The static electric quadrupole interaction in a single crystal of antiferroelectric lead Hfo(3) studied by perturbed angular correlation of 132-480 keV cascade in tantalum-181.

Ng’andwe K. Mumba

University of Windsor

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LA THÈSE A ÉTÉ MICROFILMÉE TELLE QUE NOUS L'AVONS REÇUE
THE STATIC ELECTRIC QUADRUPOLE INTERACTION
IN A SINGLE CRYSTAL OF ANTIFERROELECTRIC
PbHfO$_3$ STUDIED BY PERTURBED ANGULAR CORRELATION
OF 132-480 keV CASCADE IN $^{181}$Ta

by

Ng'andwe K. Mumba

A Thesis
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the Degree of Master of
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1977
ABSTRACT

The static electric quadrupole interaction at Hf-sites in antiferroelectric single crystalline PbHfO$_3$ is investigated at both room and high temperatures by the perturbed angular correlation method. For the application of this technique the crystal is irradiated to obtain the radioactive $^{181\text{Hf}}$. The $(152 + 137)$ keV - $(482 + 476)$ keV cascade in $^{181\text{Ta}}$ is used.

The quadrupole interaction frequency $\omega_q$ (= $44.444 \pm 1.350$ MHz) the asymmetry parameter $\eta$ (= $0.614 \pm 0.080$) and the frequency distribution of the smearing $\delta$ (= $14.165 \pm 8.253$ %) are determined by comparing the experimental results with the theoretical calculations. The maximal component of the quadrupole interaction $V_{zz}$ (= $46.252 \pm 0.890 \times 10^{20}$ V m$^{-2}$) is calculated the direction of the perturbing field is established by determining the polar angle $\beta$ (= $7.34^\circ \pm 0.35^\circ$) and the azimuthal angle $\alpha$ (= $5.10^\circ \pm 0.25^\circ$) defined with respect to a coordinate system with the crystal axis in the $z$-direction. Maximum sensitivity is obtained by orienting the crystal axis at $45^\circ$ with respect to counter 1 in the plane of the detectors. The effective mixing ratios for the cascade are also obtained: $A_{482}$ (ML/E2) (= $0.593 \pm 0.050$ ) and $A_{137}$ (ML/E2) (= $2.29 \pm 1.20$).

The investigations at high temperatures confirm the structural phase transformations undergone by the antiferroelectric PbHfO$_3$. In the cubic phase a small remaining quadrupole interaction is observed probably caused by lattice imperfections in the source.

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DEDICATION

This work has been dedicated to the beautiful memories of the late Mumba Nchindila, father, teacher and an African gentleman, for his love, his sternness and his high regard and expectation of his children.
ACKNOWLEDGEMENTS

I would like to thank all those who have helped me to complete my work. My special thanks go to Dr. E. E. Habib, my research supervisor; Dr. H. Ogata for the discussions I had with him during the preparations of this thesis and for his very valuable work on theoretical calculations; and Dr. F. Holuj for growing the crystal.

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CHAPTER I

ATTRACTIONS OF ANGULAR CORRELATION

The rapid improvement of the experimental techniques of nuclear spectroscopy in recent years, together with the development of nuclear models (Steffen, R.M. 1955) has provided important knowledge of the properties of low-lying nuclear levels. Information about the dynamic characteristics, such as beta and gamma transitions between these levels, as well as knowledge of the static properties of the ground state and of the first few excited states such as angular momenta and parities, magnetic moments and electric quadrupole moments are of considerable importance in the refinement of these models.

One of the most valuable tools of nuclear spectroscopy for the determination of angular momenta and parities of excited states is the study of angular correlation (H. Frauenfelder, 1953) and polarization direction correlation (F. Metzger and M. Deutsch, 1950) of successive nuclear radiation emitted from these states. The study of angular correlation in nuclear processes does not form a distinct part of nuclear physics as such; but rather a particular aspect involving a large variety of nuclear processes. A complete account of angular correlation aspects of all these processes would take us practically into every branch of nuclear physics. Angular correlation is influenced by various perturbation mechanisms such as electric and magnetic fields acting on the electric and magnetic moments of the nucleus; hence the name
of Perturbed Angular correlation. These perturbations may be externally applied fields or may be due to atomic, molecular or crystalline structure (S. Devons and LJB Goldfarb, 1957). When the lifetime of the intermediate state in a cascade emission is long enough (10^{-9}s) these interactions may become important. Though related to basic symmetry properties (total angular momentum or spin and parity), these interactions are equally coupled to more detailed properties of nuclear states such as coupling between nucleons, appropriate j-j or l-s descriptions, isotopic spin (of light nuclei) and in general detailed structures of nuclear states.

The investigation of perturbed angular correlation belongs to the field of nuclear spectroscopy in as far as methodology and equipment go. The possible applications, however, stretch from the commonly attacked problem of determination of nuclear magnetic moments and electric quadrupole moments of excited states to investigation of other fields of physics notably solid state physics. Moreover, the dependence of angular correlation on chemical and physical state of the radioactive source can provide information about the electric and magnetic fields prevailing at the decaying nucleus. As a consequence, information on atomic and molecular structure and the structure of liquids and solids can be obtained. When looked at as a physical method rather than a branch of low-energy nuclear spectroscopy, the attraction of P.A.C. to experimenters may be self-evident. Two difficulties arise when working with angular correlation; one is the
separation (or lack of it) of electric interaction from magnetic interaction and the other is complete knowledge of nuclear environment (Frauenfelder, 1965). In the conventional methods (microwave and nuclear resonance), by choosing a nucleus with spin \( \frac{1}{2} \), one can eliminate the quadrupole interaction and study the magnetic effects alone. However, in order to observe anisotropic correlation the spin of the intermediate nuclear level must be at least one. And in general a nucleus can possess a quadrupole moment. Thus it is impossible to eliminate one interaction in order to study the other using the angular correlation technique. Again, in conventional methods, the environment of the nucleus under investigation is known. It is in the ground state. In angular correlation work, however, the nuclear decay leading to the cascade (or the first radiation leading to cascade itself) very often excites the atomic shell. Thus the nuclear environment is unknown. This is more pronounced in a cascade preceded by a K-capture or an α-decay. The internal fields in solids and liquids can, as mentioned above, be investigated even if they are so large that they wash out nuclear resonance lines. It is possible also to work with metals or solid crystals (as is the case in our investigation) without difficulties arising from skin effects. And the change in atomic shell due to K-capture can be studied. It is clear, therefore that the possibilities offered by angular correlation, as mentioned above, including the g-factor determination for applied magnetic field, largely compensate for the disadvantages.
CHAPTER II

THEORY

2.1. Angular Correlation.

2.1.1. Introduction:

When a nucleus undergoes successive emissions of quanta, there exists a correlation between the directions of emission of these quanta. To facilitate a physical understanding, let us consider a large number of identical nuclei in a highly excited nuclear state about to undergo a single emission, with their spin vectors aligned in one direction. What is observed is the direction of emission of each quantum with respect to spin axis. After a large number of observations, it becomes clear that certain directions are more preferable than others; giving rise to a nonisotropic radiation distribution. For a mathematical description a probability angular distribution function is introduced $F_{L}(\theta)$ (Frauenfelder & Steffen, 1965). The function, $F_{L}(\theta)$ describes the distribution of angular probability of emission of a particle with total and its Z-component (along the spin axis) of angular momentum $L$ and $M$ respectively. For a dipole radiation pattern $L = 1$ while for $L = 2$ a quadrupole radiation pattern will be observed; a monopole radiation pattern is not observed since it never exists.

Now, consider a system consisting of a large number of nuclei randomly oriented undergoing the same kind of transition as above. In this case, the observed distribution will be
isotropic because the random orientation of the nuclei will result in random superposition of the individual radiation patterns. Suppose, now, that each of the randomly orientated nuclei undergoes two successive emissions and allow that the first radiation be energetically differentiated from the second. Since the emissions are cascaded and almost simultaneous, the second quantum may be observed by a coincidence-in-time experiment. We suppose that an arbitrary axis is constructed, through the source, along which the first quantum is detected. Certain superposition of the individual radiation patterns will have a higher probability than others along this chosen axis. The observation along this axis is equivalent to weighting the selection of the individual radiation patterns. Assuming that the emitted radiation possesses a unique angular momentum, it is deduced that the radiation patterns will differ only according to space orientation, that is, according to the M-value of the nucleus. Hence weighting the selection of individual radiation patterns is equivalent to weighting the selection of nuclear orientation. We say that the magnetic sublevels (M-values) of the nuclei have an unequal populations along the direction of the quantisation axis, after the first radiation.

Because of these unequal populations (of the M-values), certain of the radiation patterns for the second quantum in coincidence with the first quantum will have a higher overall
intensity than others. This intensity distribution of the second radiation with respect to the direction of propagation of the first one is known as the angular correlation of the two nuclear radiations. Cascade emissions involving more than two radiations is similarly defined. A necessary condition for an anisotropic angular correlation to occur is that some unequal m-level population in the intermediate state is preserved until the second radiation is emitted. In case no change of the magnetic sublevel population takes place during the lifetime of the intermediate state the correlation is termed undisturbed angular correlation (R. M. Steffen, 1955). This requires in general a rather short lifetime $\tau_n$ ($10^{-10}$s) of the intermediate state.

Angular correlation experiments identify the various magnetic sublevels of nuclei. If a magnetic and/or an electric fields are present the changes in the population of the m-substates will occur through the $\vec{u} \cdot \vec{B}$ and $\hat{Q} \cdot \vec{E}$ interactions, respectively. These changes in the m-sublevels can be studied as function of time. In other words, the interaction energy may be observed as a function of time. This topic will be the subject of Section 2.2.

2.1.2. Quantum Mechanical Description

The pioneer investigations of the quantum mechanical theory of angular correlation are due to Hamilton (Hamilton,
1940) who considered a double cascade emission of quanta from the nucleus. The emission of a quantum constitutes a transition between two states of the system i.e. nucleus + quantized radiation field. The quantized radiation is achieved by quantizing the normal amplitudes of the normal modes which, for convenience, are taken as plane waves. The idea of travelling plane waves brings in the concept of quantum mechanical oscillators with well-defined direction of propagation and polarisation, represented by the unit vectors \( \hat{\mathbf{k}} \) and \( \hat{\mathbf{\varepsilon}} \), respectively. The angular correlation function due to Hamilton suffers from many deficiencies even though it does contain some salient features which have in fact been used in the later theoretical works. Besides using the second order damping theory, the early treatment has been of limited applicability. It does not bring out the full generality of underlying features. In other words, the treatment is not rigorous enough.

A more general theory which gives ease of applications to various cases has been developed based on the first order perturbation theory (Frauenfelder H. and Steffen R., 1965). The progress in the theory has been due to the use of three tools: (i) group theory, (ii) Racah algebra, and (iii) density matrix formalism. The relations that are needed for the development of the theory are given in the Appendix, at the back.
In the following theory, some restrictions assumed by Hamilton are kept. The nuclear states are assumed to have well-defined symmetry properties, i.e., to be characterized by single values of the total angular momentum and parity. In addition, the radiations are assumed to be emitted in succession and not simultaneously.

In the discussion given here the following notation will be used:

\( I, I, I_f \) will denote the nuclear spin in the initial, intermediate and final states, respectively.

\( \Pi, \Pi, \Pi_f \) will denote the parity of initial, intermediate and final states, respectively.

\( m, m, m_f \) will denote the magnetic quantum numbers in the initial, intermediate and final states respectively.

\( m_a, m'_a, m_b, m'_b \) will denote the magnetic quantum numbers describing the end product of the first transition. In other words, \( m_a \rightarrow m_b \) will denote the mean lifetime of the intermediate state. The \( m'_a \) and \( m'_b \) are used for generality's sake.

\( R_1 \) or \( r_1 \) will denote the first emitted radiation described by quantum numbers \( I_1 \) and \( x_1 \). The second radiation \( R_2 \) or \( x_2 \) is similarly described by quantum numbers \( I_2 \) and \( x_2 \).
\( \rho_1, \rho(\hat{k}_1), \rho(\hat{k}_1, \hat{k}_2) \): will denote the density matrix of the initial state, the final state after the emission of \( R_1 \) in the direction \( \hat{k}_1 \), and the final state after the emission of \( R_2 \) in the direction \( \hat{k}_2 \).

\( \rho_a(\hat{k}_1) \rightarrow \rho_b(\hat{k}_1) \): will denote the change of density matrix in the intermediate state due to transitions between the different states of \( I \) during the time the intermediate state is exposed to extranuclear interaction.

We suppose that a nucleus decays from the initial level \( I \) with nuclear spin \( I_1 \), described by the density matrix \( \rho_1 \) to the intermediate level with spin \( I \). See Fig.2.1. The emitted radiation \( R_1 \) is observed in the direction \( \hat{k}_1 \). First order perturbation describes the process yielding the density matrix \( \rho(\hat{k}_1) \). By means of \( \rho(\hat{k}_1) \) the intermediate state is fully explained. Clearly, through \( \hat{k}_1 \), the density matrix is a function of direction of emission. The second step of the cascade, \( I \rightarrow I_f \), is treated in the same manner except that the density matrix \( \rho \) is not known a priori but is a result of the preceding transition. The second transition results in the density matrix \( \rho(\hat{k}_1, \hat{k}_2) \) dependent upon the second emission direction with respect to the first. Thus the first order perturbation together with the density matrix provide an adequate description of the correlation process.
Fig. 2.1: Two nuclear radiations emitted in cascade and the quantum numbers involved.
Fig. 2.2. The precession of nuclear angular momentum $\vec{I}$ and the magnetic moment $\vec{\mu}$ around a magnetic field $\vec{B}$.

Fig. 2.3. The precession of the nuclear angular momentum $\vec{I}$ and the electric quadrupole moment $\vec{Q}$ around the symmetry axis of an electrostatic gradient.
To derive the angular correlation function \( \mathcal{W}(\vec{k}_1, \vec{k}_2) \), we first consider the transition \( I_i \rightarrow I \). Applying Equation (Al.39) to this transition by setting \( a = m_i, b = m \) yields, for the density matrix \( \hat{\rho}(\vec{k}_1) \) in the intermediate state,

\[
\langle m | \hat{\rho}(\vec{k}_1) | m' \rangle = \int \sum_{m_i m'_i} \langle m | H_1 | m_i \rangle \langle m_i | \hat{\rho} | m'_i \rangle \times \langle m' | H_1 | m'_i \rangle^* \tag{2.1}
\]

where \( \int \) indicates summation over all unmeasured radiation properties (spin and polarization)

\[
\langle m | H_1 | m_i \rangle := \langle I, m, k, \sigma | H_1 | I, m \rangle ,
\]

\( \sigma_1 \) is given by the component of the spin of \( R_1 \) in the direction of propagation \( \vec{k}_1 \),

\( H_1 \) is the interaction operator for emission of \( R_1 \) into the direction \( \vec{k}_1 \) and polarization \( \sigma_1 \).

In Equation (2.1) angle independent factors are of no consequence and are set equal to unity. Similar application of Eqn. (Al.39) to the second transition setting \( a = m, b = m_f \) yields for the density matrix in the final state \( \hat{\rho}(\vec{k}_1, \vec{k}_2) \)

\[
\langle m_f | \hat{\rho}(\vec{k}_1, \vec{k}_2) | m'_f \rangle = \int \sum_{m, m', m_i, m'_i} \langle m_f | H_2 | m \rangle \langle m | H_1 | m_i \rangle \times \langle m'_i | \hat{\rho} | m'_i \rangle \times \langle m | H_1 | m'_i \rangle \times \langle m_f | H_2 | m'_f \rangle^* \tag{2.2}
\]

According to Equation (Al.31) the probability \( P_f(m_f) \) of finding the nucleus in the state \( m_f \) after emission of radiations \( R_1 \)
and \( R_2 \) in directions \( \vec{k}_1 \) and \( \vec{k}_2 \), respectively, is given by the diagonal elements of \( \rho \):\[
P_f(m_f) = \langle m_f | \rho(\vec{k}_1, \vec{k}_2) | m_f \rangle \quad (2.3)
\]

If the efficiency \( \varepsilon(m_f) \) of the counter system detecting \( R_1 \) and \( R_2 \) depends on the final state \( m_f \), the correlation function becomes
\[
\mathcal{W}(\vec{k}_1, \vec{k}_2) = \sum_{m_f} \varepsilon(m_f) \langle m_f | \rho(\vec{k}_1, \vec{k}_2) | m_f \rangle \quad (2.4)
\]

In directional correlation experiments, the efficiency is independent of \( m_f \) and the initial state \( I_1 \) is randomly oriented. Using Equations (A1.30) and (2.2) with \( \varepsilon(m_f) = \text{constant} \), Equation (2.4) becomes
\[
\mathcal{W}(\vec{k}_1, \vec{k}_2) = \int \sum_{m_f, m'} \langle m_f | H_2 | m \rangle \langle m | H_1 | m_1 \rangle \times

\times \langle m' | H_1 | m_1 \rangle^* \langle m_f | H_2 | m' \rangle \quad (2.5)
\]

Equation (2.5) is in a form suitable for extending to investigation of effects of extranuclear field on correlation process.

2.2. Perturbed Angular Correlation

2.2.1 Introduction

In Section 2.1.1., it has been pointed out that the undisturbed angular correlation occurs when no change of the
magnetic sublevel population takes place during the lifetime of the intermediate state. The undisturbed correlation is the maximum correlation observable; we may call it the true correlation. In general, a case of vanishing extranuclear field is not realised in practice, since, in reality, a variety of forces exist due to extranuclear environment. These forces include the commonly known hyperfine coupling and may also include externally applied magnetic and/or electric interactions, individually or in combination. The extranuclear forces induce changes in the magnetic sublevel populations giving rise to perturbation of the "true" correlation. Probably the single most distinguishing factor between perturbed and unperturbed angular correlation is the lifetime of the intermediate nuclear state. In the case of the unperturbed correlation, the time that elapses between the emission of the first and second radiations is insignificantly small. For mean lifetimes of the order of $10^{-10}$ s or less no perturbation is observed. In general perturbation effects may be observed when the mean lifetimes are $10^{-9}$ s or greater.

We have seen that observable influence of static extranuclear interactions on the angular correlation requires not only the presence of these perturbations but also sufficient time $t$ for the magnetic sublevel $m_{l}$ transitions to proceed. Where a precession frequency $\omega$, is defined the relative
attenuation of the correlation function is of the order of \( \omega t^2 \) (\( \omega t \ll 1 \)). The present sensitivity of the experimental techniques allows, under favourable circumstances, the precise criterion to become \( \omega t < 0.01 \). The angular correlation function can be given by the symbol \( \mathcal{W}(\hat{k}_1, \hat{k}_2; t) \); in which the time \( t \) dependence is explicitly emphasised.

Besides the static interactions, the time dependent interactions may also alter the "true" correlation. The lifetime of the intermediate state is still significant. However, these interactions do not form part of the subject of this work and therefore will not be discussed further.

The perturbation mechanism by which the angular correlation of a cascade is altered is through the interaction of either the magnetic dipole moment \( \vec{\mu} \) of the nucleus with extranuclear magnetic field \( \vec{B} \), or of the electric quadrupole moment \( \vec{Q} \) with the electric field gradients \( \vec{\nabla} E \). In the static case, the magnetic field \( \vec{B} \) exerts a torque on the nuclear magnetic dipole \( \vec{\mu} \) tending to align the nuclear magnetic axis in the direction of \( \vec{B} \) (Steffen R.M., 1953). The nuclear angular momentum (whose direction coincides with the magnetic axis of the nucleus) will respond to this torque by a precession around \( \vec{B} \) as axis (Fig. 2.2). Classically, this yields an angular precession velocity (Larmor frequency) independent of relative orientation of \( \vec{\mu} \) and \( \vec{B} \)

\[
\omega_m = -\frac{\vec{\mu} \cdot \vec{B}}{I \hbar}
\]  
  \[(2.6)\]
The sense of precession is determined by sign of $\mu$

Quantum mechanics restricts the angles $\theta$ between the axis of $\hat{\mu}$ and the field $\hat{B}$ to those which result in a component of $\hat{I}$ along $\hat{B}$ equal to an integer (magnetic quantum number) $I \geq m_z \geq -I$, thus allowing $2I+1$ different orientations of $\hat{I}$ with respect to $\hat{B}$. The potential energy of a magnetic dipole on a magnetic field depends upon the relative orientation i.e.

$$ E_m(m_z) = -\hat{\mu} \cdot \hat{B} = \frac{\mu B}{I} m_z $$

Different $m_z$ will produce different energies in the $2I+1$ substates. The magnetic splitting, the energy difference between two adjacent levels ($\Delta m_z = \pm 1$), is constant

$$ \Delta E_m = \frac{\mu B}{I} = \omega_m \hbar $$

The situation is slightly more complicated in the case of the electric interaction for no nuclear electric dipole exists. Hence no torque is exerted on the nucleus in the homogenous electric field. An interaction with the electric quadrupole moment of the nucleus necessitates the gradient of the electric field, $\nabla E$. This is a second order tensor quantity requiring, in general, nine components for its description (Steffen, R.M., 1953). By proper choice of axes (transformation to principal axes) and by virtue of certain properties of electric field (Laplace's Law) the number of components is reducible to two. Assuming an axial symmetric field (around $Z$-axis, say), the gradient is given by one number alone (e.g. $\frac{dE_z}{dz}$). The generalisation to non-axial (rhombic)field, however, is easily effected by introducing an asymmetry parameter $\eta$. 
\[ \eta = \left| \frac{\partial E_x}{\partial x} - \frac{\partial E_y}{\partial y} \right| / \frac{\partial E_z}{\partial z} \]  

(2.9)

To simplify the discussion axially symmetric electric gradients are assumed.

The interaction between such an electric gradient and a nuclear electric quadrupole moment gives rise to an aligning torque exerted on the nucleus. The ensuing "precession" of the angular momentum about the z-axis of the gradient field has in general more than one characteristic frequency depending upon the relative orientation of the nuclear spin axis \( \vec{i} \) with respect to z-axis (Fig. 2.3). This is reflected in unequal spacing of the \( 2I+1 \) energy levels caused by electric quadrupole coupling (Steffen, 1953). The potential energy of the quadrupole system, specifying the position of the axis of the nuclear quadrupole moment with respect to z-axis through the magnetic quantum number \( m_z \), is given by

\[ E_Q (m_z) = \frac{3 m_z^2 - I(I+1)}{4I \, (2I-1)} \, Q \, \frac{\partial E_z}{\partial z} \]  

(2.10)

Since positions of \( \vec{i} \) corresponding to \( +m \) and \( -m \) give the same energy the levels are two-fold degenerate. The classical interpretation of this energy degeneracy would make use of the picture that the quadrupole nucleus (the vector \( \vec{i} \)) precesses in one direction for the angle \( \theta < 90^\circ \) (\( +m \)) and with same precession frequency but in the opposite direction for the angle \( 180^\circ - \theta \) (\( -m \)) Fig. 2.3. Hence the quadrupole precession is not unidirectional like the magnetic precession. The characteristic frequencies, classically visualizable as precession frequencies of the quadrupole moment around the field axis corresponding
to energy differences between neighbouring levels, is

$$\omega = \frac{\Delta E}{\hbar} = \frac{E_\alpha(m_z) - E_\alpha(m_z')}{\hbar}$$  \hspace{1cm} (2.11)

The common feature of these static interactions is the occurrence of a precession of the nuclear spin around a well-defined stationary axis, the symmetry axis of the field. The latter has also been used as the axis of quantisation for which the $m_z$-values of the angular momentum projection have been defined (Steffen, 1955 & Frauenfelder, 1965). Except for phase changes between the $m_z$-sublevels, and the precession of $I$, these projections do not change. The interaction mechanism does not induce transitions between magnetic sublevels, defined with respect to the field axis, the axis of quantization. The population of the $m_z$-sublevels defined with respect to the direction of emission, as the axis of quantization, other than the field direction, is periodically changing with the precession of $I$ about the field axis as a result of the interaction. The second radiation is emitted from a level with an altered population distribution; a change, responsible for the attenuation of correlation. In the language of density matrices (Frauenfelder, 1965), the transitions among the $m_z$-states are described by a time dependence in the density matrix of the intermediate state.

If, however, the field axis $z$ coincides with the axis representing the direction of emission of radiation $k_1$ used for the introduction of unequal populated $m_{k_1}$-states then the $m_z$ are the same as the $m_{k_1}$. Since $m_z$ does not change neither does $m_{k_1}$. No perturbation correlation is possible.
A strong field may even be applied to anneal the trapped static interaction which may be present so as to restore the full undisturbed angular correlation. Only when the field axis is different from the direction of emission \( k_1 \) does perturbation in the angular correlation occur. The maximum attenuation of correlation to the point of complete disappearance occurs, in the case of static case, when the symmetry axis of the extranuclear field (z-axis) is normal to both directions of emission of nuclear radiation (Steffen, 1953).

Although, as we have said in Chapter 1, in angular correlation work both the magnetic dipole and electric quadrupole interaction can, in general, perturb the correlation, in solids, however the former interaction can be neglected except in the case of ferromagnetic materials. In the first place, the nucleus has a very small magnetic moment because the different velocities of the charges inside the nucleus are small compared to the velocity of light \( c \) (Roy R.R. and Nigam, 1967). This situation is further complicated because of quenching (C. Kittel, 1953) of the orbital contribution to the magnetic moment of the electron shell. The quenching phenomenon can be explained as follows:

In an electric field directed toward a fixed nucleus, the plane of a classical orbit is fixed in space. Denoting the orbital angular momentum by \( \mathbf{L} \), its square \( \mathbf{L}^2 \) and the magnetic angular momentum (the component of the orbital angular momentum) \( L_z \) are constant. In a noncentral field the plane of the orbit will move about; the angular momentum component is no longer constant and may average to zero. This is more so in a crystal with definite symmetry e.g. orthorhombic symmetry. When \( L_z \) averages to zero the orbital angular momentum is said to be quenched. [Hence in a solid crystal, the crystalline field is predominantly of electric quadrupole nature.]
2.2.2. Quantum Mechanical Description.

(a) General field:

We start with Equation (2.5) written in the following form (the notation follows from Section 2.1.2.)

\[ W(k, k_z) = \sum_{m_i, m_n, m_b, m'_i, m'_n, m'_b} \langle m_f | H_2 | m_b \rangle \langle m'_i | H_1 | m_i \rangle \delta_{m_n m'_n} \times \]
\[ \times \langle m'_i | H_1 | m'_b \rangle \langle m'_b | H_i | m_i \rangle \delta_{m_m m_m'} \delta_{m_n m_n'} \delta_{m_b m_b'}. \]  

(2.12)

where \( H_1 \) and \( H_2 \) represent the interaction between the nucleus and the radiation field only. In the absence of extranuclear perturbation the final states \( |m_a\rangle \) and \( |m'_a\rangle \) after the emission of the first radiation are identical with the initial states \( |m_b\rangle \) and \( |m'_b\rangle \) for the emission of the second radiation, Fig. 1.

We assume the presence of an interaction of the nucleus in its intermediate state with some extranuclear fields described by Hamiltonian \( \mathcal{E} \). This interaction acts from time \( t = 0 \) (when the first radiation is emitted) to time \( t = t \) (when the second radiation is emitted). In between this time interval, the states \( |m_a\rangle \) change to different states \( |m_b\rangle \) under the influence of the general extranuclear perturbation. This interaction may be represented by a unitary operator which describes the evolution of the state vectors \( |m_b\rangle \). The perturbed correlation can be expressed thus:

\[ W(k, k_z; t) = \sum_{m_i, m'_i} \langle m_f | H_2 \Lambda(t) | m_a \rangle \langle m_a | H_1 | m_i \rangle \langle m'_i | H_2 \Lambda(t) | m'_b \rangle \times \]
\[ \times \langle m'_a | H_1 | m'_b \rangle \langle m'_b | H_i | m_i \rangle \delta_{m_n m'_n} \delta_{m'_n m'_n} \delta_{m_b m_b'}. \]  

(2.13)
The states $|m\rangle$ form a complete set and the set vector $\Lambda(t)|m_a\rangle$ can be expressed as

$$\Lambda(t)|m_a\rangle = \sum_{m_b} |m_b\rangle \langle m_b| \Lambda(t)|m_a\rangle$$  \hspace{1cm} (2.14)$$

Similarly

$$\Lambda(t)|m'_a\rangle = \sum_{m'_b} |m'_b\rangle \langle m'_b| \Lambda(t)|m'_a\rangle$$

where the expansion coefficients are matrix elements of the time evolution operator $\Lambda(t)$ in the representation $m$. The time evolution $\Lambda(t)$ satisfies the Schrödinger equation

$$\frac{\partial}{\partial t} \Lambda(t) = -\frac{i}{\hbar} K \Lambda(t)$$  \hspace{1cm} (2.15)$$

For static interactions ($K$ independent of time $t$) the solution of Equation (2.15) is simply:

$$\Lambda(t) = \exp \left( -\frac{i}{\hbar} K t \right)$$  \hspace{1cm} (2.16)$$

Knowing the form of $\Lambda(t)$ we now write the perturbed correlation in the form:

$$\mathcal{W}(\vec{k}_1, \vec{k}_2, t) = \sum_{m_k, m'_k, m_a, m'_a} \langle m'_f|H_a|m_b\rangle \langle m_b|\Lambda(t)|m_a\rangle \langle m_a|H_i|m_i\rangle \times$$

$$\langle m'_f|H_i|m_b\rangle \langle m_b|\Lambda(t)|m'_a\rangle \langle m'_a|H_i|m_a\rangle$$  \hspace{1cm} (2.17)$$

Introducing the density matrices $\rho(\vec{k}_1)$ for the first transition and $\rho(\vec{k}_2)$ for the second transition we write for the correlation function:

$$\mathcal{W}(\vec{k}_1, \vec{k}_2, t) = \sum_{m_k, m'_k, m_a, m'_a} \langle m_a|\rho(\vec{k}_1)|m'_a\rangle \langle m'_b|\rho(\vec{k}_2)|m_b\rangle \times$$

$$\langle m_b|\Lambda(t)|m_a\rangle \langle m_b|\Lambda(t)|m'_a\rangle$$  \hspace{1cm} (2.18)$$
The discussion is restricted to the influence of extranuclear fields on directional correlations and not on circular polarisation correlations. With $r_1 = r_2 = 0$, cf. Appendix, Eqn (A.1.6) can be used to express the $D_{N,0}^k$ as spherical harmonics $Y_{N,0}^k(\theta, \phi)$. The definition of angles $\theta$ and $\phi$ with respect to the quantisation axis $z$ is shown in Fig. 2.4.

The density matrices in Equation (2.18) after a lengthy calculation (H. Frauenfelder and R. M. Steffen, 1965), for a general case can be expressed in the following form

\[
\langle m | \rho(k) | m' \rangle = \sum_{L, L', k, N} (-)^{2I - I' + m - L'} C_{k,0}^N(L', L) \times \left\{ \left( \begin{array}{ccc} k & k & k \\ N & N & N \end{array} \right) \right\} \times \langle I || L, \eta || I \rangle \langle I || L', \eta' || I \rangle^* \gamma_{k,0}^N(\theta, \phi)
\]

where $C_{k,0}^N(L, L')$ are radiation parameters for radiation of multiple orders $L$ and $L'$. $\theta, \phi$ of the spherical harmonics refer to the direction of observation of radiation with respect to arbitrary quantisation axis $z$.

Inserting Eqn. (2.19) and a similar expression for $\langle m' | \rho(k) | m \rangle$ for second radiation (Frauenfelder, 1965) we obtain the following correlation function:

\[
\mathcal{W}(k, k_2, t) = \sum_{k_1, k_2, N, N_2} A_{k_1}(I) A_{k_2}(I) \sum_{N, N_2} G_{k_1, k_2}^{N, N_2}(t) \left[ (2k_1 + 1) (2k_2 + 1) \right]^{-\frac{1}{2}} \times \gamma_{k_1}^N(\theta, \phi) \gamma_{k_2}^{N_2}(\theta, \phi)
\]

where:

\[
A_{k_2}(I) := A_k(L, \ell', I, I) = \sum_{L, \ell'} (-)^L C_{k,0}^L(L', \ell') \left\{ \begin{array}{ccc} I & I & k \\ L & \ell' & I \end{array} \right\} \times \langle I || L, \eta || I \rangle \langle I || L', \eta' || I \rangle^*
\]

(2.21)
\[ A_{k_k^{(2)}} = A_k(L_2'^{L_2} I_x I) = \sum_{L_2'^{L_2}} (-)^{L_2'} C^{*}_{k_2^{(L_2'^{L_2})}} L_2^{I_2} I_x I \times \langle I_x I_2'^{L_2} I_I \rangle \langle I_x I_2'^{L_2} I_I \rangle \]  

and where the perturbation factor \( G_{k_2,k_2}^{N,N_t_2} (t) \) is

\[
G_{k_2,k_2}^{N,N_t_2} (t) = \sum_{m_a^a, m_b^b} (-)^{L_2 + m_a + m_b} \left( \frac{2k_2 + 1}{2(k_2 + 1)} \right) \left( \frac{m_a^a - m_a^N, m_b^b}{m_b^b - m_b^N, N_2} \right) \times \langle m_a^a | \Lambda | m_a^a \rangle \langle m_a^b | \Lambda | m_a^b \rangle
\]

This general form of the perturbation factor was first derived by Abragam and Pound in 1953.

The influence of the extranuclear perturbation is completely described by the perturbation factor \( G_{k_2,k_2}^{N,N_t_2} (t) \); in general, complex.

For vanishing perturbation (indicated by \( t \approx 0 \) i.e. the lifetime of the intermediate nuclear state negligible), the evolution matrix \( \Lambda (t) \) reduces to the unit matrix. By the orthogonality relation, see Appendix, Equation (A1-13), of the 3-j symbols the perturbation factor reduces to

\[
G_{k_2,k_2}^{N,N_t_2} = \delta_{k_2,k_2} \delta_{N_2,N_t_2}
\]

The unperturbed directional correlation is obtained thus:

\[
\mathcal{W} (\theta, \phi) = \sum_k A_{k_k} P_k (\cos \theta)
\]

where

\[
A_{kk} = A_k (1) A_k (2)
\]

defined in Equations (2.21) and (2.22) above.

\( \theta \) : the angular separation of the two emissions.
(b) **Static interactions (classical fields)**

From the general perturbation case we consider now static interactions. The static interaction takes place when the perturbation of the correlation is caused by the interaction of the nuclear magnetic or electric (quadrupole) moments with a stationary external field that can be described classically. Examples include an externally applied magnetic field and, to a good approximation, a crystalline electric field. We first consider the general interaction Hamiltonian $K$ in order to discuss the perturbation factor. Later on the case of static electric quadrupole interaction will be considered.

(i) When the interaction is caused by classical fields the matrix elements of the time evolution operator $\Lambda(t)$ can easily be expressed in the $m$-representation. If $U$ is the unitary matrix diagonalising the Hamiltonian $K$, then

$$U K U^{-1} = E$$

(2.26)

where $E$ is the diagonal energy matrix with the diagonal elements (i.e. energy eigenvalues) $E_n$.

By the expansion of the exponential function the following relation holds

$$U \exp \left(-\frac{i}{\hbar} K t\right) U^{-1} = \exp \left(-\frac{i}{\hbar} E t\right)$$

(2.27)

Equation (2.24) can now be written as

$$\Lambda(t) = U^{-i} \exp \left(-\frac{i}{\hbar} E t\right) U$$

(2.28)

And the matrix elements of $\Lambda(t)$ in the $m$-representation are

$$\langle m_b | \Lambda(t) | m_a \rangle = \sum_n \langle n | m_b \rangle \exp \left(-\frac{i}{\hbar} E_n t\right) \langle n | m_a \rangle$$

(2.29)
where \( \langle m' \mid n \rangle \) are the matrix elements of the unitary matrix \( U \) that is obtained by solving the eigenvalue Equation (2.26).

The perturbation factor is then

\[
G_{N, n}^{N, n}(t) = \sum_{m_a, m_b} (-)^{2 I + m_a + m_b} \left[ (2 k_1 + 1)(2 k_2 + 1) \right]^{1/2} \times \\
\langle m_a \mid m_b \rangle \exp \left[ -(i \cdot \frac{\hbar}{2}) \left( E_a - E_{m_a} \right) t \right] \\
\langle \hat{n} \mid \hat{m}_a \rangle^* \langle \hat{n} \mid \hat{m}_b \rangle \\
\times \langle m_a' \mid m_b' \rangle \left( \begin{array}{c} \mathbb{I} \mathbb{I} \\ \mathbb{I} \mathbb{I} \end{array} \right)_{m_a' - m_a} \left( \begin{array}{c} \mathbb{I} \mathbb{I} \\ \mathbb{I} \mathbb{I} \end{array} \right)_{m_b' - m_b} \right)_{N, N} (2.30)
\]

When an axial symmetry exists in the perturbing field, for example a pure magnetic field or an axially symmetric electrostatic field, the symmetry axis of the interaction may be chosen parallel to \( \hat{z} \) and used as the quantisation axis for the eigenfunction of the Hamiltonian \( \hat{K} \). The eigenfunctions are \( \{ \hat{n} \} \) and \( \hat{K} \) and \( \Lambda(t) \) are diagonal in this representation \( (U = 1) \).

\[
\langle \hat{m}_a \mid \Lambda(t) \mid \hat{m}_b \rangle = \exp \left[ -(i \cdot \frac{\hbar}{2}) \left( E_a - E_{m_a} \right) t \right] \delta_{m_a} \delta_{m_b} \quad (2.31)
\]

The perturbation factor in this case is

\[
G_{k_1, k_2}^{N, N}(t) = \sum_{m} \left[ (2 k_1 + 1)(2 k_2 + 1) \right]^{1/2} \left( \begin{array}{c} \mathbb{I} \mathbb{I} \\ \mathbb{I} \mathbb{I} \end{array} \right)_{m} \times \\
\times \left( \begin{array}{c} \mathbb{I} \mathbb{I} \\ \mathbb{I} \mathbb{I} \end{array} \right)_{m} \exp \left[ -(i \cdot \frac{\hbar}{2}) \left( E_a - E_{m} \right) t \right] \right)_{N, N} (2.32)
\]

If the extranuclear field with axial symmetry is parallel to the radiation propagation direction of one of the two radiations e.g. \( \hat{r}_1 \), then

\[
\gamma_{k_1}^N(\theta, \varphi) = \delta_{N, \varnothing} \left[ \left( 2 k_1 + 1 \right) / 4 \pi \right]^{1/2}
\]

Only terms with \( m = m' \) in Equation 2.20 i.e. \( E_m = E_{m'} \) occur.

Using the orthogonality property of \( 3-j \) symbols, Equation (2.32) reduces to

\[
G_{k_1, k_2}^{N, N}(t) = \delta_{k_1, k_2}
\]
Fig 2.4: Angular Coordinates of the propagation directions $\vec{k}_1$ and $\vec{k}_2$

Fig 2.5: Position of $z^*$ axis defined by the Euler angles $\alpha$ and $\beta$
The foregoing argument shows that such a perturbation field will have no influence on angular correlation.

This fact can be appreciated on the basis of a semi-classical picture. Choose \( \mathbf{k}_1 \) as quantisation axis and assume, the axially symmetric field is parallel to it. The influence of this field can be interpreted as a precession of the intermediate nuclear state about \( \mathbf{k}_1 \). The projection of I on \( \mathbf{k}_1 \) is constant. Therefore the population of the \( m \)-state with respect to \( \mathbf{k}_1 \) remains the same. Hence the angular distribution of the second radiation with respect to \( \mathbf{k}_1 \) is not disturbed.

In numerous cases, angular correlations are observed using radioactive sources, in powder form, consisting of an ensemble of randomly oriented microcrystals, macroscopically isotropic. If the perturbation is caused by crystalline fields whose direction is related to the symmetry axes of the microcrystals, the observed correlation is obtained by averaging over the random directions of the symmetry axes of the microcrystals.

Suppose the interacting fields, in the individual microcrystals, are axially symmetric and denote this symmetry axis as \( z' \). The interaction Hamiltonian is thus diagonal in the \( z' \)-system, \( \mathbf{K}(z') = \mathbf{E} \) (2.33) with eigenvalues \( E_n \). The direction of the symmetry axis \( z' \) of the microcrystal is specified by the Euler angles \( (\alpha,\beta,0) \) with respect to the old \( z \)-system, Fig 2.5. The nondiagonal Hamiltonian is obtained by applying the rotation \( D^{(z)}(\alpha,\beta,\gamma) = D(1)^{-1}(\alpha,\beta,0)(\text{See Appendix}): \)

\[
K(z) = D(1)^{-1}(\alpha,\beta,0) K(z') D(1)(\alpha,\beta,0) \tag{2.34}
\]
Since \( K(z') \) is diagonal Equation (2.34) can be written as follows

\[
D^{(1)}(\alpha \beta \sigma) K(z) D^{(1)^{-1}}(\alpha \beta \sigma) = K(z') = \mathcal{E}
\]  
(2.35)

corresponding to Eqn (2.26). The unitary transformation \( D^{(1)}(\alpha \beta \sigma) \) diagonalizes \( K(z) \). The matrix elements of the evolution operator \( \Lambda(t) \) in the \( z \)-representation are, according to Eqn (2.29)

\[
\langle m_b | \Lambda(t) | m_a \rangle = \sum_n D^{(1)^*}_{n m_a} e^{-\frac{i}{\hbar} E_n t} D^{(1)}_{n m_b}
\]  
(2.36)

and the perturbation factor Eqn (2.23) is

\[
G^{N_i}_{m_i} (\pm) = \left[ (2k_i + 1)(2k_\pm + 1) \right] \sum_{m_a m_b} (-)^{m_a + m_b} \left( \begin{array}{ccc}
I & I & k_i \\

m_a & m_b & N_i \\

m_a' & m_b' & N_i \\
\end{array} \right) \times
\]

\[
x \exp \left[ -\frac{i}{\hbar} (E_{m_b} - E_{m_a}) t \right]
\]  
(2.37)

The summations over \( m_a \) and \( m_b \) can be performed by using the general contraction relation

\[
\sum_{m_a} \left( \begin{array}{ccc}
I & I & k_i \\

m_a' & -m_a & N_i \\
\end{array} \right) D^{(1)^*}_{n m_a} D^{(1)}_{n m_a} = \left( \begin{array}{ccc}
I & I & k_i \\

n' & -n & p_i \\
\end{array} \right) D^{k_i}_{p_i N_i}
\]  
(2.38)

where \( p_i \) takes any \( m_a \) 's.

Similarly for \( \sum_{m_b} \). Integrating over Euler angles \( \alpha \) and \( \beta \) Equation 2.37 gives

\[
G^{N_i}_{m_i} (\pm) = \frac{1}{4\pi} \left[ (2k_i + 1)(2k_\pm + 1) \right] \sum_{n', n} \left( \begin{array}{ccc}
I & I & k_i \\

n' & -n & p_i \\
\end{array} \right) \times
\]

\[
x \exp \left[ -\frac{i}{\hbar} (E_{m_b} - E_{m_a}) t \right] \int_0^{2\pi} \int_0^{2\pi} D^{k_i}_{p_i} (\xi \rho \sigma) D^{k_i}_{p_i} (\xi \rho \sigma) \sin \beta \ d\alpha d\beta
\]  
(2.39)

Using the orthogonality property of \( D \)-function the integration reduces to

\[
\frac{1}{4\pi} (2k_i + 1) \int \delta_{k_i k_\pm} \delta_{p_i N_i} \delta_{N_i N_a}
\]

giving rise to the following expression for perturbation.
factor $G_{kk}^{(t)}$ of a powder source:

$$G_{kk}^{(t)} = G_{k,k}^{N,N} x f = \sum_{n'}^{\infty} \left( I I k \right)^{2} \left( \left\langle n' \right| \left( E_n - E_{n'} \right) t \right)$$

Comparing with Equation (2.32), Equation (2.40) shows the following:

$$G_{kk}^{(t)} = G_{k,k}^{N,N} x f = \frac{1}{2^{k+1}} \sum_{N} G_{k,k}^{N,N} x f = G_{k,k}^{N,N} x f$$

is the perturbation factor for an axially symmetric interaction in a powder.

We consider now a case when the individual microcrystals in a powder source are not axially symmetric with respect to some crystalline axis $z'$ (Fig. 5). The interaction Hamiltonian $K(z')$ is not diagonal. Denoting by $U$ the unitary transformation that diagonalizes $K(z')$ Equation (2.35) becomes

$$U D_{\alpha\beta}^{(z')} K(z') D_{\alpha\beta}^{(z')} U^{-1} = U K(z') U^{-1} = \tilde{E}$$

the perturbation factor (H. Frauenfelder 1965) is now:

$$G_{kk}^{(t)} = G_{k,k}^{N,N} x f = \sum_{n,m}^{\infty} \left( I I k \right)^{2} \left( \left\langle n \right| \left( E_n - E_{n'} \right) t \right) \left\langle n \left| m \right\rangle \times \right.$$  

$$\times \left. \left\langle n' \left| m' \right\rangle \right. \right.$$  

Again this can be expressed in the form similar to Equation (2.41) thus:

$$G_{kk}^{(t)} = G_{k,k}^{N,N} x f = \sum_{n=-k}^{k} G_{k,k}^{N,N} x f$$

Since $G_{kk}^{(t)}$ is independent of $N_1, N_2$ the additional theorem for spherical harmonics can be applied to Equation (2.17).
The directional correlation for powder source has the form

$$W_p(\theta, t) = \sum_k A_k(1) A_k(2) G_{kk}(t) P_k(\cos \theta)$$  \hspace{1cm} (2.45)

with $A_k(1)$ and $A_k(2)$ retaining their definition as in Equations (2.21) and (2.22) and $G_{kk}(t)$ as in Equation (2.43). From Equation (2.45) we see that the effect of randomly oriented perturbation does not change the form of the angular correlation function. Only the coefficients of the $P_k(\cos \theta)$ are attenuated. The perturbation factors $G_{kk}(t)$ for macroscopically isotropic sources (no privileged direction) are thus commonly known as the attenuation factors.

The attenuation factors of Equation (2.40) can be written in the form:

$$G_{kk}(t) = \frac{1}{2k+1} \sum_{n \neq n'} \left( \begin{array}{c} I \\ n' - n \\ p \end{array} \right) \left( \begin{array}{c} I \\ k \end{array} \right)^2 \cos \left[ (E_n - E_{n'}) t \right]$$  \hspace{1cm} (2.46)

The total time-integrated attenuation factor is:

$$\overline{G}_{kk}(\omega) = \frac{1}{2k+1} + \sum_{n \neq n'} \left( \begin{array}{c} I \\ n' - n \\ p \end{array} \right) \left( \begin{array}{c} I \\ k \end{array} \right)^2 \frac{1}{1 + \left[ (E_n - E_{n'})^{1/2} \right]^2}$$  \hspace{1cm} (2.47)

A very interesting feature of the time-integrated attenuation factors for static interaction with macroscopically isotropic source is the existence of finite lower limits, the so-called hard-core values (Abragam & Pound, 1953) which are independent of interaction. Thus the time-integrated angular correlation is never completely wiped out no matter how strong the perturbation and for how long it acts (Devons & Goldfarb L.J.B. 1957). For axially symmetric fields the hard-core values (from Equation (2.47) ) are:
Because of degeneracies \( E_n = E_{n'} \) for \( n \neq n' \) the value given by Equation (2.48) will be larger, depending on the symmetry properties of the perturbing fields. These "hard-core" values refer to time-integrated correlation only. For finite delay times, other, possibly smaller, attenuation coefficients are found.

For non-axially symmetric static interaction, the time-integrated attenuation factor is

\[
\overline{G}_{kk}(\infty) = \sum_{m_a, m_b, N} (-1)^{2I + m_a + m_b} \begin{pmatrix} I & I & k \\ \cdot & m_a & N \\ \cdot & -m_b & N \end{pmatrix} \begin{pmatrix} I & I & k \\ \cdot & m'_a & N \\ \cdot & -m'_b & N \end{pmatrix} \times \\
\times \langle n | m_b \rangle \langle n | m_a \rangle \langle n' | m'_b \rangle \langle n' | m'_a \rangle \frac{1}{1 + \frac{(E_n - E_{n'})^2}{\hbar^2}}
\]

Again non-zero limiting values exist for \( E_n = E_{n'} \).

\( \text{(ii) We now consider the perturbation due to static electric quadrupole interaction. This is the perturbation which features in the experimental part of this work. The crystalline field has been approximated to classical field perturbation case.} \)
\[ K_q = \frac{4\pi}{\hbar^2} T^{(2)} V^{(2)} = \frac{4\pi}{\hbar^2} \sum (-)^q T_q^{(2)} V^{(2)} \]  

(2.50)

where \( T^{(2)} \) is the second rank tensor operator of the nuclear quadrupole moment with the components:

\[ T_q^{(2)} = \sum_p e_p r_p^2 Y_q^2 (\theta_p, \varphi_p) \]  

(2.51)

where \( e_p \) are the point charges in the nucleus specified by points \( (r_p, \theta_p, \varphi_p) \)

\( V^{(2)} \) is the tensor operator of the classical external field gradient.

We assume the electrostatic field is caused by point charges \( q \) (ions in a crystal lattice) at points \( (r_c, \theta_c, \varphi_c) \) with respect to the nuclear centre. The field tensor \( V^{(2)} \) has the components given by:

\[ V_q^{(2)} = \sum_c \frac{q_c}{r_c^3} Y_q^2 (\theta_c, \varphi_c) \]  

(2.52)

Or in an arbitrary cartesian coordinate system \( x', y', z' \) the cartesian components are given thus

\[ V_o^{(2)} = \frac{1}{4} \sqrt{\frac{\sigma}{\pi}} V_x x' \]  

\[ V_{11}^{(2)} = \pm \frac{\sigma}{6\pi} (V_{x'} \pm i V_{y'} \mp i V_{z'}) \]  

\[ V_{22}^{(2)} = \frac{1}{4} \sqrt{\frac{\sigma}{6\pi}} (V_{x'} - V_{y'} \mp 2i V_{z'}) \]  

(2.53)

If a principal axes system \( (x, y, z) \), in which mixed derivatives of \( V \) disappear, is chosen, Equation (2.53) reduces to
\[
\begin{align*}
\nu_{z}^{(2)} &= -\frac{1}{4}\sqrt{\frac{2}{\pi}} \nu_{zz} \\
\nu_{z}^{(2)} &= 0 \\
\nu_{zz}^{(2)} &= -\frac{1}{4} \sqrt{\frac{2}{\pi}} (\nu_{xx} - \nu_{yy}) = \frac{1}{4} \frac{a^2}{L^2} \eta \nu_{zz}
\end{align*}
\]

where

\[
\eta = (\nu_{xx} - \nu_{yy}) / \nu_{zz}
\]

is the asymmetry parameter (a measure of the deviation from spherical symmetry).

We choose the principal axes such that \(|\nu_{xx}| < |\nu_{yy}| < |\nu_{zz}|\) so that (together with the Laplace equation \(\sum_{i=1}^{3} \nu_{ii} = 0\))

\[0 < \eta < 1\]

The gradient tensor is determined by two parameters \(\eta\) and \(\nu_{zz}\). For axially symmetric fields (with respect to the z-axis) \(\eta = 0\) and only \(\nu_{z}^{(2)}\) is a non-vanishing component. The Hamiltonian in Equation (2.50) reduces to:

\[
K_{Q} = \sqrt{\frac{\mu}{5}} T_{o}^{(2)} \nu_{zz}
\]

The matrix elements of this Hamiltonian in the \(m\)-representation, using the Wigner-Eckart theorem, are given by:

\[
\langle \bar{I} m | K_{Q} | I m' \rangle = \sqrt{\frac{\mu}{5}} \nu_{zz} \langle \bar{I} m | T_{o}^{(2)} | I m' \rangle
\]

\[
= \frac{\mu}{6} \nu_{zz} (-)^{1-m} \langle \bar{I} 1 2 1 \rangle \langle 1 \parallel T_{o}^{(2)} \parallel 1 \rangle
\]

For \(m \neq m'\), the 3-j symbol in this equation vanishes; \(K_{Q}\) is diagonal.

By definition (conventionally) the electric quadrupole moment is:
\[ e Q = \left< \mathbf{II} \right| \sum_p e_p \left( 3 \mathbf{z}_p^2 - \mathbf{r}_p^2 \right) \left| \mathbf{II} \right> \] (2.58)

or

\[ e Q = 4 \sqrt{\frac{\pi}{6}} \left< \mathbf{II} \right| T^{(2)} \left| \mathbf{II} \right> \] (2.59)

Applying the Wigner–Eckart theorem to Equation (2.59)

\[ e Q = 4 \sqrt{\frac{\pi}{6}} \left( \frac{I}{I-1} \frac{I}{I} \right) \left< \mathbf{II} \right| T^{(2)} \left| \mathbf{II} \right> \] (2.60)

The quadrupole interaction matrix elements, Equation (2.57), can be written thus

\[ \left< \mathbf{I}_m \right| K_Q \left| \mathbf{I}_m \right> = E_m = \frac{3m^2 - I(I+1)}{4I(2I-1)} e Q V_{zz} \] (2.61)

For convenience we introduce the quadrupole frequency \( \omega_Q \):

\[ \omega_Q := -\frac{e Q V_{zz}}{4I(2I-1)\hbar} \] (2.62)

so that

\[ E_m = \left[ I(I+1) - 3 m^2 \right] \omega_Q \hbar \] (2.63)

Denoting the angular frequency for the smallest nonvanishing energy difference by \( \omega_0 \) we have

\[ \omega_0 = \begin{cases} 3 \omega_Q & \text{for even } I \\ 6 \omega_Q & \text{for odd } I \end{cases} \] (2.64)
From Equations (2.63) and (2.64) it is clear that the energy splitting due to the static quadrupole interaction is not uniform and that the states are two-fold degenerate i.e. \( \pm m \) and \( -m \) give the same energy. It is no longer possible to describe the influence of the quadrupole interaction on angular correlation by a simple semi-classical precession of the correlation pattern.

The perturbation factor for the static quadrupole interaction is, according to Equation (2.32):

\[
G_{k_1 k_2}^{NN} = \left[ (2k_1 + \Delta)(2k_2 + \Delta) \right] \sum_{m m'} \left( I \frac{k_1}{k_2} \frac{I}{I} \frac{k_1}{k_2} \right) \exp \left[ \frac{i}{\hbar} (m m' \hbar) \right] (2.65)
\]

The factor multiplying the two 3-j symbols depends on the summation index \( m \). The summation cannot be performed simply, because the orthogonality property of the 3-j symbols can not be used to cause the disappearance of the interference terms, \( k_1 \neq k_2 \). The factors \( A_{k_1} \) (1) and \( A_{k_2} \) (2) Eqn (2.45) must be known individually in order to compute the "interference" factors \( A_{k_1} \) (1) \( A_{k_1} \) (2). In general, this requires an accurate knowledge of the multiple expansion of the two radiations involved in the cascade. From Equation (2.65) it is shown that for either \( k_1 \) or \( k_2 \) equal to zero, the perturbation factor vanishes. Thus interference terms occur only if \( k_{\text{max}} \geq 4 \).

The perturbation factor Equation (2.65) can be written in a somewhat more instructive form,

\[
G_{k_1 k_2}^{NN} (t) = \sum_n S_n^{k_1 k_2} \cos (n \omega_0 t) \quad (2.66)
\]
with
\[
S_{nN}^{k_1k_2} = \sum_{m,m'}'(I^{I^I} k_1)(I^{I^I} k_2)(\frac{2k_1+1}{2k_2+1}) \frac{2k_1k_2}{2k_1k_2}
\] (2.67)
where the prime on \(\sum\) sign means that the summation over \(m\) and \(m'\) should only include those terms where \(m\) and \(m'\) satisfy the condition:
\[
|m^2 - m'^2| = n \quad \text{for integer } I
\]
\[
\frac{1}{2} m^2 - m'^2 = n \quad \text{for half-integer } I
\] (2.68)
Numerical values of the coefficients \(S_{nN}\) have been tabulated (K. Alder and Others, 1953) for some cases. By using Equations (2.66) and (2.67), the directional correlation perturbed by an axially symmetric electrostatic gradient in an arbitrary direction (e.g. for a noncubic single crystal source) can be (K. Alder and others, 1953) calculated:

In a macroscopically isotropic source, the polycrystalline powder source, the influence of an axially symmetric quadrupole interaction is represented (H. Frauenfelder, 1965) by
\[
G_{kk}(t) = \sum S_{kn} \cos (n\omega_0 t)
\] (2.69)
with
\[
S_{kn} = \sum' \begin{pmatrix} I & I & k \\ m & -m & -m+m \end{pmatrix}
\] (2.70)
where the prime on \(\sum\) implies \(m\) and \(m'\) must obey the condition given by equation (2.68).
\(\omega_0\) is given by Equations (2.62) and (2.64). The calculation of attenuation factors for powder sources where
the interaction is caused by non-axial (rhombic) electrostatic field gradients is considerably more complicated. (Frauenfelder, 1965). The rhombic field Hamiltonian must be diagonalized and the eigenvalues and eigenfunctions must be determined for different values of $\alpha_k$ and asymmetry $\eta$. The attenuation can then be computed from the general expression (2.49).

Hitherto it has been assumed that the electric field gradients acting on the nuclear quadrupole moments are the same at each nuclear site. This is an idealization. Slight variations of crystalline fields will be caused by imperfection in the lattices and also by impurity centres. In most cases, the radioactive decay process transforms the $i$th atom in lattice into an impurity centre. Because of recoil energy during the decay process, an atom may be displaced from its regular lattice position to some less well defined point. The effect is that variations in the fields experienced by the nuclei in their intermediate states occur. The frequency-averaged perturbation factor is then given by (Frauenfelder, 1965)

$$\delta_{N_k N_k^*}^{M_k M_k^*} (\omega) = \frac{\int G_{N_k N_k^*}^{M_k M_k^*} (\omega) P(\omega^*) d\omega}{\int P(\omega^*) d\omega}$$  \hspace{1cm} (2.71)

where

$$P(\omega^*)$$ : is Probability distribution of the quadrupole interaction frequency given by:

$$P(\omega^*) d\omega = \frac{1}{\sqrt{2\pi} \sigma} \exp \left[ -\frac{(\omega^* - \omega^*_0)^2}{2\sigma^2} \right] d\omega$$ \hspace{1cm} (2.72)
where

$\omega_0$: centroid

$\omega_n$: centres of the frequency distributions representing interaction frequencies of the perfect crystal

$\sigma$: width of the distribution

$\delta = \frac{\sigma}{\omega}$: the relative width of the distribution

Other factors are as defined above.

The discussion above has been simplified by assuming axial symmetry about z-axis. But the discussion in the last paragraph has shown that this assumption is but a very rough approximation. Hence the experimental investigation of electric quadrupole interactions in solids by angular correlation perturbation method will yield at least two quantities, viz the quadrupole interaction frequency $\omega_Q$ and the asymmetry parameter $\eta$ given by Equations (2.84) and (2.76), respectively.

2.3 Experimental Formulae

(i) The angular correlation function $W(\mathbf{k}_1, \mathbf{k}_2)$ given by Equation (2.5) must be reduced to a more attractive form for a more meaningful appreciation of the information contained therein. This involves the transformations of matrix elements of the type $\langle m | H | m' \rangle$ and $\langle -m | f(\mathbf{k}) | -m' \rangle$, where $\langle -m \rangle$ stands for $\langle I_m k | \sigma \rangle$, $H$ for the perturbing Hamiltonian and $f(\mathbf{k})$ stands for the density operator; $\mathbf{k}$ for the direction
of propagation of the radiation and \( \sigma \) the polarisation of the radiation. After detailed manipulation of the above matrix elements (Frauenfelder, 1965) the angular correlation function \( \mathcal{W}(\mathbf{k}_1, \mathbf{k}_2) \) is given by:

\[
\mathcal{W}(\mathbf{k}_1, \mathbf{k}_2) = \sum (-1)^{z_1 - z_2 - I_1} \left\langle I \mid \mathbf{L} \mid I_1 \right\rangle \left\langle I_1 \mid \mathbf{L} \mid I \right\rangle \left\langle I \mid \mathbf{L} \mid I_2 \right\rangle \left\langle I_2 \mid \mathbf{L} \mid I \right\rangle \times \\
x \left\langle I \mid \mathbf{L} \mid I_1 \right\rangle \left\langle I \mid \mathbf{L} \mid I_2 \right\rangle \times C_{k_1, \ell_1} \times \\
x C^*_{k_2, \ell_2} \oint_D^{k_2} \oint_D^{k_1} (\mathbf{k}_2 \rightarrow \mathbf{k}_1)
\]

(2.73)

where \( D_{k_1} \) are the rotational matrices

\( C_{k_1} \) are Racah radiation parameters defined by

\[
C_{k_1}(\ell, \ell') = \int \sum_{\ell'\mu'\nu'} (-)^{L - L' - \ell - \ell'} \left\langle L \mid \ell \mu \nu \mid k_1 \right\rangle \left\langle \sigma \mid L \mu \nu \right\rangle^* \\
\times \left\langle \sigma \mid L' \mu' \nu' \right\rangle
\]

(2.74)

and satisfying the relation,

\[
C_{k_1}(\ell, \ell') = (-)^{L - L' - \ell} \circ \mathcal{C}_{k_1}(\ell, \ell')
\]

(2.75)

These parameters \( C_{k_1} \) are characteristic of the emitted radiation through the transformation coefficients \( \left\langle \sigma \mid L \mu \mu' \right\rangle \) and of the experimental arrangement through the averaging process designated by \( S \). It is stated formally that \( C_k \) (\( \underline{\mu} \underline{\nu} \)) are eigenfunctions of the operators for the total angular momentum and the \( z \)-component of the angular momentum with eigenvalues \( k \) and \( \tau \) (\( k \) and \( \tau \) have no physical significance except they are convenient summation indices).

When only the directional correlation \( \mathcal{W}(\phi) \) is needed
(very often this is the case experimentally) only $C_{ko}$ appears in equation (2.73). In other words the angular correlation function $W(k_1, k_2)$ will be independent of Euler angles denoting rotation about the directions of propagation $\vec{k}_1$ and $\vec{k}_2$. That is $\gamma = \alpha = 0$. The representation $D^k$ in Equation 2.73 transform into Legendre polynomials (See Appendix) and expression (2.73) simplifies to

$$W(k_1, k_2) = W(\theta) = \sum_{k \text{ (even)}} A'_{kk} P_k(\cos \theta)$$

(2.76)

where

$$A'_{kk} = A_k' (L, L', \Lambda; I) A_k'(L_2, L_2', \Lambda_2 I)$$

(2.77)

with $A_k'(1)$ and $A_k'(2)$ defined by Equations (2.21) and (2.22).

The most convenient form of describing the directional correlation $W(\theta)$ for double cascade emission is (Frauenfelder, 1965)

$$W(\theta) = 1 + A_{z2} P_2(\cos \theta) + \ldots + A_{k_{max} k_{max}} P_{(\cos \theta)}$$

(2.78)

where $A_{kk} = \frac{A'_{kk}}{A'_{00}}$

For both pure and mixed multipoles $L_1$ and $L_2$ the form of Equation (2.78) holds, differing only in the values
(Frauenfelder 1965) of \( A_k(1) \) and \( A_k(2) \), that is

\[
A_k(1) = \frac{F_k(L, L', I) + 2\Delta_1(L') F_k(L, L', I) + \Delta_1(L') F_k(L, L', I)}{1 + \Delta_1(L')}
\]  

(2.79)

Similarly for \( A_k(2) \),

where

\[
F_k(L, L', I) = \frac{A_k(L, L', I)}{A'_{k}(L, L', I)}
\]  

(2.80)

\( \Delta \): is the amplitude mixing ratio between the electric multipole and the magnetic multipoles defined as the ratio of the reduced matrix elements (for the first transition).

\[
\Delta_1(L') = \frac{\langle I \mid L', \eta' \mid I \rangle}{\langle I \mid L, \eta \mid I \rangle}
\]  

(2.81)

where: \( L \), \( I \) refer to the first transition and the prime distinguishes between the electric and magnetic multipoles.

and a similar expression for \( \Delta_2(L') \) for the second transition is analogously defined.

The experimental investigation of a \( \gamma - \eta \) directional correlation will at best yield two constants \( A_{22} \) and \( A_{44} \). Higher terms have not yet been observed. This being the situation, since the energies that normally are available in radioactive decays are such that multipoles with \( L > 2 \) possess a half life \( > 10^{-6} \) sec. The half life is too long for directional correlation function for such a cascade to be measurable. The measured correlation is taken at \( 180^0 \) and \( 90^0 \) and the result expressed as a ratio, so-called anisotropy, \( R(t) \) defined by

\[
R(t \neq 0) = \frac{W(180^0)}{W(90^0)} - 1
\]  

(2.82)
or equivalently as
\[ W(t=0) = 2 \frac{W(180^\circ) - W(90^\circ)}{W(180^\circ) + W(90^\circ)} \]  
(2.83)

The latter expression has been used in this work.

(ii) The perturbed directional angular correlation function \( W(\theta, t) \) given in Equation 2.20 with \( G_{k_1k_2}^{N_1N_2}(t) \) given in Equation 2.30 is valid for a perfect crystal. In the theoretical calculation \( W(\theta, t) \) has been adapted to take into account the fact that we are dealing with a real crystal with lattice imperfections. The \( W(\theta, t) \) used has been adapted by Dr. H. Ogata and is given in the following form:

\[
W(\theta, t) = \sum_{k_1=0,2,4} \sum_{N_1=-k_1}^{k_1} \sum_{m_\alpha, m_\alpha'} \chi_1 \sum_{I} (-)^{I+m_\alpha} A_{k_1k_1}^{N_1} (\cos \theta_1) \sum_{m_\alpha, m_\alpha'} \chi_1 \sum_{I} (-)^{I+m_\beta} A_{k_2k_2}^{N_2} (\cos \theta_2) \sum_{m_\beta, m_\beta'} \chi_2 e^{-iN_1N_2} \chi_2 \sum_{n=-I}^{I} \sum_{n'=-I}^{I} \langle n \mid m_\alpha \rangle \langle n' \mid m_\alpha' \rangle^* \langle n \mid m_\beta \rangle \langle n' \mid m_\beta' \rangle \times \left< e^{-i(E(n) - E(n'))t} \sum_{n} \sum_{n'}^\omega \right> \]

(2.84)

where \( \tau_R \) is the response time of the time to amplitude.
Converter (T.A.C.) discussed in Chapter 3.

\[ A_{ki}^i (k = 0, 2, 4, \ldots; \ i = 1, 2) \] are the correlation coefficients defined in Equation 2.79.

The averaging over \( \omega_o \) is carried out because the field gradients differ at different \( H \) sites giving rise to different coupling energies. The smearing \( \delta \) (= \( \sigma / \omega_o \), Equation 2.72, \( \sigma \) = width of frequency distribution) is the relative width of the frequency distribution about some centroid frequency distribution about some centroid frequency \( \omega_o \). Other parameters including \( \alpha, \beta \) and \( \eta \) are contained in the matrix elements \( \langle n|m \rangle \) forming the last summation in Equation 2.84.

In analogy with the formal expression (2.78) the correlation function is expressible (Steffen, 1955 and Frauenfelder, 1965) as:

\[ \mathcal{W}(e, t) = 1 + A_{22} \mathcal{G}_{22}(t, \cos \theta) + \cdots + A_{kk} \mathcal{G}_{kk}(t, \cos \theta) \]  

(2.85)

where \( \mathcal{G}_{kk}(t), (k = 2, 4, \ldots) \) are the perturbation factors.

Here we restrict ourselves to the case of static quadrupole interaction in a single crystal for which the experimental work has been done. As stated above, what need be calculated is the anisotropy \( R(t) \) from the formal expression (2.83).

In order to see the relation between \( \mathcal{G}_{kk}(t) \) and \( R(t) \) and because \( A_{44} \) is usually very small, the expansion in Equation (2.85) may be limited to two terms, as follows:
\[ W(\theta, t) \approx 1 + A_2 G_{zz}(t) P_2(\cos \theta) \]

It follows that:

\[ W(\theta, t) \approx 1 + A_2 G_{zz}(t) \frac{1}{2} (\cos^2 \theta - 1) \quad (2.85) \]

so that

\[ R(t) \approx \frac{3}{2 + A_2^o} \quad (2.86) \]

where

\[ A_2^o \approx A_2 G_{zz}(t) \]

or

\[ A_2 G_{zz}(t) \approx - \frac{2}{3} \frac{R(t)}{3 - R(t)} \quad (2.87) \]

The experimental results will yield \( \omega_0 \) from Equation (2.87). From Equation (2.62) and (2.64) the nuclear quadrupole moment or the quadrupole interaction can be deduced through the knowledge of either parameter. The electrostatic gradients are (Frauenfelder, 1965) typically of the order of \( 10^{16} - 10^{18} \, \text{Vcm}^{-2} \). However, their exact calculation at nuclear sites is very difficult. In this work the experiments have been performed which established \( R(t) \). From these results the precession frequency \( \omega_P \); and electrostatic gradient \( \nabla E \) have been calculated.
CHAPTER III

EXPERIMENT

3.1. Apparatus

3.1.1. General

The block diagrams of the apparatus used are shown in Figs. 3.1 and 3.2. The directional correlation of the (132 keV and 480 keV) $\gamma - \gamma$ cascade in $^{181}$Ta has been observed time-differentially using a two-detector fast-slow-coincidence system. The scintillation detectors used consisted of 2" X 2" and $\frac{1}{4}$" X 2" NaI(Tl) crystals mounted on the 56 AVP photomultipliers. The smaller crystal detected the 132keV $\gamma$-ray and the bigger crystal detected the 480 keV $\gamma$-ray. This choice of crystal resulted in the lowering of the random coincidence rate. The nominal total range of the time-to-amplitude converter (TAC) was set to 250 ns. The time coincidence spectra were registered in either of the two 200 channel subgroups of the multichannel analyser for the detector angles 90° and 180°.

The calibration was done before and after each experiment by the use of a Helical delay line described by McAllindon, with the delay of 2.384 ns per revolution. Lateral lead shielding has been used to minimize coincidences due to scattering.

In the next subsection we give the description of the working of the apparatus.
Fig 3.1 Block diagram of Apparatus Used to Set the lower level and window.
Fig 3.2: Block diagram of Apparatus showing
time spectrum
3.1.1. **Electronics and the Selection of 132-480 keV Cascade**

The pulse output from the anode (14th dynode) of the photomultiplier tube was fed into the comparator, Fig. 3.1. The anode was grounded for safety. The comparator was set at some specific voltage to which all input pulses were compared. A pulse was formed in the comparator when the height of the input pulse was greater than the set voltage. In this way, noise due to thermal emission of electrons from the photocathode was minimized. This procedure was independently followed for both detectors. The output pulses from the comparator were fed to a time-to-amplitude converter, Ortec Model 447. The T.A.C. was able to determine the time interval between $\gamma_1$ and $\gamma_2$-pulses by utilizing the start-pulse-stop-pulse principle. In the experiments conducted, the $\gamma_1$-pulse was used as a start pulse and the $\gamma_2$-pulse, delayed by 30 ns, was used as the stop pulse. A length of cable (Amphenol Canada - RG 58 A/V Serial 03554) was used to produce the required delay. The entire line from the anode through the T.A.C. constituted the fast pulse system. The output of the TAC was fed to the multichannel analyser.

The slow pulse output risetime approximately 0.1 $\mu$s and positive from the 10th dynode was fed through the amplifiers to the single channel analyser (SCA). By means of the SCA, the 132 keV-pulses and the 480 keV-pulses (detected by counters 1 and 2, respectively), forming the cascade were selected, Fig. 3.3. The slow pulses were also fed to the
Fig 3.4: Hf$^{181}$ Decay Scheme (Table of Isotopes)

(Not Drawn to Scale)
kicksorter through a 2 μs delay line (Technical Measurement Corp, Model 404). The kicksorter was gated by the output of the single channel analyser and therefore analysed only pulses accepted by the window of the SCA. In this way the windows could be easily set to the photopeaks of the 132 keV and 480 keV gamma rays. In the final analysis, therefore, the slow pulse system was used to ensure that only the \( \gamma_1 \)-pulses and the \( \gamma_2 \)-pulses forming the cascade in the \(^{181}\)Hf decay were used in the final coincidence analysis.

With the SCA's adjusted as described above, the final set up, for time analysis of the coincidence counting between \( \gamma_1 \) and \( \gamma_2 \), was connected as shown in Fig. 3.2. The outputs of the SCA were fed into the double coincidence circuit. The double coincidence circuit worked on the principle that a coincidence count would occur between \( \gamma_1 \) and \( \gamma_2 \) only if they are genetically related. The output of the double coincidence circuit was used to gate the kicksorter. The kicksorter produced a spectrum which was a coincidence rate as a function of time, the channel number being proportional to time. The time calibration was carried out by the method described by McAllindon and also by Graham (Graham R.L. etc, 1957). The calibration apparatus included the pulse generator (Tektronics Type 110) and the delay cable (Tektronics Type 113) and the Helical delay line which has been built locally and described by McAllindon (McAllindon, 1965). McAllindon established that one rotation of the delay line introduced a relative time delay of 2.384 ns to within 1%. Using the
<table>
<thead>
<tr>
<th>Delay Line No. (for every 2 Rotations)</th>
<th>Centroid</th>
<th>Channels</th>
</tr>
</thead>
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<tr>
<td>10</td>
<td>39.197</td>
<td>0</td>
</tr>
<tr>
<td>12</td>
<td>43.278</td>
<td>4.081</td>
</tr>
<tr>
<td>14</td>
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<td>4.100</td>
</tr>
<tr>
<td>16</td>
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<td>4.188</td>
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<td>4.227</td>
</tr>
<tr>
<td>20</td>
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<td>4.172</td>
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<tr>
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<td>4.030</td>
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<tr>
<td>24</td>
<td>68.306</td>
<td>4.301</td>
</tr>
<tr>
<td>26</td>
<td>72.488</td>
<td>4.183</td>
</tr>
</tbody>
</table>

\[ \text{Mean} = 4.160 \]

4.160 ch : = 4.76 ns = 2 rotations

or 1 ch : = 1.145 ns

Table II. Channel-Time Calibration
Fig. 3.6: Coincidence Spectrum (less background)

Coincidence Rate

Channel No.

PbHfO₃ 181 Hf
apparatus mentioned above together with the apparatus shown in the block diagram of Fig. 3.2, the number of channels corresponding to each rotation of the delay line was determined. Using the method of centroids it was determined that 1 channel was equivalent to about 1.15 ns. Typical calibration results are shown in Table II.

The calibration then established the relative time dependence of the coincidence spectrum. By introducing the delay cable in the experimental arrangement the time-zero point was shifted to some other point along the spectrum. Therefore there need to evaluate the channel corresponding to the time-zero point. To accomplish this the coincidence experiment using $^{60}$Co decay was carried out. See $^{60}$Co-decay scheme in Fig 3.7. The SCA windows were set at the values used for the 132-480 keV cascade. The $^{60}$Co-decay was chosen because the mean lifetime in its intermediate state is negligibly small — only 0.7 ps. In other words coincidence counting would be non-zero only for time-zero on the coincidence time spectrum. This type of distribution would only be realised in principle. Owing to the time difference in the arrival of the cathode photoelectrons at the first dynode of the photomultiplier tubes, there would be a definite spread of coincidence counting about the time-zero point. The time difference was a result of the statistical nature of processes. It is clear then that the narrower the spread the better the apparatus used. In other words, the experiment with $^{60}$Co source would determine not only the channel
corresponding to the time-zero point but also the resolving time of the entire coincidence apparatus. The coincidence spectrum consisted of a flat part on which was superimposed the peak. The flat part of the spectrum was identified as the background originating from the accidental coincidences and the peak the 'true' coincidences. The resolving time, full width at half maximum, was 4 ns and time-zero point was at channel 44, Fig. 3.8. These quantities remained constant through the studies on PbHfO₃.

3.2. Preparation of the Source and Detector Geometry

The method due to Dernier-P. B. and others (Mat. Res. Bull, 1975) was closely followed in growing the single crystal using lead oxide PbO and boron oxide B₂O₃ as the high temperature solvent. Powders of hafnium oxide HfO₂, B₂O₃ and PbO were weighed into a 100 ml platinum crucible. The crucible was covered with a platinum lid and loaded into a horizontal, resistively powered furnace. The temperature was raised to over 1300°C and held for 16 h and then cooled at the rate of 5.0°C h⁻¹ to about 500°C when the crucible was removed and allowed to cool to room temperature. The extraction of the crystal was achieved using a volume ratio 1:3 of nitric acid HNO₃ and water. The resulting crystal was a light tan prismatic rectangle. One face had "frames" on it and it was assumed that the crystal axis was perpendicular to this surface. The crystal was mounted with its axis in the plane of the counters, see Fig. 3.9.
Fig 3.9: PbHfO$_3$ Single Crystal

Fig 3.10: Crystal and Detector Geometry.
The fixed counter 1 was placed at the distance of 8.2 cm from the source and the movable counter 2 at the distance of 6.3 cm for 180° - detector position and at the distance of 6.2 cm for 90° - detector setting. The detectors were aligned along the radii extending from the radioactive source. The radial direction associated with the detector 1 was \( \hat{\mathbf{k}}_1 \) (the direction of propagation of the 132 keV \( \gamma \)-ray); while the radial direction associated with detector 2 was \( \hat{\mathbf{k}}_2 \) (the direction of propagation of the 480 keV \( \gamma \)-ray). The geometry of the detectors for \( \hat{\mathbf{k}}_1 \) - \( \hat{\mathbf{k}}_2 \) system has been schematically shown in Fig. 3.10.

The detectors subtended finite angles at the source and this had a smearing effect on the structure of the correlation function. The anisotropic calculations were corrected for the detector geometrical factors using the available tables (Yates, MJL, 1963). A factor of 0.93 was used to correct the observed anisotropy.

3.3. Experimental Procedure

The lead-hafnate (Hafnium - 181) crystal of approximately 0.065 g was irradiated using the thermal neutrons (neutron flux \( 1.2 \times 10^{13} \text{ n s}^{-1} \)) for a period of just over an hour, at the McMaster Nuclear Reactor, to an activity of 0.1 millicuries (mCi). The crystal was mounted as shown in Fig 3.9 with the side containing the "frames" facing the fixed detector. By rotating the crystal (Fig. 3.9), the 'crystal'-axis was set at 0°, 30°, 40° and 45° with respect to \( \hat{\mathbf{k}}_1 \).
The counters for the detection of the two \( \gamma \)-rays were connected appropriate high voltages — detector 1 to 2kV and detector 2 to 2.236 kV. Next the windows for each of the two energy peaks of interest were set as discussed in Section 3.1.1. The outputs of the TAC and the double coincidence circuit were fed into the multichannel analyser for the collection of the coincidences as a function of time. Depending on the activity of the source (half-life of hafnium-181 is 45 d) experimental settings were arranged to run for 24, 36 or 48 h. Such runs were done for the detector angles (\( \theta \) in the correlation function \( W(\theta) \)) 90° and 180°.

After each run, data from the multichannel analyser was printed on paper using the printer (Model 500) and punched on the paper tape. The single counts of \( \gamma_1 \) and \( \gamma_2 \) pulses as obtained from the SCA outputs were counted by using Philips timers (Model PW4260) and scalers (Model PW4230) and printed out every \( 4 \times 10^2 \) s or \( 10^3 \) s automatically, depending on the specific activity of the source.

The experiments were done at both the room temperature (~24°C) and above the room temperature (Temperature = 160°C, 170°C, 200°C and 300°C). Experiments at temperatures above the room temperature were conducted in order to investigate the series of structural phase transformations which the perovskite compound PbHfO₃ does undergo (Dernier, P.D. etc, 1975). The change in the structure would have a bearing on the crystalline field. Therefore, these experiments were designed to investigate the temperature dependence of the quadrupole perturbation.
interaction; or in other words, the effect of temperature on anisotropy.

The crystal was heated to the required temperatures in a locally-made heater. The heater was made of 2.75 metre heat coil (of resistance 6.48 ohm/ft) wound on a 5-cm long cylindrical glass tubing of outside diameter 2.5 cm. The temperature was monitored by means of chromel-alumel thermocouple and the Digital Multimeter counter (Model 4440) above room temperature and with respect to ice-water.

3.4. Evaluation of Experimental Correlation Function

In this section we relate the theoretical perturbed correlation function \( W(\theta) \), given in Section 2.3 with the experimental correlation \( K(\theta) \). Here the angle \( \theta \) will have two values i.e. \( \pi \) and \( \pi/2 \). The counting will be denoted by \( N \) and \( C \) for the single counts and coincidences, respectively. From measured data, the "true" values \( C^t(\theta) \) and \( N^t(\theta) \) are obtained by subtracting the background, accidental coincidences. Symbolically,

\[
C^t(\theta) = C^{\text{meas}}(\theta) - C^{\text{acc}}(\theta)
\]  

(3.1)

where:

\[
C^{\text{acc}} = 2 \tau_0 N_1^{\text{meas}}(\theta) N_2^{\text{meas}}(\theta)
\]  

(3.2)

\( \tau_0 \) : the resolving time

The accidental coincidence counting may be due to the following: The coincidence circuit discussed in Section 3.1.1, in principle, is designed to analyse 132- and 480-keV gamma rays. This circuit may not analyse, for example, the 345-keV
γ-ray because it does not occur in coincidence with either of
the two energy peaks. However, because of the large number of
nuclei decaying in the source, it is possible that a γ₁ from
one nucleus will occur in coincidence with a γ₂ from another
nucleus. The coincidences of this type are called the
accidental coincidences.

The explicit form of the single and the coincidence
counting can be written as, (Frauenfelder)

\[ N_i(\theta) = M_i \cdot \Omega_i \cdot \epsilon_i \]  \hspace{1cm} (3.3)

\[ C(\theta) = M \cdot \Omega_1 \cdot \epsilon_1 \cdot \Omega_2 \cdot \epsilon_2 \cdot c \cdot K(\theta) \]  \hspace{1cm} (3.4)

where

- \( M \): number of nuclear disintegration per unit time,
- \( P_i \): the probability per disintegration that the radiation
  selected in detector \( i \) is emitted,
- \( \Omega_i \): the solid angle in units of \( 4\pi \),
- \( \epsilon_i \): the photoelectric efficiency of the counter \( i \),
- \( \epsilon_c \): the efficiency of the coincidence circuit.

Due to a finite deadtime of the TAC some pulses are not analysed,
so that \( \epsilon_c \) is not unity. However during the time taken for an
experimental run it remains essentially constant.

Equation (3.3) is valid if counter 1 detected only \( \gamma_1 \) and
counter 2 detected only \( \gamma_2 \). The setup has been that the window
of the counter 1 may accept, besides 132 keV gamma rays, the
137 keV photopeak and the 345 and 480 keV gamma rays due to
Compton processes in the crystal of the Counter 1. The window
of counter 2 may also accept, apart from the 480 keV photopeak,
the tail of 345 keV peak and the Compton pulses from the higher energy gamma rays, the 615 keV and 619 keV. The single counts for \( t_1 \) are given by
\[
N^{t}_{t_1} = M \cdot \rho_1 \cdot \alpha_1 \cdot \epsilon_1 + M \cdot \rho_{130} \cdot \alpha_1 \cdot \epsilon_1 + M \cdot \rho_{370} \cdot \alpha_1 \cdot \epsilon_1 + M \cdot \rho_{460} \cdot \alpha_1 \cdot \epsilon_1 + \ldots \quad (3.5)
\]
where the \( \rho \)'s are constant and the \( \alpha \)'s the efficiencies of detection of these gamma rays by counter 1 are constant provided that the window set remains constant during the experiment.
\[
N^{t}_{t_1}(\theta) = k_1 M \cdot \rho_1 \cdot \alpha_1 \cdot \epsilon_1 \quad (3.6)
\]
where \( k_1 \) is a constant.

Similarly for counter 2 we have
\[
N^{t}_{t_2} = k_2 M \cdot \rho_2 \cdot \alpha_2 \cdot \epsilon_2 \quad (3.7)
\]
The \( N^{t}(\theta) \) are the average single counts for a specific counting time interval; \( 4 \times 10^2 \) s and \( 10^3 \) s depending on the specific activity of the source. The ratio of the coincidences to the singles is given thus
\[
\text{ratio} = \frac{\text{Coincidence}}{N^{t}_{t_1}(\theta) \cdot N^{t}_{t_2}(\theta)} = \frac{M \cdot \rho_1 \cdot \alpha_1 \cdot \epsilon_1 \cdot \rho_2 \cdot \alpha_2 \cdot \epsilon_2 \cdot K(\theta)}{k_1 M \cdot \rho_1 \cdot \alpha_1 \cdot \epsilon_1 \cdot k_2 M \cdot \rho_2 \cdot \alpha_2 \cdot \epsilon_2} \quad (3.8)
\]
Equation (3.8) shows that the ratio is independent of the solid angle. Large angles are even found to be advantageous (Devons and Goldfarb). In analogy with Equation (2.83) we
evaluate the experimental anisotropy $R_{\exp}^e(t)$,
\[ R_{\exp}^e(t) = \frac{\epsilon_c}{M k_2 k_1} \left( \frac{K(\pi) - K(\pi/2)}{K(\pi/2)} \right) \times 2 \]
or
\[ R_{\exp}^e(\theta) = \frac{2 \left( K(\pi) - K(\pi/2) \right)}{K(\pi) + K(\pi/2)} \]
The disintegration rate $M$ was not constant throughout the experiment but since the half-life of $^{181}$Hf is 45 days, and the mean times between the accumulation of the data at $180^\circ$ and $90^\circ$ were 2 days or less the change in $M$ was $\leq 1\%$.

The coincidence counting (proportional to $K(\theta)$) spectra have been plotted in Figs. 3.5 and 3.6. The former plot refers to coincidences with background while in the latter the accidental coincidences have been subtracted. The peak in the graphs is assumed to represent the true coincidences. Fig 3.5 shows an approximate exponential background distribution on which a peak is superimposed.

In order to compare with the theoretical derivation of Chapter II, $K(\theta)$ has been fitted by means of the equation (Frauenfelder, 1965).

\[ K(\theta) = K_0 \left\{ 1 + A_{22}^{exp} P_2(\cos \theta) + \cdots \right\} \]  \hspace{1cm} (3.9)

using the method of least squares (Nallettamy F.P., 1971)

where

$A_{kk}^{exp}$ are defined similar to $A_{22}^0$

of Equation (2.86)

From the discussions of Section 2.3 only two terms in Equation (3.6) need be used in the calculation.
The coincidence rate $K(\theta)$ corresponds to the correlation function $W(\theta)$ only on the assumption of centred point sources and point detectors. When the necessary corrections (a factor of .93 has been used) are performed for finite geometries the coefficients $A_{kk}^0 \exp$, compare with those of the theoretical calculation, Equation (2.86).
CHAPTER IV

RESULTS

A total of twenty-two runs were carried out for the calculation of anisotropy, R(t). Each run consisted of two experimental settings — viz the $180^\circ$ and $90^\circ$ counter angles. In addition, before and after each experiment a time calibration using the Helical delay line (McAllindon) was carried out, as described in Chapter III, to determine the time-channel relationship. Besides the calibration, the $^{60}$Co-experiment, also described in Chapter III, was done to determine the channel corresponding to time zero. For the purpose of computing the anisotropy, the coincidence data for both $180^\circ$ and $90^\circ$ counter setting were fed remotely in the programmable calculator (Tektronix, Model 31) through the tape reader on the teleprinter (Marsland, Model 811). The two pieces of the apparatus were connected by the interface (Tektronix, Model 154).

The paper tape carried information of the coincidence spectrum, i.e. the coincidence counts per channel, for the total of two hundred channels. The Tektronix calculator was programmed to remove the channel number and to carry out the exponential subtraction of the background. The approximate exponential distribution of background has been indicated by the dotted line in Fig. 3.5. The calculator was also programmed to carry out the computation of the anisotropy $R_{\text{expt}}(t)$ and error $\sigma$ as a function of channel number. The "stop" pulse from gamma 2 (as observed in counter 2) was delayed by about 50 ns so that zero time appeared at about channel number 44.
This avoided the non-linearities in the T.A.C. response at small time intervals. So the calculator was programmed to begin the anisotropy calculation at the 40th channel. Because of statistics, the errors at the end of about three half-lives are very large. Therefore the calculations were terminated after about 50 ns. An example of the print-out is shown in Table II.

The results are presented graphically in Fig. 4.1-4.10. The value of the quadrupole interaction was deduced by the fitting process discussed in Chapter V.
Fig. 4.1: Perturbed Angular Correlation of $^{181}$W in Pile 0, Cylindrical Coincidence Channels 1-51 per Channel.

C - Axis 0°
Temperature = 24°C
Figure 4.21: Perturbed Angular Correlation of 141I in Phosphor Crystal. Calibration 1.142 ns/channel.

Electric field applied (constant = 500 V/cm)

- c - axis rotated 25°
- Temperature = 24°C
Fig. 4.3: Perturbed angular correlation of $^{190}$Hg in phosphor cryystal calibration 1.4 ns/Channel.

- Time-zero
- Anisotropy
- Temperature = 24°C

C-axis rotaed 30°
Calibration 1.15 ms/channel.

Fig. 4.5: Perturbed angular correlation of 181Ir in Rhilco single crystal.

- Axis rotated 45°
- Temperature = 24°C
Fig. 4.6: Perturbed angular correlation of 191 Yb in P1510 2 single crystal, calibration 1.14 ns/channel.

Constant Electric Field applied = 500 V cm⁻¹

C-axis rotated 30°

Temperature = 24°C
Figure 4.81: Perturbed angular correlation of 181Ir in PdH03 single crystal Calibration 1.142 ns/Channel

Anisotropy

Temperature = 200°C
<table>
<thead>
<tr>
<th>CHANNEL NO</th>
<th>ANISOTROPY</th>
<th>ERROR (±)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>-0.445</td>
<td>0.070</td>
</tr>
<tr>
<td>41</td>
<td>-0.296</td>
<td>0.032</td>
</tr>
<tr>
<td>42</td>
<td>-0.262</td>
<td>0.017</td>
</tr>
<tr>
<td>43</td>
<td>-0.172</td>
<td>0.012</td>
</tr>
<tr>
<td>44</td>
<td>0.139</td>
<td>0.009</td>
</tr>
<tr>
<td>45</td>
<td>-0.049</td>
<td>0.008</td>
</tr>
<tr>
<td>46</td>
<td>0.001</td>
<td>0.008</td>
</tr>
<tr>
<td>47</td>
<td>0.085</td>
<td>0.008</td>
</tr>
<tr>
<td>48</td>
<td>0.126</td>
<td>0.009</td>
</tr>
<tr>
<td>49</td>
<td>0.156</td>
<td>0.009</td>
</tr>
<tr>
<td>50</td>
<td>0.129</td>
<td>0.010</td>
</tr>
<tr>
<td>51</td>
<td>0.069</td>
<td>0.010</td>
</tr>
<tr>
<td>52</td>
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<td>0.011</td>
</tr>
<tr>
<td>53</td>
<td>-0.069</td>
<td>0.012</td>
</tr>
<tr>
<td>54</td>
<td>-0.107</td>
<td>0.012</td>
</tr>
<tr>
<td>55</td>
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<tr>
<td>56</td>
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<tr>
<td>57</td>
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<td>0.021</td>
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<tr>
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<td>-0.054</td>
<td>0.023</td>
</tr>
<tr>
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<td>78</td>
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<tr>
<td>79</td>
<td>-0.040</td>
<td>0.062</td>
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<tr>
<td>80</td>
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<td>0.066</td>
</tr>
<tr>
<td>81</td>
<td>0.007</td>
<td>0.079</td>
</tr>
</tbody>
</table>

**TABLE III**: Results for Fig. 4.4
CHAPTER V
DISCUSSION OF RESULTS

The curves in Figs 4.1 - 4.9 show that around time zero the values of the anisotropy vary for each graph. This variation may, in the main, be attributed to interference due to the prompt coincidences between the 345 keV and the 136 keV gamma rays, Fig 3.4. (The lifetime of the 136 keV energy level is negligibly small; only 40 ps). The effect of these coincidences is significant when there occurs a drift such that the tail of the 345 keV gamma ray falls within the window of counter 2, which is set to include the 482 keV photo peak Fig 3.3. Because of the negligible lifetime of the 136 keV level, the time dependence of the prompt coincidences is insignificant except around the time zero.

At room temperature, the correlation time spectra are in the form of damped oscillations. Such a damping of the correlation pattern may be attributed to the lattice imperfection and impurities. The oscillatory pattern of the time spectra was found to be independent of the direction of the c-axis. The different orientations of the c-axis were found to change the amplitudes of the oscillations. The maximum value of the amplitude was found when the c-axis was orientated 45° with respect to the fixed counter, in the plane of 1 and 2, Fig 4.4.

The application of the constant electric field (= 500 V cm⁻¹) normal to the "framed" side of the crystal before commencing the experiment was found to have no appreciable effect on the correlation pattern, Fig 4.5.
Fig 5.1 Geometry of the Apparatus with Definition of Euler Angles.
Fig. 5.2: Perturbed Angular Correlation of the $^{181}\text{Hf}$
in PbHfO$_3$ single crystal; solid line shows
the best fit (cf. Fig. 4.4).
(a) A projection along the 0 axis of the orthorhombic low temperature modification of PbHfO$_3$. Origin in lower right.

(b) Structure around Hf ions giving rise to crystalline field.

Fig. 5.3. PbHfO$_3$ Crystalline Structure
The application of the constant electric field was assumed to have the effect of changing the Hf ions to new stable positions, thereby changing the quadrupole interaction. This change in the quadrupole interaction energy was not large enough to be detected.

The experimental anisotropy was compared with the one obtained by the theoretical calculations, Equation 2.84 with \( A_k \) given by Equation 2.79 without any assumption of symmetry about \( z \)-axis. The following parameters, viz., the asymmetry \( \eta \), \( \omega_0 \) (defined as in Equation 2.64), smearing \( \delta \) (a measure of the distribution of \( \omega_0 \)) and the Euler angles \( \alpha \) and \( \beta \) defined as in Fig 5.1 were varied until the best fit was obtained. The theoretical calculations were done using the computer programme written by Dr. H. Ogata (and most of the work was done by him). And the best fit is shown in Fig 5.2. Using the Equations 2.62 and 2.64, the electric quadrupole frequency \( \omega_0 \) (\( \pm 1.35 \) MHz) and the maximal component of the quadrupole interaction \( V_{zz} = 46.252 \pm 0.89 \times 10^{-20} \text{Vm}^{-2} \) were evaluated. The asymmetry parameter was found to be equal to \( 0.814 \pm 0.080 \).

The fact that the asymmetry parameter \( \eta \) was found to be near unity indicates the extent of the axially asymmetric nature of the quadrupole field. The other parameters are shown in Table III.
In Fig. 5.1 we have shown the existence of a principal axis $Z'$, different from the c-axis (z-axis). This may be interpreted as arising from shifts of the Hf sites resulting in the deformed octahedral shapes about the Hf ion, shown in Fig. 5.3. The shifts occur mainly in the x-y plane. Fig 5.1 is but a representative of the many shifts. In the theoretical calculations it was found necessary to diagonalise the Hamiltonian $K$ using the unitary matrix $U$. Equation 2.26 giving rise to $\langle m|n \rangle$ matrix elements, as in Equation 5.1. This operation is indicative of the existence of the principal axis described by $\alpha$ and $\beta$. The Euler angles have been so determined because of the regular crystalline nature of PbHfO$_3$. In the case of a complex crystalline structure (Matthias E., etc., 1963) the principal axis may prove to be very difficult to describe. For the polycrystalline source the identification of the Euler angles would have no meaning.

From the least squares fitting $\omega_0 \approx V_{Z'Z'}, Q_{Z'Z'}$ was determined. Unlike the Euler angles the value of $W_0$ is unique. It is not a function of the physical nature of the source. In order to compute $V_{Z'Z'}$, the value of $Q_{Z'Z'}$ ($= 2.53 \times 10^{-28} \text{ m}^{-2}$) reported by Sommerfeldt (Sommerfeldt, 1965) using the coulomb excitation method.
<table>
<thead>
<tr>
<th>$\omega_2$ (MHz)</th>
<th>$\eta$</th>
<th>$\delta$ (%)</th>
<th>$\alpha$ (deg)</th>
<th>$\beta$ (deg)</th>
<th>$\Delta_{482}^{(Ml/E2)}$</th>
<th>$\Delta_{137}^{(Ml/E2)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Value</td>
<td>44.444</td>
<td>0.814</td>
<td>14.165</td>
<td>7.34</td>
<td>5.10</td>
<td>0.593</td>
</tr>
<tr>
<td>Error ($\pm$)</td>
<td>1.350</td>
<td>0.080</td>
<td>8.253</td>
<td>5%</td>
<td>5%</td>
<td>0.050</td>
</tr>
</tbody>
</table>

Table III  Values of Various Parameters

The time spectra for experiments conducted at higher temperatures showed the loss of the oscillatory pattern. This loss is attributed to the structural phase transformation of the perovskite antiferroelectric compound PbHfO$_3$. The structure of PbHfO$_3$ has been found to transform from orthorhombic at room temperature through rhombohedral at about 180$^\circ$C to cubic at about 250$^\circ$C (Dernier, P.D. etc., Mat. Res Bull, 1975). See Fig 5.3. The fact that a complete loss of oscillation could not be achieved in the cubic phase is due to the fact that we are dealing with a real crystal with a certain amount of lattice irregularities. Such imperfections will destroy the cubic symmetry at some lattice sites and thus produce a small remaining interaction.

A quantitative analysis of the dependence of quadrupole frequency $\omega_2$ on temperature was not carried out. The temperature dependence of quadrupole frequency can, however, be compared to that of PbZrO$_3$ (Forker, M etc., Z. Physik 1972) an antiferroelectric crystal with properties very close to those of PbHfO$_3$. For PbZrO$_3$ the quadrupole frequency $\omega_2$ was found to decrease by approximately a factor of 10 at the transition from
the antiferroelectric to cubic phase. (Forker, M. etc, 1972). The quadrupole frequency $\omega_q$ for PbHfO$_3$ may be expected to drop by a factor of about the same order of magnitude.

Summary

The single crystal of the antiferroelectric PbHfO$_3$ ($^{181}$Hf) has been studied by the method of perturbed angular correlation of the 132 - 482 keV cascade in $^{181}$Ta. The static extranuclear perturbation utilized has been the crystalline field. The interaction energy in the form of the quadrupole frequency $\omega_q (= 44.444 \pm 1.35$ MHz) has been found. The maximal component of the interaction $V_{zz}(= 46.252 \pm 0.890 \times 10^{20}$ Vm$^{-2}$) has been calculated.

The asymmetry parameter $\eta (= 0.814 \pm 0.080$) has been determined. The fact that it was found to be nonzero indicates the absence of the axial symmetry of the field about the c-axis (the z-axis). This was rather expected because from the results of the experiment carried out with the c-axis aligned along the direction $k_1$, we noted no disappearance of the oscillation pattern, Fig 4.1. Furthermore we were able to establish the direction of the quadrupole field by determining the Euler angles $\alpha$ and $\beta$. The maximum oscillations (hence, high sensitivity) were obtained when the c-axis was aligned 45° with respect to $\gamma_1$ in the plane of the detectors.

It appears, therefore, that the use of the single crystal source, where such can be grown, is more attractive that the use of the powder source. It is possible, with a single crystal source, to obtain high sensitivity by orienting the crystal axis at 45° with respect to counter 1 and to determine the actual direction of the perturbing field by
determining the polar angle $\beta$ and the azimuthal angle $\alpha$.
Most of the published works on the crystalline field studies have used powder sources and the interaction energies
determined therefrom. It is impossible, however, to measure
the angles $\alpha$ and $\beta$ with such sources.
APPENDIX 1

We collect the formal equations that are necessary for the development of the theory. The concepts involved are:

1. The Rotations of eigenfunctions and the rotation group
2. Vector addition coefficients and Racah algebra
3. The Wigner–Eckart theory
4. The density matrix


In the approach discussed in subsection 2.2.1, the quantisation axis coincides with the direction of emission of one particle. This special choice eliminates interference terms and facilitates the description of this particle. This approach does not, however, simplify the description of the second particle and the equivalence of the two quanta is ignored. In the development of the general theory, the advantage is taken of this symmetry through the special choice of z-axis. For each of radiations $R_i$ ($i = 1, 2, \ldots$) a separate coordinate system is introduced in which the z-axis of each system coincides with the direction of emission $\vec{k}_i$ of $R_i$. The direction of polarisation is taken as x-axis. The two radiations are connected through the introduction of an arbitrary quantisation axis z (origin of z coincides with the source of radiation) using the transformation properties of the eigenfunctions of $R_i$. 
The eigenfunction of $R$ describes a system with total angular momentum $\hat{L}$ and thus transforms according to the $(2L+1)$-dimensional irreducible representation $D^L$ of the three-dimensional rotation group. It is assumed that a radiation $R$ be emitted in the direction $\hat{k}$ with spin $\sigma$. The eigenfunction corresponding to the eigenvalues $L, M$, and $\pi$ of the operators of angular momentum, $z$-component of angular momentum and parity, respectively, are denoted by $\langle k\sigma | L M \pi \rangle$ defined with respect to arbitrary quantisation axis $z$.

The direction $\hat{k}$ of emission of radiation $R$ is characterised by polar angles $\theta$ and $\varphi$. If $z$-axis coincides with $\hat{k}$, that is, $\theta = 0$, the corresponding eigenfunctions are denoted by $\langle \sigma | L \pi \rangle$. The functions in the two systems are related by

$$\langle k\sigma | L M \pi \rangle = \sum_{\mu} \langle \sigma | L \mu \pi \rangle D^L_{\mu M} (\hat{k} \rightarrow \hat{z}) \quad (A1.1)$$

where $D^L_{\mu M} = \langle \nu | D^L | M \rangle$ are elements of unitary matrix $(\hat{z} \rightarrow \hat{k})$ stands for Euler angles ($\psi, \theta, \varphi$) describing the rotation that carries the arbitrary quantisation system $z$ over into the coordinate system of the radiation.

Some useful properties of $D^L$ functions follow (star denotes complex conjugation):

$$D^L_{\nu M} (k \rightarrow z) = D^{L\ast}_{M \nu} (z \rightarrow k) \quad (A1.2)$$
\[
D_{\rho M}^L (\kappa \rightarrow z) = (-)^{\rho - \rho'} D_{\rho M}^L (\kappa \rightarrow z) \quad (\text{Al.} 3)
\]
\[
\sum_{\rho M} D_{\rho M}^L (\kappa \rightarrow z) D_{\rho' M'}^L (z' \rightarrow z) = D_{\rho' M'}^L (\kappa \rightarrow z) \quad (\text{Al.} 4)
\]

The product of two matrix elements of the rotation group can be expressed in terms of a sum over matrix elements (Clebsch-Gordan series):
\[
D_{\rho M}^L D_{\rho' M'}^L = \sum_{k = |L' - L|}^{L + L'} \langle L' M' | \kappa \tau \rangle \langle L M | \kappa N \rangle D_{\gamma N}^\kappa \quad (\text{Al.} 5)
\]
where:
\[
N = M + M', \quad \tau = \rho + \rho'
\]

For special choices of the quantum numbers \(M\) and \(\rho\), the matrix elements take on particularly simple forms:
\[
D_{\rho 0}^L (\phi \theta 1) = \left( \frac{4 \pi}{2L+1} \right)^{\frac{1}{2}} \gamma^\rho_L (\theta, \phi) \quad (\text{Al.} 6)
\]
\[
D_{\rho M}^L (\phi \theta 1) = \left( \frac{4 \pi}{2L+1} \right)^{\frac{1}{2}} \gamma^{-M}_L (\theta, 1) \quad (\text{Al.} 7)
\]
\[
D_{\rho 0}^L (\phi \theta 1) = P_L (\cos \theta) \quad (\text{Al.} 8)
\]

Tables exist for Legendre polynomials \(P_L (\cos \theta)\) and spherical harmonics \(Y^M_L (\theta, \phi)\) (Frauenfelder, H., 1965).
2. **Vector addition, coefficients and Racah algebra**

(Brink, D.M. and Satchler, G.R., 1971). Vector addition (also called Clebsch-Gordan or Wigner) coefficient arise where more than one angular momenta from two or more systems are coupled together. We denote total angular momentum quantum numbers by \(j\) and the corresponding magnetic quantum numbers (z-components) by \(m\). The Clebsch-Gordan coefficients for the vector addition \(j_1 + j_2 = j_3; m_1 + m_2 = m_3\) are defined by the transformation

\[
|j_1 j_2 j_3, m_3\rangle = \sum_{m_1 m_2} |j_1 j_2 m_1 m_2\rangle \langle j_1 m_1 j_2 m_2 | j_3 m_3\rangle \tag{Al.9}
\]

The Clebsch-Gordan coefficients are chosen to be real; tables exist (for example Condon and Shortley). Calculations are easily handled if the Clebsch-Gordan coefficients are replaced by Wigner 3-j symbols related by the relation

\[
\begin{pmatrix} j & j_2 & j_3 \\ m & m_2 & m_3 \end{pmatrix} = (-)^{j-j_2-m_3} (j_2 j_3 + 1)^{-1/2} \begin{pmatrix} j_3 & j_1 & j_2 \\ m_3 & m_1 & m_2 \end{pmatrix} \tag{Al.10}
\]

The 3-j symbols possess simpler symmetry properties. An even permutation of the columns leaves the coefficient unchanged while an odd permutation or an interchange of all \(m\) to \(-m\) is equivalent to multiplication by \((-)^{j_1 + j_2 + j_3}\)

\[
\begin{pmatrix} j & j_2 & j_3 \\ m & m_2 & m_3 \end{pmatrix} = \begin{pmatrix} j_2 & j_3 & j_1 \\ m_2 & m_3 & m_1 \end{pmatrix} = \begin{pmatrix} j_3 & j_1 & j_2 \\ m_3 & m_1 & m_2 \end{pmatrix} \tag{Al.11}
\]
\begin{align*}
( - )^{j_1 + j_2 + j_3} 
\begin{pmatrix}
  j_1 & j_2 & j_3 \\
  m_1 & m_2 & m_3
\end{pmatrix}
= 
\begin{pmatrix}
  j_2 & j_1 & j_3 \\
  m_2 & m_1 & m_3
\end{pmatrix} & \text{(Al.12)}
\end{align*}

\begin{align*}
\begin{pmatrix}
  j_1 & j_2 & j_3 \\
  m_1 & m_2 & m_3
\end{pmatrix}
= (-)^{j_1 + j_2 + j_3} 
\begin{pmatrix}
  j_1 & j_2 & j_3 \\
  m_1 & m_2 & m_3
\end{pmatrix} & \text{(Al.13)}
\end{align*}

The 3-j symbols satisfy the following orthogonality relations

\begin{align*}
\sum_{j_3 m_3} (2j_3 + 1) 
\begin{pmatrix}
  j_1 & j_2 & j_3 \\
  m_1 & m_2 & m_3
\end{pmatrix}
\begin{pmatrix}
  j_1 & j_2 & j_3 \\
  m_1' & m_2' & m_3'
\end{pmatrix}
= \delta_{m_1 m_1'} \delta_{m_2 m_2'} & \text{(Al.14)}
\end{align*}

\begin{align*}
\sum_{m_1 m_2} (2j_{12} + 1) 
\begin{pmatrix}
  j_1 & j_2 & j_3 \\
  m_1 & m_2 & m_3
\end{pmatrix}
\begin{pmatrix}
  j_1 & j_2 & j_3 \\
  m_1 & m_2 & m_3
\end{pmatrix}
= \delta_{j_{12} j_{12}} \delta_{m_1 m_1'} & \text{(Al.15)}
\end{align*}

Additional properties are given in the cited work.

In the calculation of the correlation function sums over products of 3-j symbols appear. These sums are better handled by using Wigner 6-j symbol or the related Racah coefficients:

\begin{align*}
\sum_{m_4 m_5 m_6} (-)^{j_4 + j_5 + j_6 + m_4 + m_5 + m_6} 
\begin{pmatrix}
  j_1 & j_5 & j_6 \\
  m_1 & m_5 & m_6
\end{pmatrix}
\begin{pmatrix}
  j_1 & j_2 & j_3 \\
  m_1 & m_2 & m_3
\end{pmatrix}
\begin{pmatrix}
  j_4 & j_2 & j_6 \\
  m_4 & m_2 & m_6
\end{pmatrix}
& \times
\sum_{m_4 m_5 m_6} 
\begin{pmatrix}
  j_4 & j_5 & j_6 \\
  m_4 & m_5 & m_6
\end{pmatrix}
\begin{pmatrix}
  j_1 & j_2 & j_3 \\
  m_1 & m_2 & m_3
\end{pmatrix}
\begin{pmatrix}
  j_4 & j_5 & j_6 \\
  m_4 & m_5 & m_6
\end{pmatrix}
= \delta_{j_{12} j_{12}} \delta_{m_1 m_1'} & \text{(Al.16)}
\end{align*}

The Wigner 6-j symbol, \{\}, is independent of magnetic quantum
numbers. This symbol has simple symmetry properties, being invariant against any permutation of the columns and against interchange of the upper and lower arguments in each of any two columns:

\[
\begin{align*}
\{i_4, j_5, j_6\} &= \{j_2, j_3, j_1\} = \{j_1, j_5, j_6\} \\
\{i_4, j_5, j_6\} &= \{j_2, j_3, j_1\} = \{i_4, j_2, j_3\}
\end{align*}
\]  
(Al.17)

The Wigner 6-j symbol is related to Racah coefficient \( W \) by the relation

\[
\begin{align*}
\{i_4, j_2, j_3\} &= (-)^{j_1 + j_2 + j_4 + j_6} W(i_4, j_2, j_3; j_1, j_5, j_6)
\end{align*}
\]  
(Al.18)

If we denote \( a, b, c, d \) and \( e, f \) for vectors and \( \alpha, \beta, \gamma, \delta, \epsilon \) and \( \varphi \) for the corresponding z-components, respectively, the Racah coefficients are expanded as follows:

\[
W(a, b, c, d; e, f) = \frac{1}{\sqrt{(2a+1)(2f+1)}} \sum \langle a, b \alpha \beta | e, c \alpha' \beta' \rangle \times
\]

\[
\times \langle e, c \alpha' \beta' | d \delta \rangle \langle bc | f, \gamma + \delta \rangle \langle a, \alpha' \beta' \gamma | d \delta \rangle.
\]  
(Al.19)


This theorem states that the matrix element of a tensor operator \( T_q^{(a)} \) of tensor rank \( a \) can be written as a product of a 3-j symbol (geometrical factor) and a scalar
factor, the reduced matrix element or double-bar matrix
element which does not depend on any magnetic quantum number

\[ \langle I \bar{m} | T^{(a)}_Q | I_i m_i \rangle = (-1)^{I-m} \left( \begin{array}{cc} I & I_i \\ -m & m_i \end{array} \right) \langle I \bar{m} | T^{(a)}_i | I \rangle \]

(Al.20)

This equation defines the reduced matrix element of a tensor
operator. An equivalent definition is of the form

\[ \langle I \bar{m} | T^{(a)}_Q | I_i m_i \rangle = (-1)^{\lambda + I_i + I} \left( \begin{array}{c} \lambda \\ 2 I_i + \frac{1}{2} \end{array} \right) \left( \begin{array}{cc} I & I_i \\ -m & m_i \end{array} \right) \times \langle I \bar{m} | T^{(a)}_i | I \rangle \]

4. The density matrix (Brink, D.M. and Satchler, G.R., 1971)

Assume that the eigenstates of some operator \( F \),
form a complete orthonormal set \( \{ m \} \). If the system is in
a pure state \( \{ n \} \) then it can be expanded in terms of the
states \( \{ m \} \):

\[ \langle n | = \sum_m a_{n,m} | m \rangle \]

(Al.21)

The expectation value of \( F \) in the state \( \{ n \} \) is

\[ \langle n | F | n \rangle = \sum_{m,m'} a_{n,m}^* a_{n,m} \langle m' | F | m \rangle \]

(Al.22)

If the system is in a mixed state its description by a single
state \( \{ n \} \) is inadequate. Instead, it must be given as an
incoherent sum of pure states \( |n\rangle \) with weights \( \hat{g}_n \). The expectation value of \( F \) then becomes

\[
\langle F \rangle = \sum_n \hat{g}_n \langle n | F | n \rangle = \sum_{n \rightarrow m} \hat{g}_n a_n^* a_m \langle m' | F | m \rangle
\]

(Al.23)

We define the matrix elements of a density operator \( \rho \) by

\[
\langle m | \rho | m' \rangle = \sum_n \hat{g}_n a_n^* a_n
\]

(Al.24)

giving Equation (Al.23) thus:

\[
\langle F \rangle = \sum_{m \rightarrow m'} \langle n | \rho | m' \rangle \langle m' | F | m \rangle
\]

(Al.25)

or

\[
\langle F \rangle = \text{Tr}(\rho F) = \text{Tr}(F \rho)
\]

(Al.26)

where \( \text{Tr} \) denotes Trace or sum of diagonal elements of matrix \( \rho F \) while \( \langle n | \rho | m' \rangle \) is the density matrix. If \( |n\rangle \) is not normalised Eq (Al.26) becomes

\[
\langle F \rangle = \frac{\text{Tr}(\rho F)}{\text{Tr} \rho}
\]

(Al.27)

Without going into the properties of the density, suffice it to mention that it is Hermitean,
\[ \langle m | \rho | m' \rangle = \langle m' | \rho | m \rangle^* \]  
\text{(Al.28)}

and that Eqn (Al.26) remains unchanged under unitary transformation of density matrix.

Using Dirac's notation consistently the Equations (Al.21) and (Al.23) can be written more elegantly, thus

\[ |n\rangle = \sum_m |m\rangle \langle m | n \rangle \]  
\text{(Al.21')} 

and

\[ \langle F \rangle = \sum_{m,m'} \langle m' | F | m \rangle \langle m | n \rangle \langle n | m' \rangle \]  
\text{(Al.23')} 

so that the density operator \( \rho \) is defined by

\[ \rho = \sum_n |n\rangle \langle n| \]  
\text{(Al.29)}

We now consider four applications of the density matrix formalism, useful in the development of correlation theory.

(i) We assume that (2I+1) states \( |n\rangle \) exist, having equal weight and being equally populated (magnetic sublevels at elevated temperatures). The density matrix \( \rho \) is diagonalised by choice of appropriate states \( |m\rangle \).
\[ \langle m' | p | m \rangle = (2I + 1)^{-1} \delta_{m m'} \]  \hspace{1cm} (Al. 30)

(ii) From Eqn (Al. 24), it is clear that the probability \( P(m) \) of finding in state \( |m\rangle \) any member of a mixed ensemble described by the incoherent superposition of states \( |n\rangle \) is given by \( \hat{\varphi}_n a_{nn}^r a_{nn} \) or

\[ P(m) = \langle m | p | m \rangle \]  \hspace{1cm} (Al. 31)

Thus the diagonal elements of the density matrix give the probability \( P(m) \) of finding the ensemble in the state \( |m\rangle \)

(iii) Consider transitions from level A to level B. Letters \( a, a', \ldots \) and \( b, b', \ldots \) stand for the set of quantum numbers describing the eigenstates of level A and level B, respectively. The operator \( H \) which induces the transition \( A \rightarrow B \) is assumed linear but not necessarily Hermitean.

\[ \langle f | H | i \rangle^* = \langle i | H^* | f \rangle \]  \hspace{1cm} (Al. 32)

Where \( H^* \) denotes the adjoint of \( H \). If the system is initially in eigenstate \( |a\rangle \) of level A, the transition results in state:

\[ |f\rangle = H|i\rangle, \quad \langle f | = \langle i | H^* \]  \hspace{1cm} (Al. 33)

not necessarily an eigenstate \( |b\rangle \) of level B. The probability
$P_B(b)$ of finding the system after transition in a certain eigenstate $|b\rangle$ is given by absolute square of the corresponding expansion coefficient:

$$P_B(b) = \left| \frac{\langle b | f \rangle}{Z} \right|^2 = \left| \frac{\langle b | H | a \rangle}{Z} \right|^2 \quad (Al.34)$$

(iv) We generalise (iii) by assuming that the system is initially not in an eigenstate but only described by a density operator

$$\rho_A = \sum_n |n\rangle \otimes_\delta \langle n| \quad (Al.35)$$

After the transition due to $H$, the density operator in level $B$ will be

$$\rho_B = \sum_n H |n\rangle \otimes_\delta \langle n| H^+ \quad (Al.36)$$

Since each state $|n\rangle$ changes according to $(Al.32)$, taking matrix elements yields

$$\langle b | \rho_B | b \rangle = \sum_n \langle b | H | n \rangle \otimes_\delta \langle n | H^+ | b \rangle \quad (Al.37)$$

The form of Eqn (Al.37) is not satisfactory because matrix element is expressed in terms of $|n\rangle$ instead of $|a\rangle$.

However we employ Eqn (Al.21') between $|n\rangle$ and $|\langle n\rangle$ to get
\[ \langle b | \rho_B | b \rangle = \sum_{a, a', n} \langle b | H | a \rangle \langle a | n \rangle \hat{g}_n \langle n | a' \rangle \langle a' | H^+ | b \rangle \]  
(A1.38)

Introducing density matrix \( \rho_A \) and using Eqn (A1.32) finally yields

\[ \langle b | \rho_B | b \rangle = \sum_{a, a'} \langle b | H | a \rangle \langle a | \rho_A | a' \rangle \langle b' | H | a' \rangle^* \]  
(A1.39)

Constant factors which may appear in (A1.39) are independent of \( a \) and \( b \) and hence are of no consequence here.
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VITA AUCTORIS

Place of Birth: Mbabala Island, Samfya, Zambia.
Date: June 21, 1947.

Education

1968: Cambridge "O" Level
Malole Secondary School,
Zambia.

1972: Bachelor of Science (Mathematics/Physics)
University of Zambia.

1974: Entered Graduate School,
University of Windsor.

Awards

Research (Zambia) Scholarship.

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