modulated. Because the frequency is counted with an electronic counter, the time at which the gate of the counter opens or closes may take place anywhere in the modulating cycle. An uncertainty of the width of the modulation should then be expected on the frequency.

The first resonances, however, were observed in the laboratory with two different methods of frequency modulation: a vibrating reed (17) and a "hypersensitive voltage variable capacitor diode"(19). The first made use of a relay switch; a d.c. current was superimposed on the modulation for the following reason. The magnetic force exerted by an a.c. current on an iron reed has no polarity, and always acts in the same direction whatever the sense of the current; a modulation of twice the applied a.c. frequency is thus obtained, and cannot be detected by the phase sensitive detector. When a d.c. component was superimposed to the a.c. field, the effect disappeared, since the magnetic force was no longer exerted in the same direction for the positive and negative parts of the cycle. The vibrating reed was placed across the tank circuit of the oscillator, and frequency modulation was obtained. The second frequency modulator was essentially made of a diode whose capacity is sensitive to the applied voltage. When it was connected in parallel with the main capacitor of the oscillator and an audio voltage was applied to it, frequency modulation appeared. Besides the inaccuracy in the frequency determination,



A· SCHEMATIC



B· BIASING CIRCUIT

FIG. 3·3 VIBRATING REED

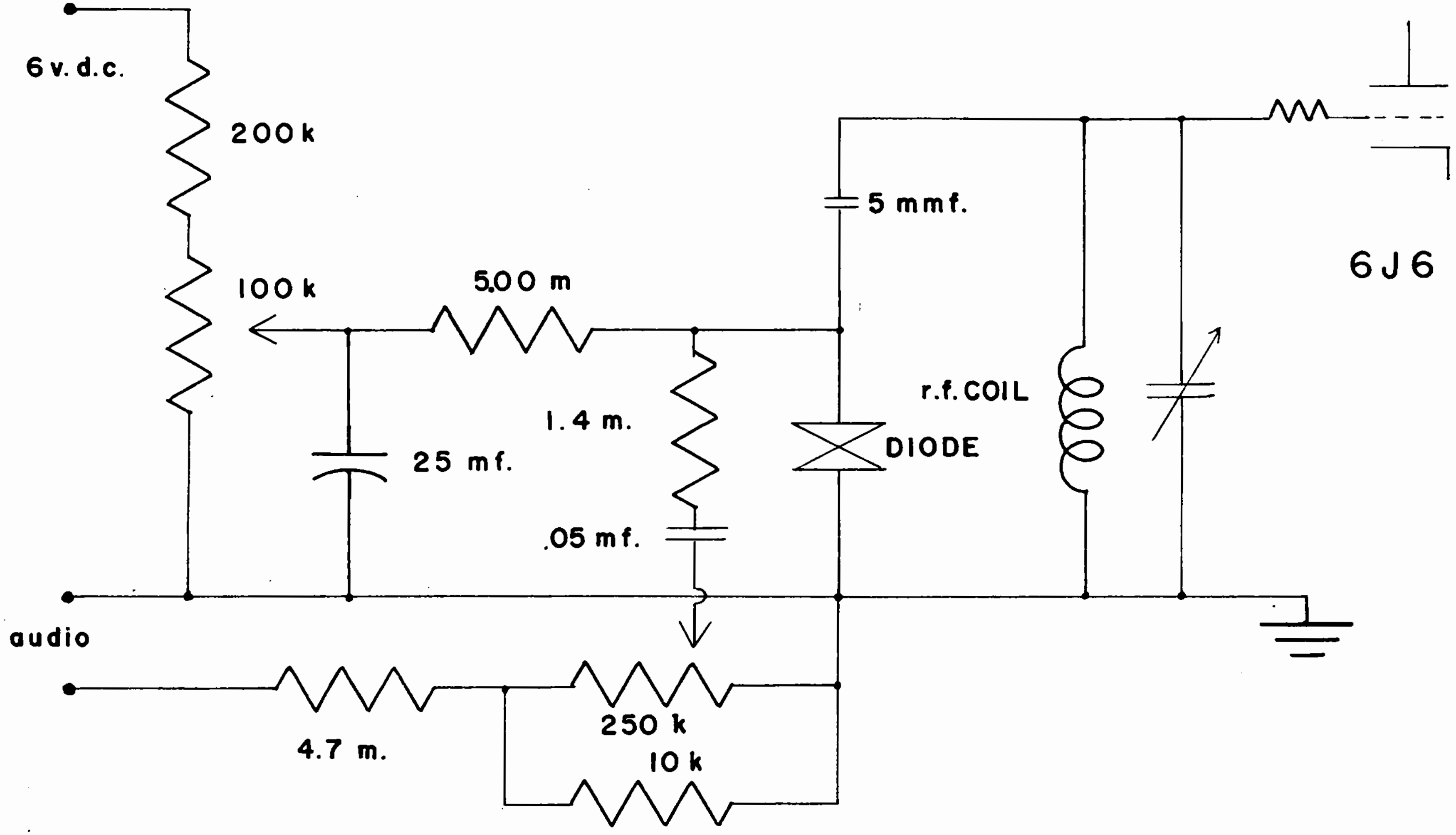


FIG. 3.4 VERICAP CIRCUIT

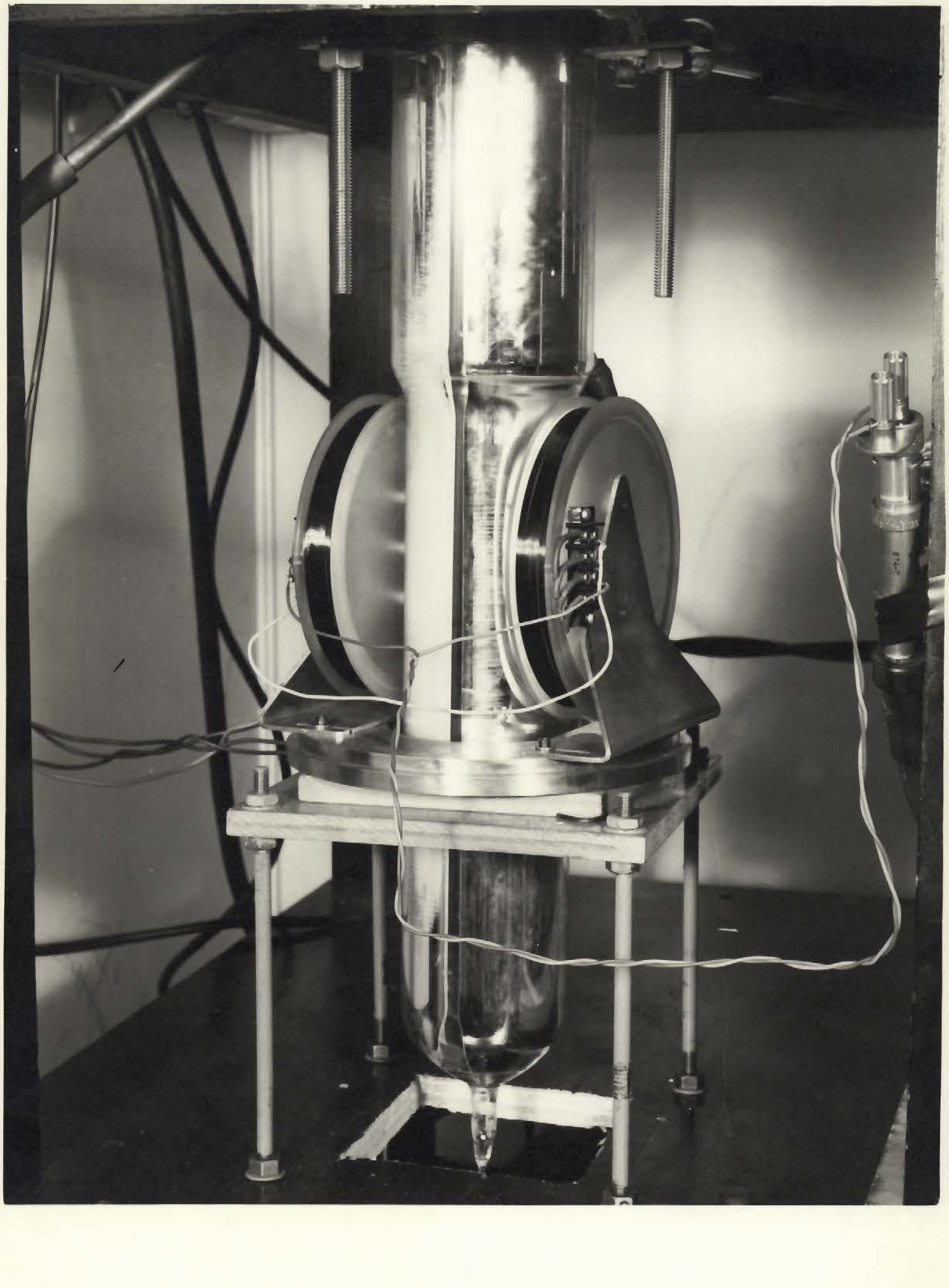


Figure 3.5 Helmotz Coil Assembly

another defect was inherent in the described systems: a strong leakage signal output was observed and saturated the following amplifiers unless the modulation was reduced to a minimum.

The method described below has been used extensively by other workers (8, 11, 12, 15) and has proved best in the present experiment. Zero based magnetic field pulses, also called "on-off" field modulation, were applied to the sample. On the "on" part of the cycle, the resonance line was spread out over several kilocycles for the reason given in section 1(c); on the "off" part, transitions were excited between the nuclear energy levels by the r.f. field, and absorption was taking place. The resonance line was then displayed by sweeping the radio frequency across it: in most experiments the sweep rate was 3 kilocycles per minute.

The on-off field was created by two Helmotz coils of 1000 turns of No. 30 copper wire each. The current necessary to obtain pulses of 20 oersteds was about 100 m.a. supplied by a Tektronic Square Wave Generator No. 105. The experimental rise-time observed for such an arrangement was approximately 2 milliseconds, which is relatively short compared to the duration of half the 35 cycles modulation which is 14 milliseconds. A rotation of 360 degrees could be made around the r.f. coil, reducing the leakage signal to a minimum, when this r.f. coil was at right angles with the Helmotz coils.

(e) Detection and Recording of the Signal.

Since the N.Q.R. signals are not strong and are comparable to the noise of the oscillator tube, a special technique for an accurate determination of the frequency of the line centre had to be used. The reduction of the noise was first accomplished by a selective amplifier that rejected all but the modulating frequency. This was done by incorporating a twin tee network in the feedback circuit of an ordinary audio amplifier. This amplifier was followed by a phase sensitive detector whose synchronous signal was taken from the square-wave generator supplying the on-off field to the sample. A d.c. output proportional to the amplitude and phase of the input signal was obtained. The noise was reduced by the use of long time-constants in the phase sensitive circuit, and strong absorption lines were observed. In most experiments a time-constant of about 5 seconds was used. The whole unit, often called "lock-in amplifier", was available since it already had been built in the laboratory.(20)

(f) Frequency Measurements.

The frequency was measured with a Hewlet Packard 524B electronic counter. A coil was placed inside the oscillator chassis and interacted very little with the spectrometer. A small r.f. signal was induced in this coil, and after sufficient amplification the frequency was counted. A diode and a microammeter were also incorporated to indicate the oscillator level.

While the frequency was swept slowly through the resonance line and the recorder was tracing the line shape, the gate of the counter was opened manually at certain characteristic points of the chart. The gate closed automatically after 1/10 of a second. If linear frequency sweep is assumed, the reading was an average of the frequencies at the start and at the end of counting. Hence, a period of time Δt existed between the time the needle of the recorder crossed a characteristic point on the chart and the time at which the frequency would have been read if it had been counted instantaneously. The frequency error was $(\nu_1 - \nu_m)$

or $\frac{1}{20}\Delta\nu$ where $\Delta\nu$ was the change in frequency per second. When the line centre was determined while the frequency increased, $\nu(T)$ plus an error

$$\frac{1}{20}\Delta\nu + \Delta\nu_L$$

was read directly on the chart. $\Delta\nu_L$ was the frequency error introduced by the time-constant of the phase sensitive detector. The apparent line centre ν_{ai} read on the chart was thus

$$\nu_{ai} = \nu(T) + \frac{1}{20}\Delta\nu + \Delta\nu_L$$

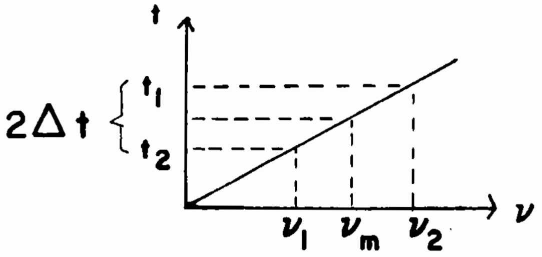
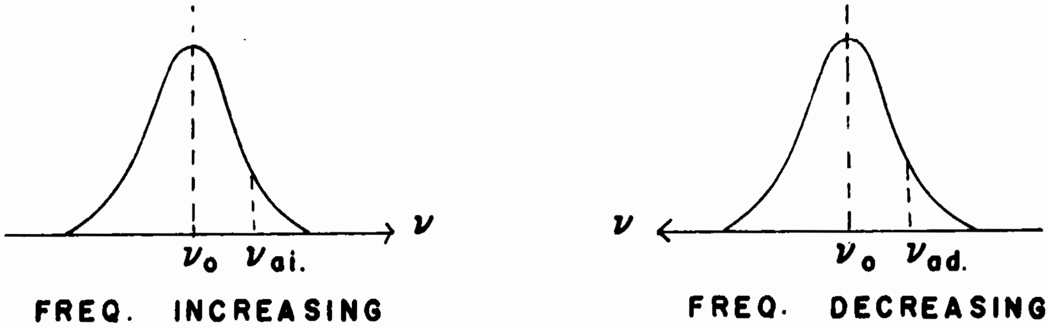


FIG. 3.6 LINEAR FREQUENCY SWEEP



FREQ. INCREASING

FREQ. DECREASING

FIG. 3.7 LINE CENTER DETERMINATION

When frequency was decreased the apparent line centre was

$$\nu_{ad} = \nu(T) - \frac{1}{20}\Delta\nu - \Delta\nu_L$$

The true line centre was then simply

$$\nu(T) = \frac{\nu_{ai} - \nu_{ad}}{2} \quad .$$

Hence, two measurements, one while the oscillator frequency was increased and another while it was decreased, gave the true line centre.

Due to an error in the time of opening the gate of the counter, fluctuations arose in $\nu(T)$. By repeating the line 8 times at 0°C the r.m.s. deviation from the mean was $\pm$ 11 c.p.s. which is 1 part in 3×10^6. The temperature of the bath, however, was not known to better than $\pm$ 0.5°K. This corresponds to a possible variation of $\pm$ 1000 c.p.s. of the resonance frequency at 60°K, because the N.Q.R. change of frequency with temperature is about 2×10^2 c.p.s.per degree kelvin at that temperature.

(g) Low Temperature Dewar Vessel.

For temperatures near that of liquid air, no problems are encountered in practice. A simple Dewar vessel is sufficient to keep an appreciable amount of liquid for several hours.

An important part of the temperature dependence of the N.Q.R. frequency occurs in the range 10°K to 70°K. At these low temperatures a double Dewar vessel must be used. The inner vessel containing the sample is first cooled down by filling the outer vessel with liquid air. Then being sufficiently cold, its walls are evacuated and it can be filled with liquid He.

Many devices are described in the literature for the purpose of obtaining intermediate temperatures between 10°K and 50°K. One of

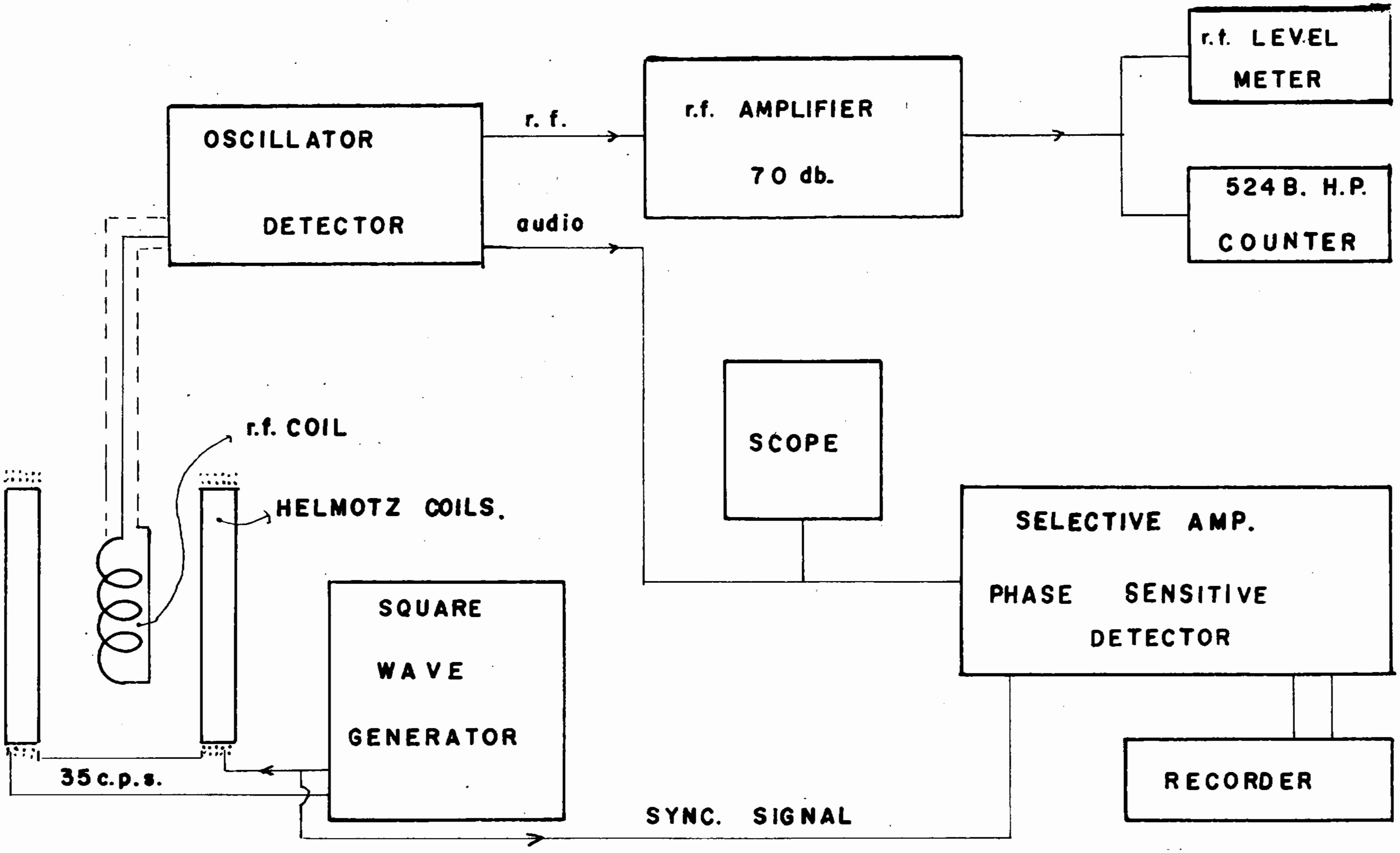


FIG. 3.8 BLOCK DIAGRAM

the simplest is a desorption system in which the sample is kept at a low temperature by cold helium vapour.(21) This vapour is desorbed from some activated charcoal placed at the bottom of a Dewar vessel and saturated with helium. The temperature of the sample is then stabilized at a fixed value by controlling the rate of flow of the helium gas; this is done by reducing the pressure over the charcoal.

The system had been built, but difficulties were met concerning the rate of pumping to be used. Nevertheless, since the sample temperature was increasing at a rate less than 0.3°K per minute, measurements could be made while the sample was heating up.

Liquid nitrogen was used to obtain temperatures between 58°K and 77°K. By reducing the pressure over the liquid, any temperatures could be obtained between these two limits.

(h) Temperature Measurements.

The temperature of the sample below and above 77°K was measured with a thermocouple Au-Co, Au-Ag. calibrated at M.I.T. against a gas thermometer. It has the advantage of being rather sensitive in the range below 77°K (still 4 μv per degree at 4°K). Its accuracy is expected to be better than ± 0.5°K. The e.m.f. was measured with a Leeds and Northrup K_2 potentiometer, on which readings could be made to ± 0.25 μv assuming enough sensitivity from the galvanometer (null indicator).

The thermocouple junction was soldered to the brass shield of the coil containing the sample and was also covered by a brass plate: hence, the temperature read was the true temperature of the sample and not of the neighbouring gas or liquid. The reference function was placed in a liquid nitrogen bath. When the inner Dewar vessel was filled with liquid N_2, an e.m.f. of about 12 μv was observed, whose polarity was such that it meant that the sample was at a higher temperature than liquid N_2. After 5 minutes the e.m.f. was reduced to 10 μv, and after an hour it was less than 2μv. In general we can thus say that the sample was not at the temperature of the neighbouring liquid, and that the thermocouple was reading the temperature of the sample and not of the liquid. The same effect observed at liquid helium temperature was far more marked. The thermocouple read 8^{o}K a few minutes after the vessel had been filled with helium. After half an hour it read 7^{o}K. The thermocouple leads were not cut at any places; that way no spurious e.m.f. should have been obtained. The liquid N_2 experiment is verifying this statement. The fact that it took a long time for the sample to cool down may be explained by the presence of a big mass of charcoal and a heavy sample container having large heat capacities.

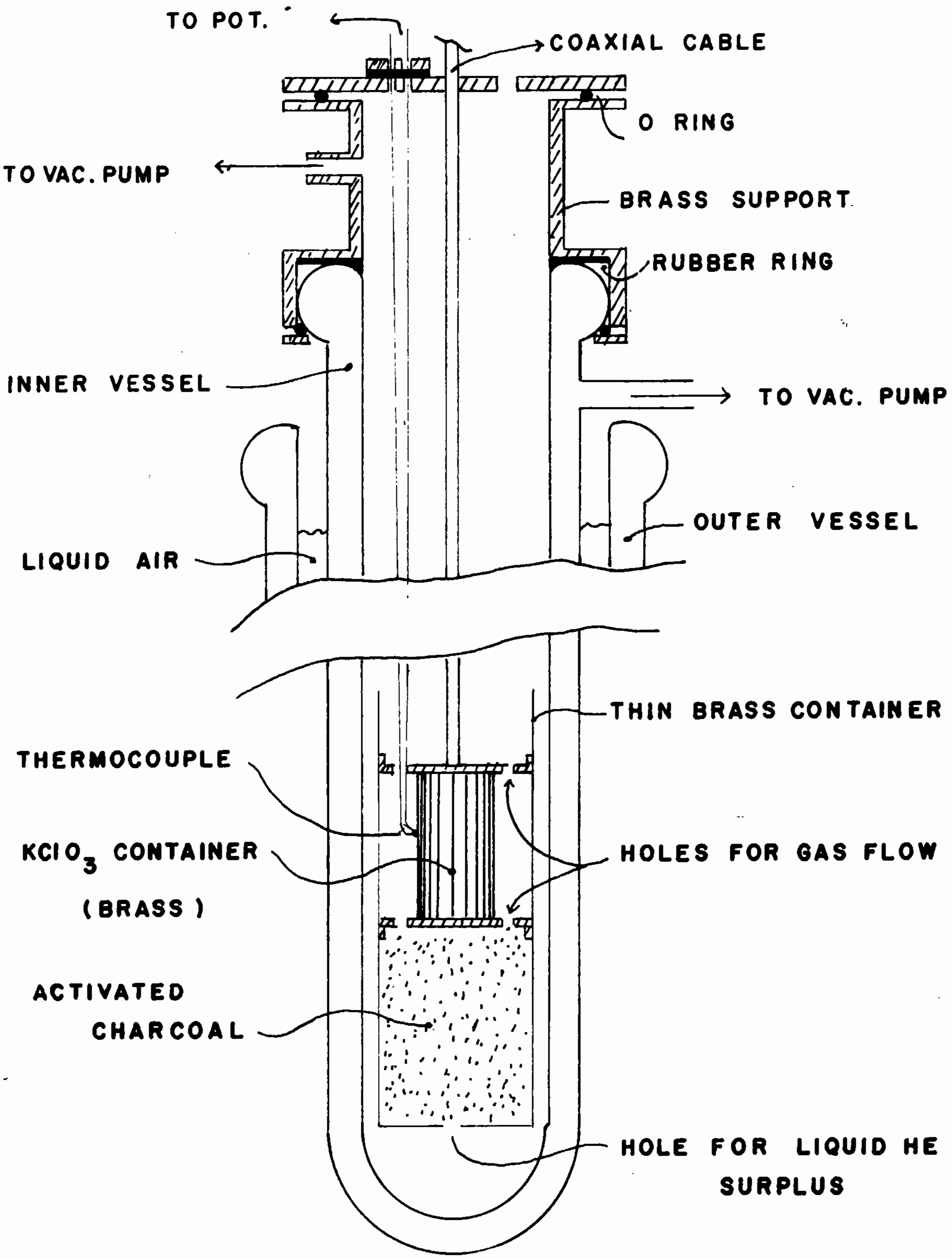
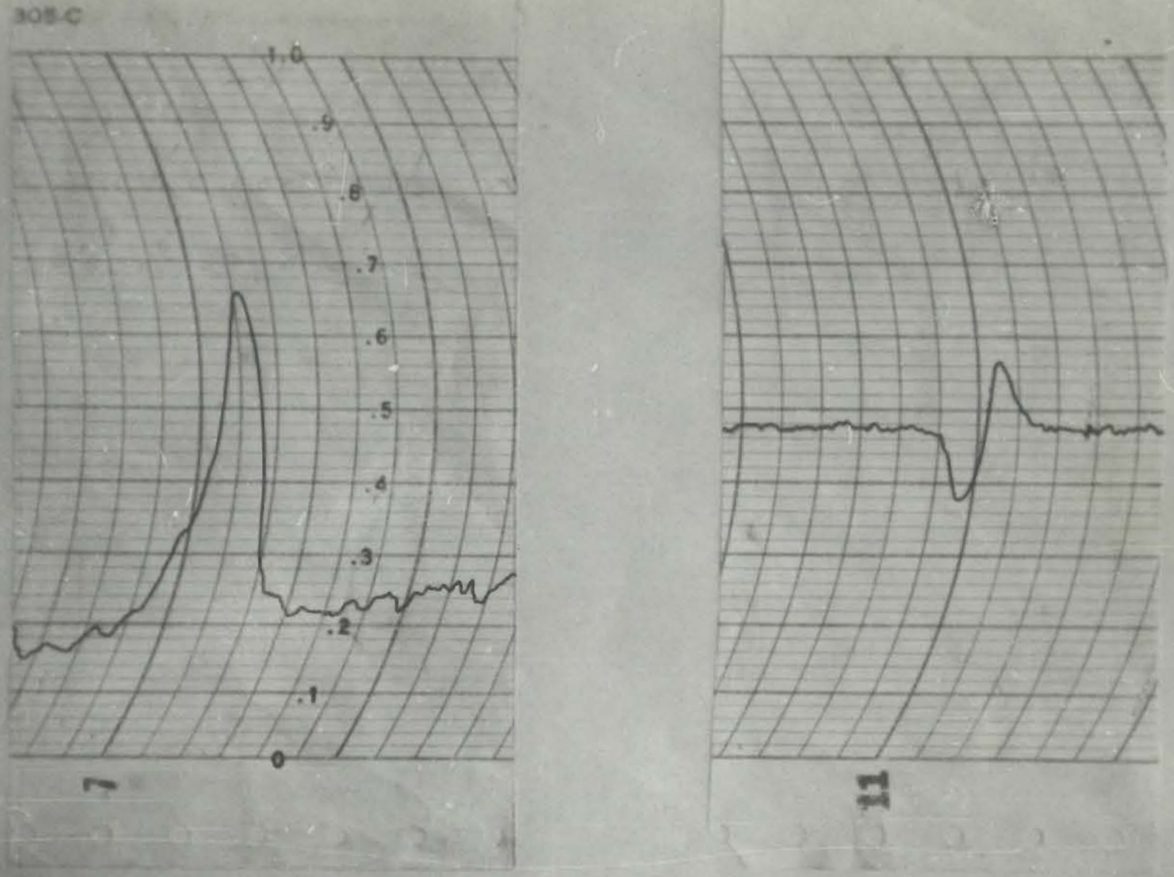


FIG. 3.9 LOW TEMP. SYSTEM



MAGNETIC FIELD MOD.

FREQUENCY MOD.

FIG 3.10 RESONANCE LINE SHAPES.

Figure 3.11 Whole Apparatus

4. EXPERIMENT AND RESULTS

(a) Purity of the sample.

The N.Q.R. frequency, as said previously, is a fundamental property of matter, depending only on temperature. This statement is true within certain limits. Other workers (11) have found that the impurity content of the sample was broadening the resonance line and was accompanied by a shift in the resonance frequency. Fortunately, the effect was negligible over a certain purity of the sample.

The purity of the substance is easily determined in practice by the width of the resonance line. The line width depends on three main factors:

1) presence of chemical impurities,
2) presence of mechanical strains,
3) effect of the earth's magnetic field.

When the line width is less than 1000 c.p.s. after effects 2. and 3. have been eliminated, Benedek and Kushida (11) have verified that the first effect was negligible as far as shifts in frequency were concerned.

The sample used in the present experiment was a powder made of very small crystals, taken from an E. + A. tested Purity Reagent lot No. 443, 121 which contained less than 0.01% of impurities.

The observed line width was 950 c.p.s. at room temperature without elimination of the third effect; sufficient purity could be assumed and the resonance frequencies observed should be the fundamental frequency of the $C\ell^{35}$ nucleus in $K\,C\ell\,O_3$.

The resonance frequency was determined at 0°C as another verification of the quality of the sample. The frequency was

$$\nu(0^{\circ}C) = 28,\ 213,\ 270 \pm 11 \text{ c.p.s.}$$

This figure does not agree exactly with the value given by Benedek and Kushida for a sample obtained by double recrystallisation. They found

$$\nu(0^{\circ}C) = 28,213,345 \pm 10 \text{ c.p.s.}$$

The disagreement can be explained: the temperature of a bath made with ice and water is not reproducible with great accuracy. The difference between the two resonance frequencies corresponds to a difference of 0.016°K between the two baths; this is certainly better than expected.

(b) Line centre determination versus temperature.

The low temperature experiment was carried out in two parts for two different ranges of temperatures.

1. From liquid air to solid nitrogen temperatures.

The resonance frequency was first determined at liquid air temperature. The thermocouple indicated 82.4 ± 0.5°K. This is reasonable since liquid air is a mixture of liquid oxygen at 90°K and liquid nitrogen at 77°K. Liquid nitrogen evaporates faster than liquid oxygen, and any temperatures between these two limits can be expected from a liquid air bath.

A measurement was also made with a liquid nitrogen bath. The thermocouple e.m.f. was less than 3 μv with the reference junction in liquid nitrogen. This corresponds to a difference of 0.1°K between the two baths.

Finally, four measurements were made between 77.4 and 58°K; these temperatures were obtained by pumping over liquid nitrogen. The accuracy obtained by repetition of the line is given in table 4.1. The 72.8°K and 73.2°K measurements were made while the temperature was drifting; hence, less accuracy should be expected from these last readings.

The temperature difference between two measurements necessary to determine a line centre was less than 0.15°K. This difference corresponds to a change of 270 c.p.s. in resonance frequency at these temperatures. The possible accuracy on the determination of the resonance frequency at these two temperatures is thus assumed to be ± 270 c.p.s.

The lowest temperature obtained by pumping over nitrogen was 58°K ± 0.5°K. At this temperature the nitrogen was solid. In that state the temperature was not as steady as it was in the liquid state under stmospheric pressure.

2. From liquid helium to solid nitrogen temperatures.

No resonance has been observed at liquid helium temperature; resonance appeared only at around 15°K. The fast increase in spin-lattice relaxation time at temperatures below 20°K explains this phenomena. Theory predicts a spin-lattice relaxation time of more than two hours at liquid helium temperature. Dautreppe and Dreyfus (9) have found a relaxation time of 100 sec at 15°K for a sample made of para-dichlorobenzene. Absorption lines were observed above 16.5°K up to 53.4°K while the sample was slowly heating in an atmosphere of cold helium vapour desorbed from the activated charcoal. The rate of increase of the temperature was around 0.3°K per minute in the whole range covered. Because of this slow increase in temperature, one can assume that thermal equilibrium existed within good limits between the thermocouple junction and the sample. Temperature gradients would have existed in the sample if thermal equilibrium had not been obtained. These gradients would have been reflected by a relatively large broadening of the absorption lines. A line broadening was observed. It is difficult, however, to separate a natural broadening at low temperatures, as observed by Wang (22) for similar substances, from a broadening due to a gradient of temperature. At room temperature the line width was 950 c.p.s.; in liquid air where no temperature gradients should exist, it was 1.4 kc; in the helium vapour, it did not much exceed 1.6 kc. One can conclude that temperature gradients, if they existed, were small and that the thermocouple, soldered to the r.f. coil shield, was giving the temperature of the sample to an accuracy of $\pm 1^{\circ}$K.

Another observation in favour of the accuracy of the measurements can be made: the experimental curve of the resonance frequency as a function of the temperature is smooth (see fig 4.3). If a large error in the temperature measurements had existed the curve would be broken at the point of junction of the two separate parts, one being obtained while temperature decreased and the other while temperature increased.

The difference in temperature between two measurements necessary to determine a line centre, except in a few cases, did not exceed half a degree. In each case, this difference corresponded to a change in the resonance frequency. This change is the figure given in table 4.1 as the accuracy of the measurements.

(c) Results and theory.

The equation of the resonance frequency of $C\ell^{35}$ in $KC\ell O_3$ as a function of temperature has been obtained in the theoretical section:

$$\nu(T) = \nu_0 \left\{ 1 - \frac{3}{2} \sum_i \frac{\hbar}{\omega_i \Theta_i} \left(\frac{1}{2} + \frac{1}{e^{\frac{\hbar\omega_i}{kT}} - 1} \right) \right\}$$

It has been suggested that only a motion of the $C\ell O_3^-$ group as a whole should be effective on the change of the resonance frequency with temperature. Following this consideration, the constant A_i was replaced by

TABLE 4.1: Experimental Results

T °K	± ΔT °K	$\nu(T)$ c.p.s.	± $\Delta\nu$(max) c.p.s.
16.5	± 1°K	29,038,530	200
17.9	"	29,038,376	200
20.8	"	29,037,699	200
22.2	"	29,036,905	125
23.7	"	29,036,588	200
26.5	"	29,035,368	200
28.8	"	29,034,590	500
30.4	"	29,033,688	300
31.9	"	29,031,702	125
32.4	"	29,031,112	250
34.9	"	29,029,440	400
36.6	"	29,027,781	200
38.0	"	29,026,416	400
43.3	"	29,020,580	600
46.6	"	29,015,622	800
49.5	"	29,011,853	300
*53.4	-	29,005,497	-
58.0	0.5	28,995,306	120
64.9	0.5	28,981,333	120
72.8	0.5	28,963,849	270
73.2	0.5	28,962,555	270
77.4	0.1	28,952,763	36
82.4	0.5	28,939,838	25
273.16	±0.02	28,213,270	11

* this reading is not corrected for the "lock-in" time constant.

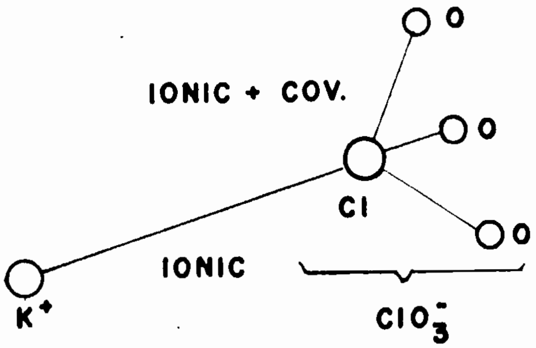


FIG. 4.1 $KClO_3$ MOLECULE

Θ_i^{-1} , the reciprocal of the moment of inertia of the $Cl0_3^-$ ion. The K Cl 0_3 molecule is shown on figure 4.1. The arrangement of the molecules in the crystals is such that they form a lattice very similar to Na Cl 0_3 extensively discussed by Kushida, with the only difference being that the crystal structure is monoclinic rather than cubic.

The $Cl0_3^-$ group forms a trigonal pyramid whose figure axis coincides with the principal z-axis of the field gradient tensor. Three normal modes can be associated with the motion of this ion. These are a hindered rotation about the symmetry axis of the molecule and two torsions around two orthogonal axis both perpendicular to the z-axis.

It seems obvious that the hindered rotation about the symmetry axis of the molecule will not affect the gradient of the field at the Cl^{35} nucleus, since the field is very nearly symmetric ($\eta = 0.006$) (24). We are left with the two other modes corresponding to a rocking motion of the ion. These are shown on figure 4.2.

Kushida has calculated the moment of inertia of such a pyramid for each mode. He has found, for three magnitudes of r (see fig 4.2), values between 83 and 89 x 10^{-47} kg m^2.

Since the moment of inertia is almost the same for the two modes and since the restoring forces in the solid state should be approximately equal for these two modes, equation (27) can be written with the sum over i ($\sum_i$) replaced by a multiplying factor two:

$$\nu(T) = \nu_0 \left\{ 1 - \frac{3\hbar}{\omega_m \Theta_m} \left(\frac{1}{2} + \frac{1}{e^{\frac{\hbar\omega_m}{kT}} - 1} \right) \right\}$$

Θ_m is the mean value of the two moments of inertia around the two axis and ω_m is the mean of the two possible vibration frequencies consistent with the previous remark on restoring forces.

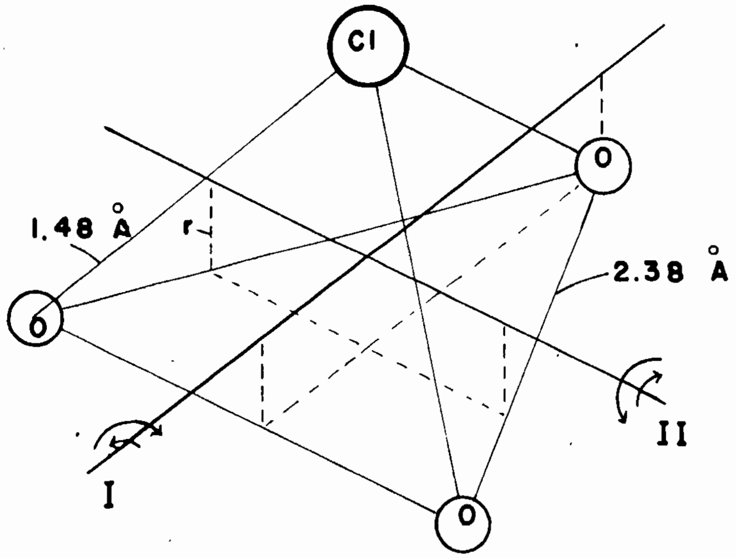


FIG. 4.2. TWO NORMAL MODES OF VIBRATION OF THE ClO_3^- GROUP

Negligible variation of the volume should be expected for the range of temperature covered. In consequence, we can assume that ω_m is a constant and write

$$\nu(T) - \nu(o) = - \frac{a}{e^{\frac{\hbar\omega_m}{kT}} - 1} \tag{29}$$

where

$$\nu(o) = \nu_o(1 - \frac{3}{2}\frac{\hbar}{\omega_m \Theta_m}) \tag{30}$$

$$a = \frac{3\nu_o \hbar}{\omega_m \Theta_m} \tag{31}$$

Transforming equation (29), writing θ_m for $\frac{\hbar\omega_m}{k}$ and taking logarithms on each side, one gets

$$\ell n \, \Delta\nu_T \, (1 - e^{-\theta_m/T}) = \ell n \, a - \frac{\theta_m}{T}$$

where $\Delta\nu_T$ has been written for $\nu(o) - \nu(T)$. The last equation is rectified when the left side is plotted against 1/T. The slope of the line is "θ_m" and its intercept is "ℓn a". The exponential term is a function of θ_m but is rather small for the usual Raman frequency. Furthermore, at 85°K, an error of 10% on an assumed trial value for this θ_m will be reflected by an error less than 0.1% on the logarithm; this error should decrease as T decreases since the exponential term becomes smaller. The procedure to follow for an evaluation of θ_m is the following: one assumes a first trial value for θ_m obtained from the results of other workers; the straight line then gives a new θ_m which must be nearer the true value than the previous θ_m assumed.

Kushida has found that his data was in agreement with an approximate equation good for $T \geqslant \theta_m$ when a value of $2\pi \times 3.08 \times 10^{12}$ c.p.s. was chosen for ω_m. The closest line in the Raman spectrum is $2\pi \times 2.94 \times 10^{12}$ c.p.s.

Inserting this value for ω_m, one gets

$$\Theta_m = 141^\circ K.$$

Evaluating $e^{-\Theta/T}$ for each temperature considered, the correction to $\Delta\nu_T$ can be worked out. The only uncertainty is reduced to the extrapolation to $0^\circ K$, to obtain $\nu(o)$. At temperatures above $45^\circ K$, $\Delta\nu_T$ is already more than 20 Kc. Hence, an error of a few hundred cycles in $\nu(o)$ do not affect much the logarithm, and all the high temperature points should coincide with a straight line. The error in $\nu(o)$ may be more effective at low temperatures where $\Delta\nu_T$ is reduced to a few kilocycles or less. By a first graph with a trial $\nu(o)$ one will find, at low temperatures, marked deviations from a straight line coinciding with high temperatures points. The deviations, however, will have all the same sign and all the points may be made to coincide with a straight line by a correction on $\nu(o)$.

The procedure has been used for interpolated values of $\nu(T)$ at every 5 degrees from $15^\circ K$ to $85^\circ K$. The best value of $\nu(o)$ found for a straight line fit for all these points is

$$\nu(o) = 29{,}038{,}270 \text{ c.p.s.}$$

The slope is $\Theta_m = 141^\circ K$ coinciding with the assumed Raman line. The intercept is

$$\ln a = 6.1 \Rightarrow a \simeq 445{,}860 \text{ c.p.s.}$$

This last figure should not be expected to be very accurate since an error of 2% on "$\ln a$" is reflected by a relative error of 13% on "a". It will be seen below that a better accuracy can be obtained with a least square analysis of all the points.

Having found the Θ_m which gives the best fit to the observed curve, this value can be used to make a least square analysis of the experimental points. Equation (29) can be written simply as

$$\nu(T) = \nu(o) - aX$$

where

$$X = \frac{1}{e^{\Theta_m/T} - 1}$$

This is again a straight line whose slope is "a" and whose intercept is $\nu(o)$. Evaluating X for each experimental temperature, one gets from a least square analysis (assuming T exactly known)

$$\nu(o) = 29{,}037{,}800 \text{ c.p.s.}$$

The figure differs by less than 0.002% from the value assumed to obtain Θ_m. It is only 0.0025% lower than the last measurement at 16.5°K. The slope of the line is

$$a = 440.903 \text{ c.p.s.}$$

This last value is expected to be more accurate than the one found by the first method, since it is obtained directly from a slope and not from a logarithm. The two values do not differ by much more than 1%.

The value of ν_o can be obtained in the following way. From (30) and (31) we can write

$$\nu_o = \nu(o)_{obs} + \frac{a_{obs}}{2}$$

It gives

$$\nu_o = 29{,}258{,}321 \text{ c.p.s.}$$

This value would be the resonance frequency obtained at 0°K if the model used in equation (25) had been classical instead of quantum-mechanical. In other words, it would be the resonance frequency observed at 0°K if atomic vibrations obeyed classical rather than quantum mechanical laws.

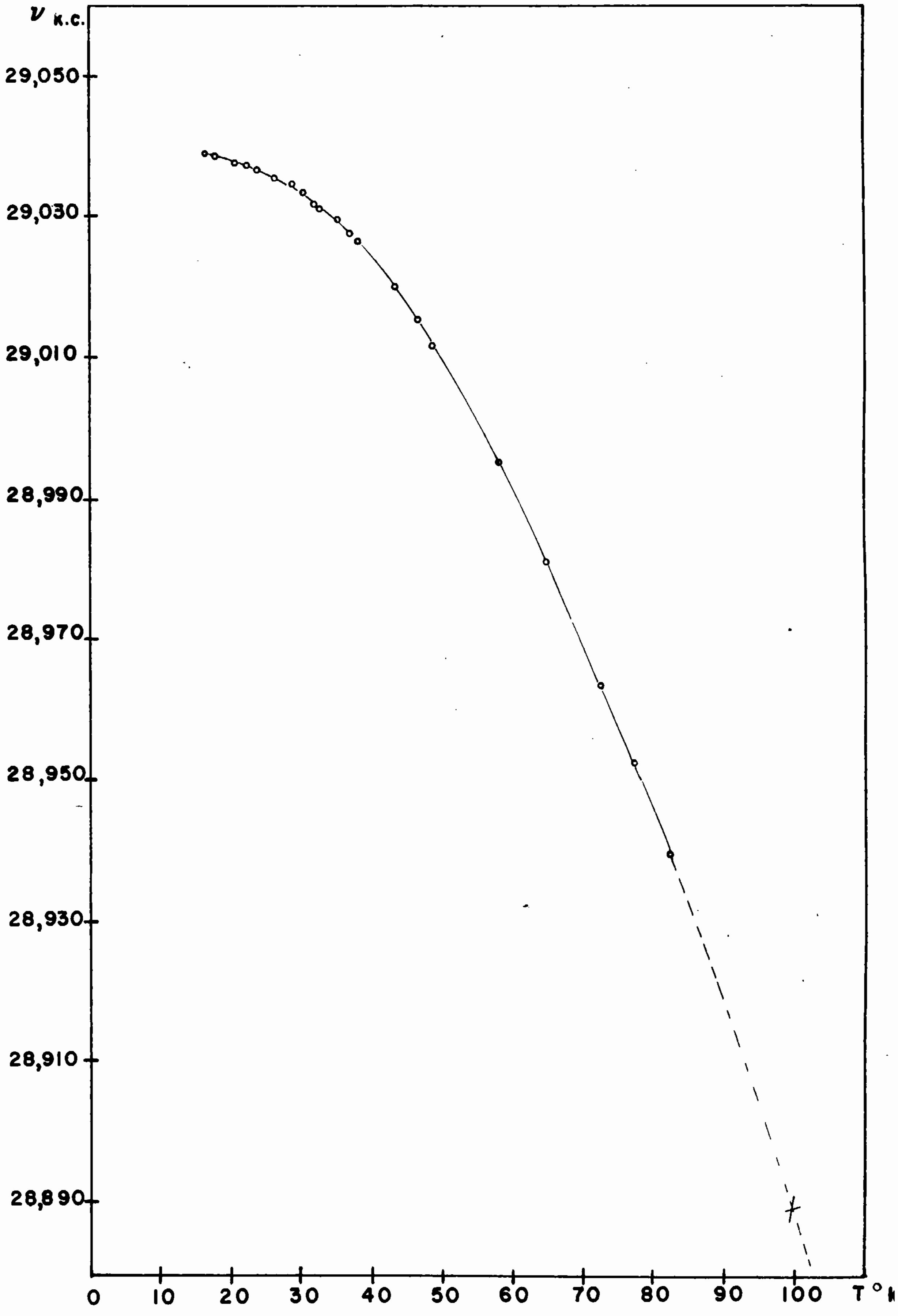


FIG. 4.3 ν(T) vs. T FOR $KClO_3$ (Cl^{35})

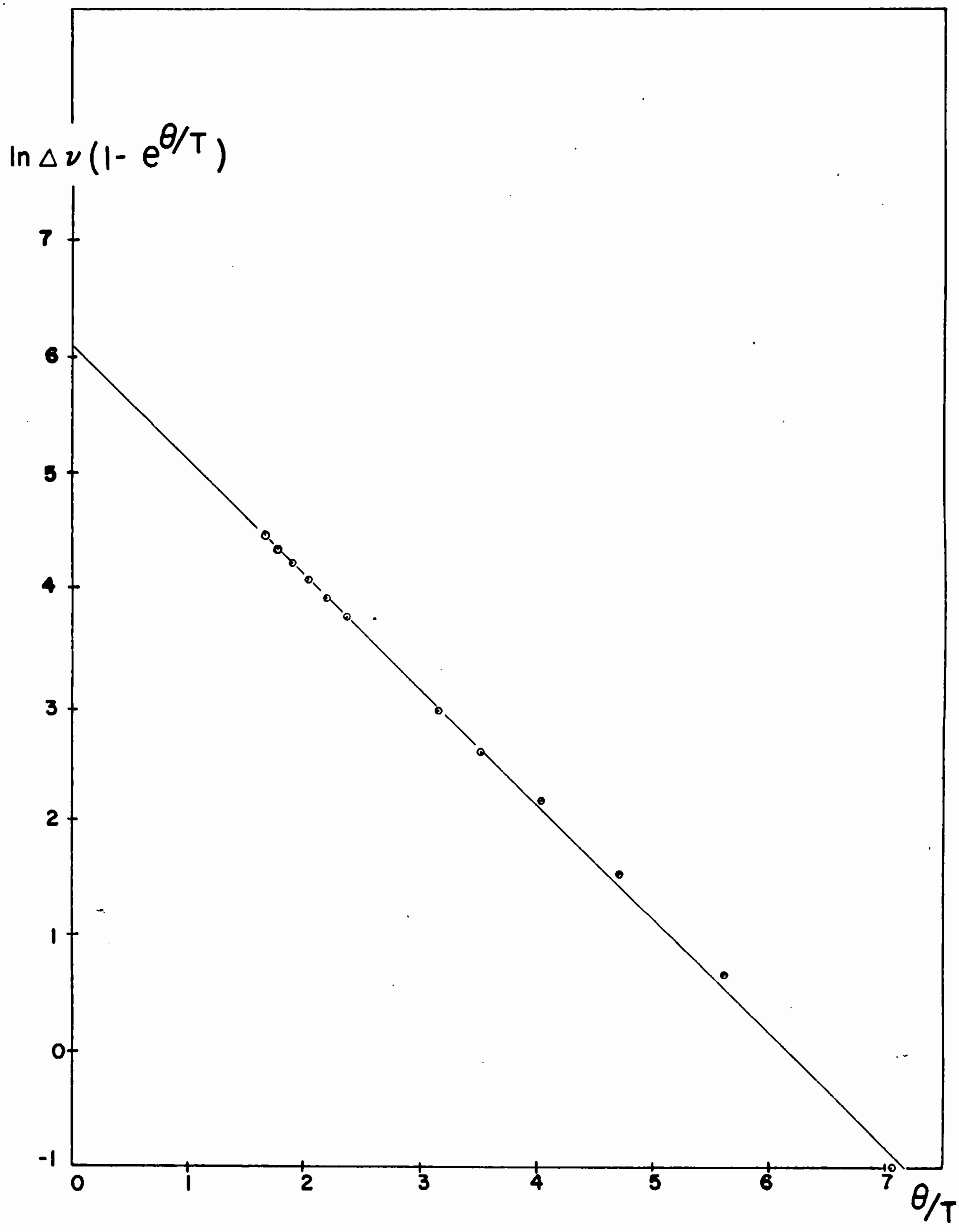


FIG. 4.4 DETERMINATION OF θ

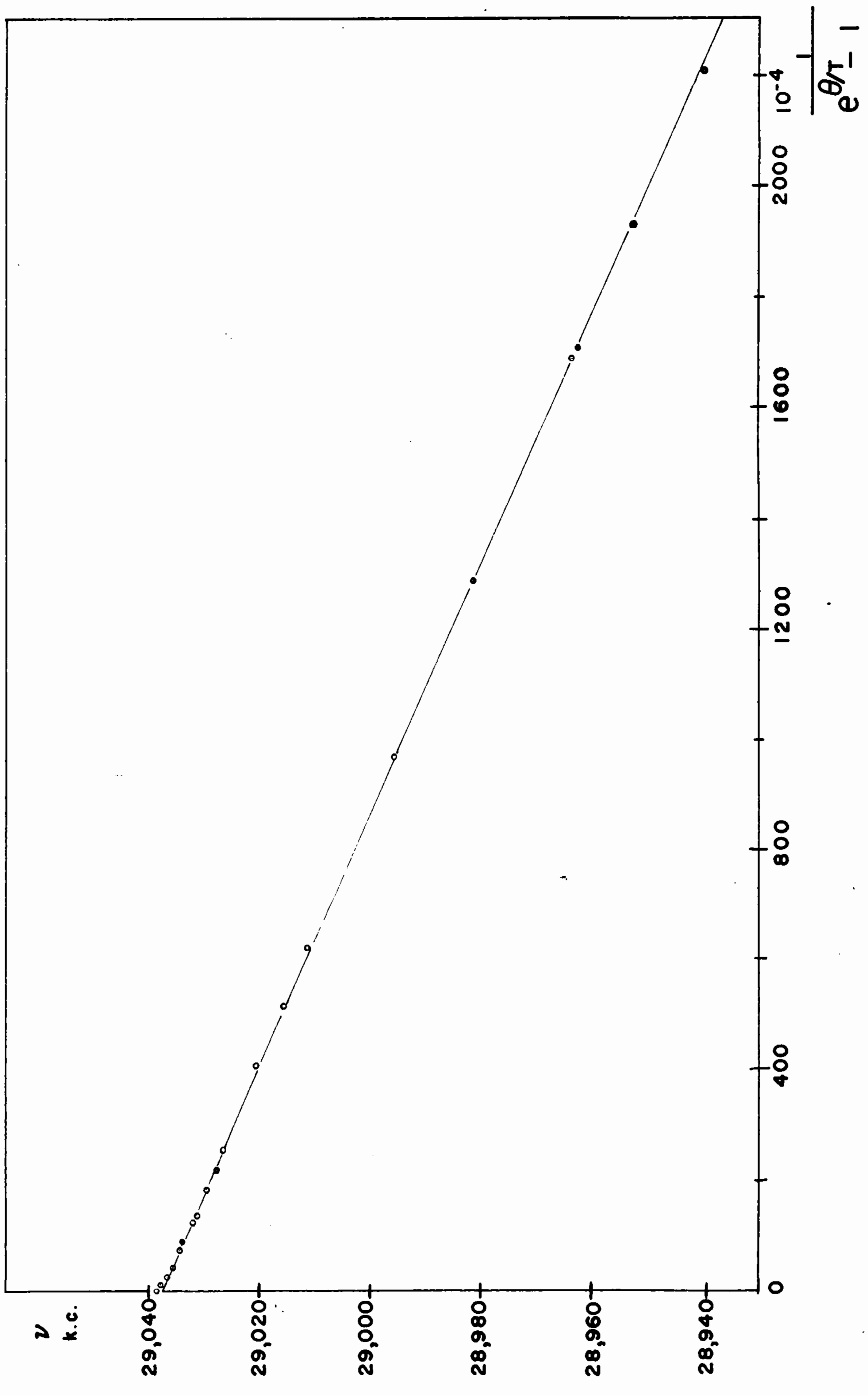


FIG. 4.5 DETERMINATION OF ν_0 AND Θ

The accuracy on ν_o is rather difficult to calculate, but it should be high: $\nu(o)$ is known to approximately 0.003%, and "a" being obtained from a slope should be as much accurate. This slope, however, depends on θ_m; an error of 1% on this last one is reflected by an error of more than 1% on the slope. θ_m is thus the determining factor, but the precision on this parameter should be high since it is also obtained from a slope. From (34) it can also be seen that an error of 1% on "a" is reflected by an error of only 0.008% on ν_o.

The moment of inertia of the $C\ell O_3^-$ group can be calculated from (30) and (31).

$$\Theta_m = \frac{3h}{\omega_m} \left(\frac{\nu(o)\,obs}{a_{obs}} + \frac{1}{2}\right).$$

It gives

$$\Theta_m = 112 \times 10^{-47} \text{ kil m}^2.$$

which is far from the calculated value. The calculation made by Kushida, however, is applicable to a free $C\ell O_3^-$ ion. In the situation encountered in a real crystal, the ion is bound to other atoms. For instance, in the $Na\,C\ell\,O_3$ crystal, which is similar to $K\,C\ell\,O_3$, Kushida suggests that each "O" of the $C\ell O_3^-$ group is coupled ionically to two neighbouring sodium atoms. With this picture it is then difficult to give an exact meaning to the moment of inertia.

Knowing the value of "a" and ν_o, one can extrapolate to find what would be the resonance frequency at higher temperatures if lattice expansion was absent. Evidently the theoretical and the experimental values will not coincide since lattice expansion is not negligible at high temperatures. For example, at 0°C the difference between theory and experiment is already 20% of the whole change in resonance frequency from 0°K.

Kushida, Benedek and Bloembergen have studied this lattice expansion effect at temperatures higher than 77°K. They have measured the resonance frequency as a function of pressure and temperature in that range. Constructing an equation of state and knowing the thermal expansion of the substance, they have transformed their isotherms $\nu(T)$ versus P to isotherms $\nu(T)$ versus V. They could then calculate what would be the resonance frequency, if no thermal expansion was taking place. These are shown in table 4.2, compared with the theoretical extrapolated values, calculated with $\nu(o)$ and "a" obtained from the present experiment.

It is seen that the theory and experiment are in excellent agreement below 80°K. Except in one case the difference does not exceed 1 kc which corresponds to 0.003%. Marked differences exist at high temperatures between the values obtained by Kushida and the values obtained here. On the basis of the excellent fit at low temperatures, it could be believed that a transformation through an equation of state of the solid, not being absolutely wrong, is not as accurate as one would expect. The disagreement explains the difference between Kushida's ω_m and Θ_m and the figures found in the present experiment. (Kushida (8) has calculated ω_m and Θ_m to be respectively $2\pi \times 3.08 \times 10^{12}$ and 84×10^{-47} kg m^2. A calculation done by the present writer with his data gave 95×10^{-47} kg m^2 for Θ_m; the lattice vibration frequency was found to be in agreement with the published value.)

Figure 4.6 is an overall view of the resonance frequency of Cl^{35} in K Cl O_3 as a function of temperature. The curve called Dehmelt approximation is the temperature dependence that would be observed if the Planck's oscillator mean energy in (25) was replaced by the mean classical energy $\frac{1}{2}$ kT associated with every mode. At 0°K the resonance frequency would be ν_o.

TABLE 4.2: Comparison between theory and experiment

T	$\nu(T)$ c.p.s. (observed)	$\nu(T)$ c.p.s. corrected by Kushida for lattice expansion	$\nu(T)$ c.p.s. calculated with Bayer's equation	Difference between $\nu(T)$ calculated and $\nu(T)$ observed c.p.s.	%
16.5	29,038,530		29,037,714	+ 816	0.0028
17.9	29,038,376		29,037,649	+ 727	0.0025
20.8	29,037,699		29,037,299	+ 400	0.0014
22.2	29,036,905		29,037,026	- 121	0.0004
23.7	29,036,588		29,036,650	- 62	0.0002
26.5	29,035,368		29,035,974	- 606	0.0021
28.8	29,034,590		29,034,475	+ 115	0.0004
30.4	29,033,688		29,033,798	- 110	0.0004
31.9	29,031,702		29,032,430	-728	0.0025
32.4	29,031,112		29,032,046	- 934	0.0032
34.9	29,029,440		29,029,904	- 464	0.0016
36.6	29,027,781		29,028,234	- 453	0.0016
38.0	29,026,416		29,026,738	- 322	0.0011
43.3	29,020,580		29,020,120	+ 460	0.0016
46.6	29,015,622		29,015,314	+ 308	0.0010
49.5	29,011,853		29,010,667	+1,186	0.0040
*53.4	29,005,497		29,004,913	+ 584	0.0020
58.0	28,995,306		28,995,184	+ 122	0.0004
64.9	28,981,333		28,981,188	+ 145	0.0005
72.8	28,963,849		28,963,508	+ 341	0.0012
73.2	28,962,555		28,962,582	- 27	0.0001
77.4	28,952,763	28,960,000	28,952,750	+ 13	0.0001
82.4	28,939,838		28,940,581	- 743	0.0026
196.0	28,550,000	28,610,000	28,618,678	-8,678	
297.6	28,090,000	28,280,000	28,310,310	-30,310	
357.7	27,750,000	28,080,000	28,123,367	-40,367	

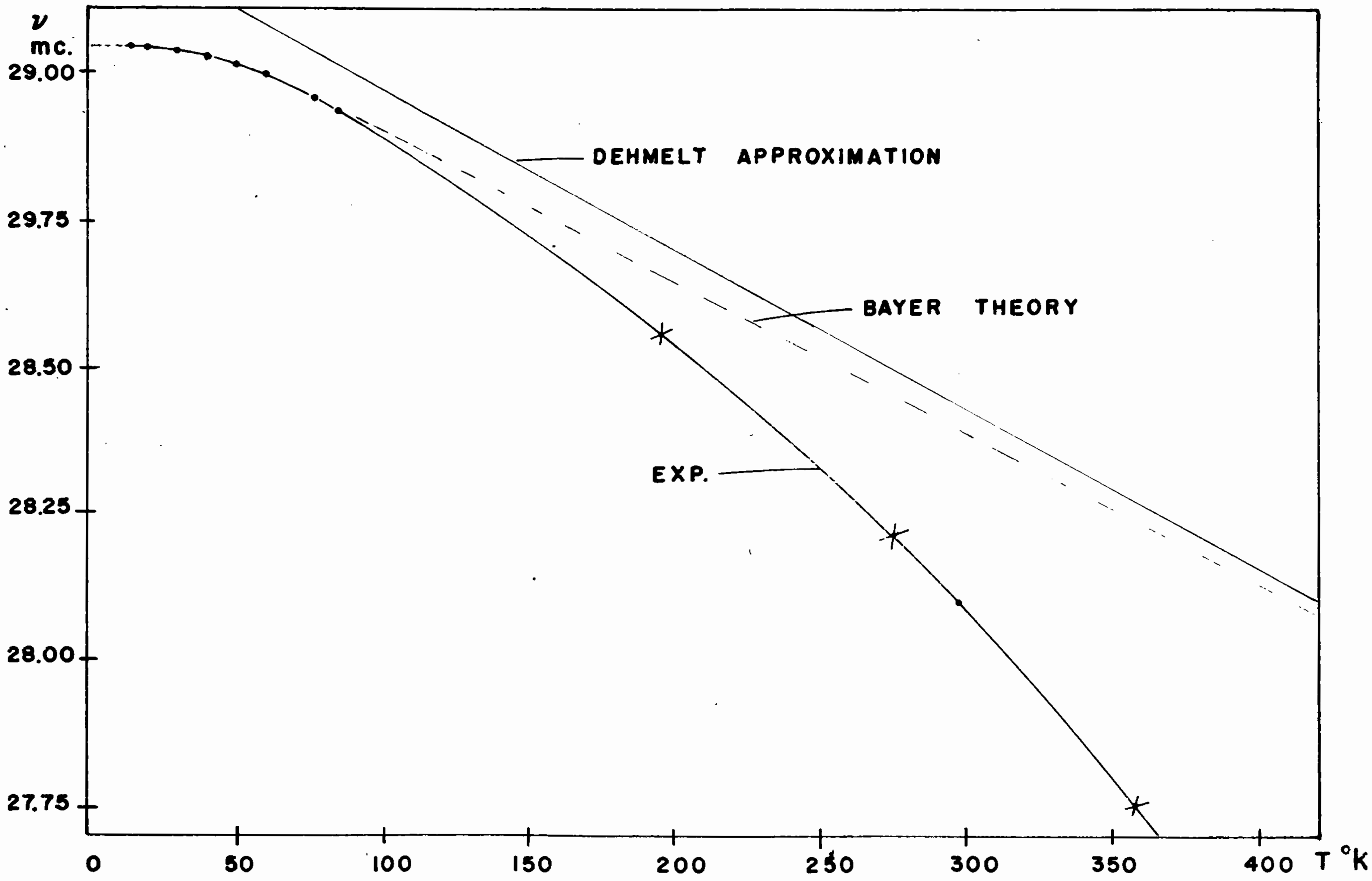


FIG. 4.6 ν(T) vs. T FOR A WIDE TEMPERATURE RANGE

(CROSSED POINTS ARE FROM KUSHIDA (7))

5. N. Q. R. THERMOMETER

Owing to the observed temperature dependence of the N.Q.R. frequency of $C\ell^{35}$ in $K\,C\ell\,O_3$, it is seen that, following the suggestion made by C. Dean and R. V. Pound (10), an accurate thermometer can be built using the effect. As mentioned in the theory, this is due to the fact that, if sufficient purity is attained, the resonance frequency is a function only of the temperature, insensitive to variationsin the atmospheric pressure.

This possibility has been studied by Benedek and Kushida for temperatures higher than 77°K. It is studied here for lower temperatures.

From the experimental curve $\nu(T)$ versus T a sensitivity curve has been derived and is shown in figure 4.7 for the range 15°K to 140°K. For higher temperatures the sensitivity increases almost linearly. The numbers written on the right hand side of the graph are figures representing the accuracy with which the temperature could be determined, assuming a line centre determination of ± 10 c.p.s. It is seen that below 60°K the sensitivity drops very rapidly, being only 200 c.p.s. per degree at 20°K. This would correspond to a temperature determination of ± 0.05°K.

It could be added that if the thermometer does not seem to be very practical to measure temperatures, it could be used, after accurate calibration has been done, as a laboratory secondary standard. Its characteristics would be:

1. Good sensitivity over 20°K.
2. Precise reproducibility since below a definite inpurity content, the resonance frequency is a fundamental property of matter. Purity is easily determined by the line width.
3. Absence of hysteresis.

The last two statements have been verified by Benedek and Kushida, and the first one is deduced from figure 4.7.

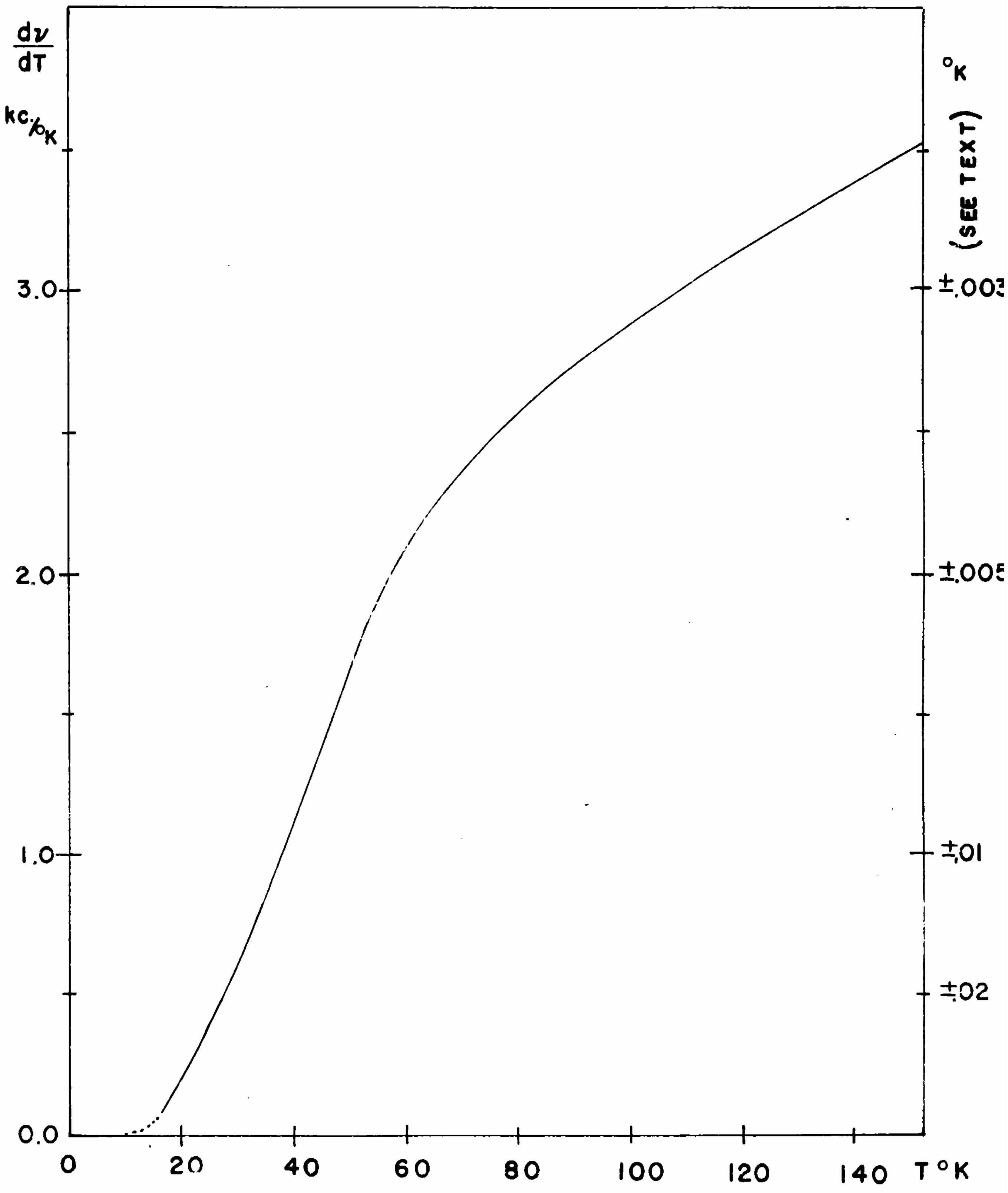


FIG. 4.7 SENSITIVITY OF THE N.Q.R. THERMOMETER

6. SUMMARY AND CONCLUSIONS

Nuclear Quadrupole Resonance frequency of the Cl^{35} nucleus in $K\,Cl\,O_3$ has been measured as a function of temperature from 16.5° to 273.2°K. Estimated accuracy of the temperature measurements made with a thermocouple was ± 1°K for temperatures lower than 50°K and better than ± 0.5°K for higher temperatures. The accuracy on the resonance frequency determination was in most cases better than ± 300 c.p.s. At 0°C it was measured to ± 11 c.p.s.

Below 80°K agreement between theory and experiment was found to be better than 0.004%. Above this temperature where thermal expansion is no longer negligible the agreement is not as good: near 1% at room temperature. The transformation through an equation of state made by Kushida to account for the thermal expansion, was found to be not as accurate as it was expected, and deviations are observed from the high temperature, extrapolated, theoretical values.

With the accuracy obtained, a very good value for the gradient of the electric field at the Cl^{35} nucleus can be calculated. Knowing this value, a comparison could be made with the theoretical one obtained from approximate wave-functions.

Finally, it has been seen that a useful thermometer can be built using the temperature dependence of the resonance frequency. Its accuracy would be ± 0.003°K at 120°K and still ± 0.05°K at 20°K.

APPENDIX

1. Tensor Transformation

The fundamental relation for a tensor transformation is

$$V_{i'j'} = a_{i'i} \; a_{j'j} \, V_{ij} \qquad A(1)$$

where the a(s) are the directional cosines of the primed system of axis in respect to the system fixed with the molecule. In that notation it should be understood that a subscript appearing twice must be summed; $i'j'$ and $i\,j$ hold for any x', y', z' and x, y, z. Hence, from figure 1.1

$$\begin{pmatrix} a_{x'x} & a_{x'y} & a_{x'z} \\ a_{y'x} & a_{y'y} & a_{y'z} \\ a_{z'x} & a_{z'y} & a_{z'z} \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\theta & -\sin\theta \\ 0 & \sin\theta & \cos\theta \end{pmatrix} \qquad A(2)$$

From A(1) one obtains the component $V_{z'z'}$:

$$\begin{aligned} V_{z'z'} &= a_{z'i} \; a_{z'j} \; V_{ij} \\ &= a_{z'x} a_{z'j} V_{xj} + a_{z'y} a_{z'j} V_{yj} + a_{z'z} a_{z'j} V_{zj} \\ &= a_{z'x} \; a_{z'x} V_{xx} + a_{z'y} \, a_{zy} V_{yy} + a_{z'z} \, a_{z'z} V_{zz} \, . \end{aligned}$$

All $V_{ij} = 0$ when $i \neq j$ for the assumed symmetry of the field. Thus

$$V_{z'z'} = \sin^2\theta \quad V_{yy} + \cos^2\theta \quad V_{zz}. \qquad A(3)$$

Using Laplace equation and the fact that

$$V_{xx} = V_{yy}$$

one obtains

$$V_{z'z'} = \frac{1}{2} V_{zz} \ (3 \cos^2 \theta - 1) \qquad A(4)$$

which is relation (10) written without proof.

2. In the discussion of the theory of temperature dependence it has been stated that the relation A(4) was symmetrical. This is easily seen here since all the directional cosines hold, whatever the "new" or "old" system is. Hence, a relation can be written at once

$$V_{zz} = V_{y'y'} \sin^2 \theta + V_{z'z'} \cos^2 \theta$$

The tensor ellipsoid is now fixed with the primed system of axis and we have

$$V_{y'y'} = V_{x'x'}$$

One can write

$$V_{zz} = \frac{1}{2} V_{z'z'} (3 \cos^2 \theta - 1)$$

which is relation (20).

3. Special mode of vibration.

In figure 2.2 is shown a special mode of vibration of a molecule. In that case it can be shown easily that A_i can be interpreted as a (moment of inertia)$^{-1}$. The displacement of the atoms in a molecule or in a crystal can be expressed by the superposition of the displacement of all normal co-ordinates. Call $x_i \ y_i \ z_i$, the displacement co-ordinates of the ith atom.

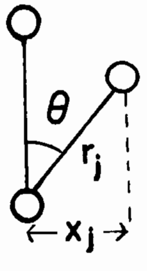


FIG. 2.2 SPECIAL MODE OF VIBRATION: BENDING

Then we can write

$$x_1 = a_{11}\xi_1 + a_{12}\xi_2 + a_{13}\xi_3 + \ . \ . \ .$$

$$y_1 = b_{11}\xi_1 + b_{12}\xi_2 + a_{13}\xi_3 + \ . \ . \ .$$

$$z_1 = c_{11}\xi_1 + c_{12}\xi_2 + c_{13}\xi_3 + \ . \ . \ .$$

$$. \ . \ .$$

$$z_N = c_{N1}\xi_1 + c_{N2}\xi_2 + c_{N3}\xi_3 + \ . \ . \ .$$

where the coefficients must satisfy the normalization condition imposed on the kth normal co-ordinate

$$\sum_i m_i \left(a_{ik}^2 + b_{ik}^2 + c_{ik}^2\right) = 1$$

The α_i in A_i is simply

$$\alpha_i = \frac{\partial \theta}{\partial \xi_i}$$

and θ is a function of all the displacements

$$\theta = \theta\,(x, y, z, \ . \ . \ . \ z_N).$$

Following these considerations one can write

$$\alpha_i = \sum_j \frac{\partial \theta}{\partial x_j}\,\frac{\partial x_j}{\partial \xi_i} = \sum_j \frac{\partial \theta}{\partial x_j}\, a_{ji}$$

For the special type of motion shown in figure 2.2 corresponding to a tilting motion of the molecule

$$\frac{\partial \theta}{\partial x_j} = \frac{1}{r_j} \qquad \text{since} \quad x_j \simeq r_j\,\theta.$$

For j = 1 and using the normalization condition we have

$$\alpha_1 = a_{11}\,\frac{1}{r_1} = \frac{1}{\sqrt{m_1}\,r_1}$$

or

$$\alpha_{11}^{2} = \frac{1}{\Theta_1}$$

The term δ_{ii} which is related to a stretching motion of the molecule, can be shown in a similar way to have the order of magnitude of a (moment of inertia)$^{-1}$. In K Cl O_3 this stretching motion would take place between K^+ and Cl O_3^-. Since the contribution of K^+ to the field gradient is not expected to be greater than a few percent (8), its variation should have a negligible effect and we may neglect that type of contribution in the case of interest here. Hence

$$A_i = \Theta_i^{-1}$$

which is the wanted relation.

REFERENCES

1. H. G. Dehmelt, H. Kruger, Naturwiss 37, 111, (1950).
2. H. Schuler, T. Schmidt, Z. Physik 94, 457, (1935).
3. J. M. B. Kellogg, I. I. Rabi, N. F. Ramsey, J. R. Zacharias, Phys. Rev. 55, 318, (1939); 57, 677, (1940).
4. D. K. Coles, W. E. Good, Phys. Rev. 70, 979 (1946).
5. R. V. Pound, Phys. Rev. 79, 685, (1950).
6. H. Bayer, Z. Physik. 129, 401, (1951).
7. T. Kushida, J. Sci. Hiroshima Univ. A19, 327 (1935).
8. T. Kushida, G. B. Benedek, N. Bloembergen, Phys. Rev. 104, 1364 (1956).
9. D. Dautreppe, B. Dreyfus, Soutif, M.Comptes Rendus 238, 2309, (1954).
10. C. Dean, R. V. Pound, J. Chem. Phys. 20, 195 (1952).
11. G. B. Benedek, T. Kushida, Rev. Sci. Inst. 28, 92, (1957).
12. H. G. Dehmelt, Am. J. Phys. 22, 110 (1954).
13. H. Kruger, Z. Physik. 130, 371, (1951).
14. C. Kittel, Introduction to Solid State Physics (Wiley) 2nd ed., p.152.
15. G. Watkins, (thesis not published) Harvard University, 1952.
16. R. V. Pound, W. D. Knight, Rev. Sci. Inst. 21, 219, (1950).
17. H. W. Knoebel, E. L. Hahn, Rev. Sci. Inst. 22, 904, (1951).
18. J. A. Cowen, W. H. Tantilla, Am. J. Phys. 26, 381, (1958).
19. D. Jennings, W. H. Tantilla, Rev. Sci. Inst. 30, 137, (1959).
20. R. A. McFarlane, "Eaton Electronics Res. Lab. Annual Report", 1957.
21. R. F. Broom, A. C. Rose-Innes, J. Sci. Inst. 33, 420, (1956).
22. T. C. Wang, Phys. Rev. 99, 566, (1955).
23. J. C. Slater, Int. to Chem. Phys. (McGraw-Hill) 1939.
24. T. P. Das, E. L. Hahn, Nuclear Quadrupole Resonance Spectroscopy, Solid State Physics sup. 1 AC Press Pub 1958, p.108.