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THE EFFECT OF RANDOM AND APPLIED STRESS ON PARAELECTRIC RESONANCE SPECTRA

by

JESS GALE CARNES, Jr.

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Doctor of Philosophy

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CHAPTER I

INTRODUCTION

Paraelectric resonance is a technique for studying the properties of substitutional impurities which have an orientable electric dipole moment (provided the possible orientations of the electric dipole are discrete). Two types of impurities are known which may exhibit this property. One type is an ion which has minimum energy at several positions which are not on the site of the ion for which it is substituted. This type of ion is referred to as an off-center ion. If one considers only the charges on the ions, creating a vacancy at the lattice site is the same as placing a charge of the opposite sign on the lattice site. The substitutional ions have charges of the same sign as the ion for which it was substituted. If the impurity ion does not lie on the lattice site, there are effectively two charges of opposite sign separated by the distance between the lattice site and the position of the substitutional impurity. Therefore, the ionic impurity has an electric dipole moment. If there are high potential energy barriers which restrict the motion of the ion around the lattice site, the electric dipole moment will have discrete values for its direction. If these potential energy barriers are not infinitely high, the electric dipole moment may change its orientation by tunneling through the energy barriers.

Another type of substitutional impurity which may exhibit paraelectric resonance is a diatomic molecule which has an intrinsic electric dipole moment. In a manner similar to the off-center ion, the molecular ion may not be free to rotate about its center. There
may be potential energy barriers which prevent this type of motion. These barriers create discrete orientations for the dipole moment of the impurity. In order for the dipole moment to change orientation, it must tunnel through these barriers.

The only difference between these two types of impurities is the manner in which they change the orientation of their electric dipole moment. The off-center ion changes the direction of its electric dipole by translational motion around the lattice site, the molecular ion by rotational motion. It should be noted, however, that the molecular ion does not necessarily have to be on the lattice site. It could be off-center as well. In this case, the reorientation of the dipole moment is effected by a combination of both rotational and translational motion. The important characteristics for both types of impurities are: (1) the dipole moment has discrete orientations, and (2) the dipole moment can change from one orientation to another only by tunneling through the energy barriers separating the possible orientations. Whether the ion reorients itself by translation, rotation, or a combination of the two is immaterial. The method of reorientation can not be determined by the technique of paraelectric resonance.

In studying the impurity ion, one must also include the effect of the impurity on the surrounding atoms of the lattice. When the impurity ion is placed in the crystal, all of the other ions in the vicinity of the impurity must shift their positions in order to accommodate the impurity with the lowest possible energy for the system. If one changes the position or orientation of the impurity, the other ions will shift their positions so that the total energy will always be minimized for the impurity ion in any particular
position or orientation. Since the change in position or orientation of the impurity ion causes the shifting of the surrounding ions, one may consider the change in energy as a function of the position of the impurity alone. In a similar manner, there will be a contribution to the dipole moment of the impurity from the shifting of the surrounding ions, but since the shifting of the surrounding ions is due to the presence of the impurity ion, the dipole moment of the impurity ion and the surrounding ions can be attributed solely to the impurity ion.

In order to show how a system of the sort described above can exhibit paraelectric resonance, consider an impurity for which the electric dipole is frozen in one of its possible orientations. There is a possible state for the impurity corresponding to each of the orientations of the dipole moment. If there are N possible orientations for the dipole, there are N states for the impurity. All of these states are equivalent, and their energy is the same. If the Hamiltonian for the system were expressed in matrix form, it would be diagonal. The wavefunction describing the impurity would be one of the wavefunctions for the various orientations.

If, however, the impurity is allowed to tunnel from one orientation to another, the wavefunctions for the impurity are no longer just the wavefunctions for the various orientations, but are linear combinations of the functions for all of the orientations. The Hamiltonian for the impurity, expressed in terms of the wavefunctions for the various orientations, will have off-diagonal matrix elements. These off-diagonal matrix elements of the Hamiltonian will lead to splittings of the energy between the states of the system. This is the zero field splitting of the tunneling multiplet.
The application of an electric field can further split this multiplet. An electric field applied to the system can change the energy of a dipole in a given orientation, depending on the direction of the electric field. The Hamiltonian for this interaction is given by
\[ H = -\vec{\mu} \cdot \vec{E} \]
where \( \vec{\mu} \) is the electric dipole moment in the given orientation and \( \vec{E} \) is the electric field applied to the impurity.

An oscillating electric field can induce transitions between some of the energy levels of the multiplet. The Hamiltonian for this interaction is
\[ H_x = -\vec{\mu} \cdot \vec{E} e^{i\omega t} \]
where \( \vec{E} \) is the amplitude of the oscillating electric field, and \( \omega \) is the angular frequency of the oscillation.

In the technique of paraelectric resonance, the tunneling multiplet is split by the application of an electric field. When the difference in energy between two levels for which there is an allowed transition is equal to the microwave quantum, \( h\omega \), more power is absorbed from the microwave field. This causes a change in the power being reflected from the sample cavity. From this information, one can deduce some of the behavior of the tunneling multiplet in the presence of an electric field.

This paper will deal with two systems for which good quality paraelectric resonance spectra have been obtained. The host crystals for both systems have the NaCl-type structure, which exhibits octahedral symmetry. The first system is probably the most studied of all paraelectric systems: Li\(^+\) substituted for K\(^+\) in KCl. This is an example of an off-center paraelectric impurity. It is found
to have possible orientations for its dipole moment along the eight [111]-type directions. The second system is OH\(^-\) substituted for Cl\(^-\) in NaCl. This is a molecular impurity which is found to have possible orientations for its dipole along the six [100]-type directions. All well documented paraelectric systems seem to have properties similar to one or the other of these two systems.

Two types of data were taken for both systems. The first type of data is plain paraelectric resonance spectra in which an electric field is applied and the absorption of microwave energy is measured as a function of the applied field. This was done in both the straight back reflection mode and the phase sensitive detection mode. The second type of data is the effect on the spectra of uniaxial stress applied parallel to the electric field. This was done in the phase sensitive detection mode.

The effect of random internal stresses was calculated for the NaCl:OH\(^-\) system. This type of calculation has previously been done for the KCl:Li\(^+\) system\(^1\). The effect of applied stress on the zero-intrinsic stress allowed transitions was calculated for both NaCl:OH\(^-\) and KCl:Li\(^+\).
CHAPTER II

GENERAL THEORY OF PARAELECTRIC RESONANCE

In order to make theoretical calculations of the properties of a paraelectric impurity, a model for the defect must be formulated. As stated in the introduction, we are only concerned with two characteristics of the impurity: (1) the discrete orientations of the dipole moment of the impurity, and (2) the potential energy barriers which prevent the change in orientation of the dipole except by tunneling.

MODEL FOR THE PARAELECTRIC IMPURITY

First, consider the form of the potential energy barrier which prevents the reorientation of the dipole moment. Most of the calculations which are made do not require an exact knowledge of the form of the potential. However, it may be useful from time to time to have an approximate form for the potential in order to gain more insight into the results of a calculation.

The potential energy of the ion in the region near a minimum may be expressed in terms of a Taylor series about the minimum.

\[ V(g_i) = V(g_i = 0) + \frac{\partial V}{\partial g_i} g_i = 0 \cdot g_i + \frac{1}{2} \sum_{j \neq i} \frac{\partial^2 V}{\partial g_i \partial g_j} g_i = 0 \cdot g_i \cdot g_j \cdot \ldots \]

where for an off-center ion, the \( q_i \)'s are the position coordinates, and for a molecular ion, they are the angular coordinates. The value \( q_i = 0 \) is the position of the minimum. Since this is true, \( \frac{\partial V}{\partial g_i} g_i = 0 \) is zero. One may set \( V(q_i = 0) \) equal to zero, and get an approximation to the actual potential.

\[ V(g_i) \approx \frac{1}{2} \sum_{i \neq j} k_{ij} g_i \cdot g_j \]

where \( k_{ij} = \frac{\partial^2 V}{\partial g_i \partial g_j} g_i = 0 \). By rotation of the coordinate system, one can eliminate the cross terms of \( q_i q_j \) and one is left with
\[ V(q_z) = \frac{1}{2} \sum_{z} \frac{k_z^2}{2} q_z^2 \]

which is the potential for an anisotropic three dimensional harmonic oscillator. One may therefore use harmonic oscillator wavefunctions as approximations to the actual wavefunctions. In all cases studied in this paper, the temperature and frequency are low enough that the only state it is necessary to consider is the ground state or zero point vibrational wavefunction. Some work has been done on transitions between the ground state and the first excited state, but these transitions are at much higher frequencies than those used in microwave spectroscopy.

One can assume that there is an anisotropic harmonic oscillator centered at each position of minimum energy for the ion. The ion is considered to be under the influence of the potential for the minimum to which it is closest. Each of the potential energy minima is labeled with a number, \( j \), and each minimum is assigned a wavefunction, \( |j\rangle \), which describes the ion in that well.

In order to show what the matrix elements of the Hamiltonian for this model will be like, consider the simple one dimensional model illustrated in Figure 1. There are two minima for the ion which are separated by a distance \( 2a \). A harmonic oscillator potential energy function is used. The potential energy of the ion is given by

\[
\begin{align*}
V(\kappa) &= \frac{1}{2} k_0 (\kappa + a)^2 & \text{for } \kappa < 0 \\
V(\kappa) &= \frac{1}{2} k_0 (\kappa - a)^2 & \text{for } \kappa > 0
\end{align*}
\]

The left well is labeled 1, and the right well is labeled 2. A ground state vibrational wavefunction is used to describe the ion in each of the wells. These would be the exact wavefunctions if the wells were infinitely separated. The wavefunctions used are

\[
|1\rangle = N e^{-\kappa^2 (\kappa + a)^2 / 2} \quad |2\rangle = N e^{-\kappa^2 (\kappa - a)^2 / 2}
\]
FIGURE 1: POTENTIAL FOR A ONE-DIMENSIONAL TWO WELL HARMONIC OSCILLATOR
where \( N = \alpha^{1/2}/\pi^{1/4} \) and \( \alpha = m \omega / \hbar \). The overlap integral, \( S_{12} = \langle 1 | 2 \rangle \), is given by

\[
S_{12} = \int_{-\infty}^{\infty} N^2 e^{-\alpha^2(\kappa+a)^2/2} e^{-\alpha^2(\kappa-a)^2/2} \, d\kappa.
\]

and the off-diagonal matrix element of the Hamiltonian, \( H_{12} = \langle 1 | H | 2 \rangle \), is given by

\[
H_{12} = \int_{-\infty}^{\infty} N^2 e^{-\alpha^2(\kappa+a)^2/2} \left[ -\frac{\hbar^2}{2m} \frac{d^2}{d\kappa^2} + \frac{1}{2} \hbar (\kappa+a)^2 \right] e^{-\alpha^2(\kappa-a)^2/2} \, d\kappa
\]
\[
+ \int_{0}^{\infty} N^2 e^{-\alpha^2(\kappa+a)^2/2} \left[ -\frac{\hbar^2}{2m} \frac{d^2}{d\kappa^2} + \frac{1}{2} \hbar (\kappa-a)^2 \right] e^{-\alpha^2(\kappa-a)^2/2} \, d\kappa.
\]

The results of these integrations are

\[
S_{12} = e^{-\alpha^2a^2}, \quad H_{12} = \left( \frac{1}{2} \hbar \omega - a \sqrt{\frac{\hbar \omega}{\pi}} \right) S_{12}
\]

In microwave spectroscopy, constant components of the energy are not of interest, since they represent only a shifting of the zero of energy. Therefore, we neglect the term \( \frac{1}{2} \hbar \omega \) in the matrix elements of the Hamiltonian. The diagonal matrix elements become 0, and the off-diagonal matrix elements become

\[
H_{12} = -a \sqrt{\frac{\hbar \omega}{\pi}} S_{12}
\]

In this simple case, the matrix element, \( H_{12} \), will always be negative, so it is assumed that this will be the case for the more complicated three dimensional situation. The matrix elements of the tunneling Hamiltonian are expressed as follows:

\[
H_{12} = -\Delta_{ij} (i \neq j) \quad H_{ii} = 0 \quad (i = j)
\]

The parameter \( \Delta_{ij} \) is called the tunneling parameter, and is assumed to be positive.

In systems where tunneling is the only method for reorienting the dipole, the overlap integral, \( S_{ij} \), must be small in comparison to the normalization, \( \langle i | i \rangle \). Therefore, the overlap is neglected with respect to the normalization. The matrix element, \( \langle i | j \rangle \), will equal \( \delta_{ij} \).

Even if the overlap is not neglected, the results will be approximately the same, and neglecting them makes the calculations much easier.
USE OF GROUP THEORY IN PARAELECTRIC RESONANCE CALCULATIONS

Calculations of the properties for paraelectric impurities are greatly simplified by taking advantage of the information contained in the symmetry of the problem. This is done by the use of group theoretical methods. The following is a brief justification for the use of group theory in this type of problem. The problem is to determine the eigenfunctions for the Hamiltonian using as basis functions the vibrational wavefunctions corresponding to the various wells. As stated in the previous section, these eigenfunctions are linear combinations of the vibrational wavefunctions.

\[ \psi_i = \sum_j a_{ij} \phi_j \]

The vibrational wavefunctions can be used as a basis for a representation of the operations of the point group for the Hamiltonian. This group contains all of the rotations and inversions which will leave the Hamiltonian invariant. Another way of stating this is that all of the members of the group commute with the Hamiltonian. Since the \( \psi_i \)'s are eigenfunctions of the Hamiltonian,

\[ H \psi_i = E_i \psi_i \]

Consider the effect of operating on this equation with one of the members of the point group for the Hamiltonian.

\[ R H \psi_i = R E_i \psi_i \]

Since \( R \) commutes with \( H \) and \( E_i \) is just a number,

\[ H(R \psi_i) = E_i (R \psi_i) \]

From this argument, it can be seen that operating on an eigenfunction of the Hamiltonian with one of the elements of the point group for the Hamiltonian gives the same eigenfunction or one which has the same energy.
In group theory, a set of functions which transform into each other under the operations of the point group is called the basis for an irreducible representation for the point group. Therefore, the eigenfunctions corresponding to a given energy level form an irreducible representation for the point group of the Hamiltonian. This fact gives one a method for determining the number of levels into which the tunneling multiplet splits and the degeneracy of these levels. All that is required is to determine the number and types of irreducible representations contained in the reducible representation based on the vibrational basis functions.

In order to find the irreducible representations, it is necessary to consider the character of the reducible representation based on the vibrational wavefunctions. The character for this representation may be found by observing the operation of an element of each class on the vibrational wavefunctions. From this knowledge and a knowledge of the character of the various irreducible representations of the point group, it is possible to determine the number of irreducible representations of a given type from the formula

\[ \alpha_i = \frac{1}{N} \sum_{\alpha} N_{\alpha} \chi_i^\ast (C_{\alpha}) \chi_\alpha (C_{\alpha}) \]

where \( \alpha_i \) is the number of times the \( i \)-th irreducible representation appears in the \( \alpha \) representation; \( N \) is the number of elements in the group; \( N_{\alpha} \) is the number of elements in the class, \( C_{\alpha} \); \( \chi_i (C_{\alpha}) \) is the character of the \( i \)-th representation for the class, \( C_{\alpha} \); and \( \chi_\alpha (C_{\alpha}) \) is the character for the representation using the vibrational wavefunctions for the class, \( C_{\alpha} \). The sum is over all of the classes of the group. This gives the number of energy levels and their degeneracies. From the properties of the basis functions for the irreducible representations, one can determine the \( a_{ij} \)'s in
\[ \psi_i = \sum_j a_{ij} |j\rangle \]

In this way, the eigenfunctions have been determined simply by using the symmetry of the problem. For a more complete explanation of the techniques of group theory as they are applied to quantum mechanics, see the book by Tinkham. The symmetry labels assigned to states in this paper are taken from this book.

Since the matrix elements of the Hamiltonian are known in terms of the vibrational wavefunctions, the actual zero field splittings can be determined by calculating the expectation value for the Hamiltonian in a given state.

\[ \langle \psi_i | H | \psi_i \rangle = \sum_i a_{ij} \langle i | H \sum_k a_{jk} | k \rangle = \sum_j a_{ij} a_{jk} \langle i | H | k \rangle \]

\[ \langle \psi_i | H | \psi_i \rangle = -\sum_j a_{ij} a_{jk} \Delta_j \]

Group theory will tell one only which levels are allowed to split and their degeneracies. It will be seen later that the possible transitions for a system can be determined by using group theoretical methods. Group theory cannot give the actual splittings or the probability of a transition. In order to determine these things, actual calculations must be made. By using group theory, however, one has an independent check on calculations. If a splitting or transition is not allowed by the symmetry of the system, and a calculation shows that it is allowed, then it is necessary to recheck the calculation for possible errors.

**EFFECT OF ELECTRIC FIELDS ON THE TUNNELING MULTIPLET**

When an electric field is applied to the system, the symmetry of the Hamiltonian is reduced and the irreducible representations for the zero field Hamiltonian may become reducible. This means that there is a further splitting of the energy levels due to the application of an electric field. The electric field induced splittings can be
determined by the same methods as were used in the zero field case, or
one may use the compatibility tables contained in most collections of
group theory tables. Perhaps the most comprehensive collection of
group theory tables is contained in the book, Properties of the Thirty-
Two Point Groups.\textsuperscript{3} One might attempt to determine the eigenfunctions
for this problem using the same methods as for the zero field case, but
this is a very tedious task. Instead, numerical methods are used to
diagonalize the Hamiltonian and obtain the wavefunctions.

In order to determine the effect of electric fields on the system,
one must determine the effect of the electric field on the vibrational
basis states. The Hamiltonian for the interaction has the form \(-\vec{\mu} \cdot \vec{E}\).
Therefore, the matrix elements of the electric field Hamiltonian are
\[ \langle i | -\vec{\mu} \cdot \vec{E} | j \rangle = -\langle i | \vec{\mu} | j \rangle \cdot \vec{E} \]
Since the overlap between states in different wells is being neglected,
the matrix elements of \(\vec{\mu}\) become
\[ \langle i | \vec{\mu} | j \rangle = \vec{\mu}_i \cdot \vec{S}_{ij} \]
where \(\vec{\mu}_i\) is the dipole moment when the ion is in state \(i\). We may
assign a dipole moment to each well.

One can also determine which transitions are allowed by the
symmetry of the problem. This can be done by the use of group theory.
The intensity of a transition is proportional to the absolute square
of the matrix element, between the two states of the system, for the
interaction between the electric dipole and the oscillating electric
field.

\[ I \propto | \langle \psi_i | \vec{\mathcal{H}} | \psi_j \rangle |^2 \]

The Hamiltonian for the interaction between the electric dipole and
the oscillating electric field is given by
\[ H_x = -\mathbf{A} \cdot \mathbf{E}, \]
where \( \mathbf{E} \) is the magnitude of the oscillating electric field.

Therefore, the intensity of a transition becomes

\[ I \propto |\langle \psi_i, H_x, \psi_j \rangle \cdot \mathbf{E}|^2 \]

One can see from this expression that if \( \langle \psi_i, H_x, \psi_j \rangle \) is zero, the transition between states \( i \) and \( j \) is not allowed. Because of the symmetry of the system, this matrix element will always be zero for certain transitions. These transitions may be determined by the use of group theory.

In order to see how this is done, consider the operator, \( \mathbf{A} \).
This is a polar vector with the same symmetry properties as \( \mathbf{A} \). One can consider \( \mathbf{A} \) as a three dimensional representation for the operations belonging to the symmetry group of the Hamiltonian. \( \langle \psi_i, H_x, \psi_j \rangle \) will form the basis of a direct product representation. If the representation using \( \langle \psi_i, H_x, \psi_j \rangle \) does not contain one of the same irreducible representations as the representation containing \( \langle \psi_i \rangle \), then \( \langle \psi_i, H_x, \psi_j \rangle \) will be zero, and the transition between states \( i \) and \( j \) is not allowed by symmetry.
One may determine the character of the direct product representation based on \( \langle \psi_i, H_x \rangle \) by the formula

\[ \chi_{\langle \psi_i, H_x \rangle}(C_k) = \chi_{\mathbf{A}}(C_k) \chi_{\langle \psi_i \rangle}(C_k) \]

Then by using the decomposition formula, one may determine the irreducible representations contained in the representation based on \( \langle \psi_i, H_x \rangle \). Another method is to determine the irreducible representations contained in a representation based on \( \mathbf{A} \), and use the multiplication tables for the representations to determine which transitions are allowed.

There are two rather general rules which make the determination of which transitions will occur much simpler. The first is concerned
with transitions for a system which exhibits inversion symmetry. This would be the zero field case and the case where only a stress is applied to the system. The states of a system with inversion symmetry can be characterized by their parity. If the parity is even, the inversion operator does not change the state.

\[ I \psi_g = \psi_g \]

If the state is odd, the inversion operator changes the sign of the state.

\[ I \psi_o = -\psi_o \]

The g and o stand for "gerade" and "ungerade", which is German for "even" and "odd". The parity of the product of two functions is even if the functions have the same parity. It is odd if the functions are of different parity. \( \mathcal{A} \) or any polar vector has odd parity. Therefore, operating with \( \mathcal{A} \) on a wavefunction will give a function of the opposite parity from the original wavefunction. This indicates that the only transitions which will occur are between even and odd states. It does not mean that all transitions between even and odd states are allowed. To determine which ones are allowed, one must examine the problem more closely.

The second general rule is concerned with transitions in the presence of an electric field. When the oscillating electric field is parallel to the applied field, the only component of \( \mathcal{A} \) which can induce transitions is the component parallel to the field. Since the operators of the group for the Hamiltonian do not affect the electric field, they will not affect the component of the electric dipole parallel to the field. This means that the component of the dipole parallel to the field belongs to the symmetric representation for the group. The direct product of the symmetric representation
with any representation is that same representation. Therefore, as a general rule, there will be transitions only between states belonging to the same representation.

Group theory only gives an indication of which transitions are allowed. To determine the actual intensities of a transition, it is necessary to evaluate the matrix element of the interaction Hamiltonian between the two states of interest.

**EFFECT OF STRESS ON THE TUNNELING MULTIPLET**

A stress applied to the system will also split the energy levels. The stress distorts the lattice and changes the energy of the ion. The amount of change depends on which of the minima about the lattice site is occupied by the ion. The change is due to the interaction between the stress field and the localized strain caused by the presence of the impurity. The Hamiltonian for the interaction between the stress and the localized strain is given by

$$\mathcal{H}_c = -\vec{\tau} \cdot \hat{\sigma}$$

where $\vec{\sigma}$ is the stress at the site of the impurity, and $\hat{\tau}$ is the localized strain due to the impurity. The localized strain, $\hat{\tau}$, has properties which are analogous to the electric dipole moment, $\hat{\mu}$. They are both associated with the presence of the impurity, and they both react to an applied field by changing the energy of the impurity. Because of this close analogy, one can call $\hat{\tau}$ the elastic dipole moment of the impurity. In analogy to the electric dipole moment, an elastic dipole moment is associated with each state of the ion.

Because of the tensor form of $\hat{\tau}$, it is not as simple to evaluate as $\hat{\mu}$. In order to evaluate $\hat{\tau}$ for the various wells, it is necessary to use the symmetry of the system and the fact that one neglects constant shifts in the energy due to the application of a stress.
The splittings of the tunneling multiplet due to an applied stress may be determined in the same manner as for an applied electric field. The stress lowers the symmetry of the system, and causes some of the levels for the unstressed system to decompose. These splittings can be found by using the decomposition formula or by looking them up in a compatibility table.

One may also induce transitions between levels by the application of an oscillating stress. This is a variation of the paraelectric resonance technique known as paraelastic resonance. Another important process concerned with oscillating stress fields is the relaxation of the impurity by the lattice phonons. Both of these problems are treated using techniques analogous to those used to treat electric field induced transitions.

One may formulate a general rule for which stress induced transitions will occur in a system exhibiting inversion symmetry. The stress field possesses inversion symmetry, so its parity is even. By arguments similar to those used for electric field induced transitions in a system with inversion symmetry, it can be shown that the stress induced transitions can only take place between states of the same parity. As always, one must examine the individual situation to determine if a transition between two states will actually occur.

The stress and electric fields which are used in the Hamiltonian are the fields at the site of the individual ion. It must be remembered that the electric field at the site of an impurity is not the same as that applied to the crystal macroscopically. There is an extra contribution due to the polarizability of the other ions of the lattice. One may, however, calculate the actual field from a knowledge of the field applied $\tilde{E}$ AND the electric susceptibility
of the dielectric, $\chi_e^4$

$$\mathcal{E} = \mathcal{E}_0 \left( 1 + \chi_e / 3\varepsilon_0 \right)$$

Another thing to bear in mind is that this field may vary from ion to ion due to inhomogeneities in the host crystal. This distribution of fields will lead to broadening of the resonance lines, because one can get transitions for several different values of the electric field.

The resonance lines may also be broadened by the presence of random internal stresses due to dislocations and other imperfections in the crystal. Another consequence of the random internal stresses is that some transitions which were not allowed in the presence of the electric field become allowed when the stress is present. This does not appear to occur as easily for the case of random internal electric fields.$^1$
CHAPTER III

APPLICATION OF THE TUNNELING MODEL TO KCl:Li⁺ AND NaCl:OH⁻

Both KCl and NaCl are alkali halides with the same cubic structure. This section will describe the consequences of the use of the tunneling model for a system exhibiting octahedral symmetry. The methods used are similar to those employed by Gomez, Bowen, and Krumhansl.⁵

The point group of KCl and NaCl is the full octahedral group. It consists of all the rotations and inversions which will leave a cube invariant. The elements of the group and a character table for the group are presented in Table 1. There are several possible symmetries which the paraelectric impurity could exhibit. The simplest arrangement is for the dipole to have possible orientations along the six [100]-type directions. This type of system is called the six ⟨100⟩ dipole system. The OH⁻ ion appears to have this type of symmetry in NaCl. The next more complicated arrangement is a dipole with possible orientations along the eight [111]-type directions. This type of system is called the eight ⟨111⟩ dipole system. The Li⁺ ion in KCl seems to have this symmetry.

There are more complicated systems possible in octahedral symmetry, but there does not appear to be any well documented system with a more complicated symmetry than the eight ⟨111⟩ dipole system. A schematic representation of both the six ⟨100⟩ and eight ⟨111⟩ dipole systems is shown in Figure 2. The numbering system for the states is also shown.
TABLE 1: ELEMENTS AND CHARACTER TABLE FOR THE FULL OCTAHEDRAL GROUP

ELEMENTS OF THE FULL OCTAHEDRAL GROUP

<table>
<thead>
<tr>
<th>CLASS</th>
<th>NUMBER IN CLASS</th>
<th>TYPE OF ELEMENT</th>
</tr>
</thead>
<tbody>
<tr>
<td>E</td>
<td>1</td>
<td>Identity</td>
</tr>
<tr>
<td>8C₃</td>
<td>8</td>
<td>120° rotations about the body diagonals of a cube</td>
</tr>
<tr>
<td>3C₂</td>
<td>3</td>
<td>180° rotations about axes through the origin perpendicular to the faces of a cube</td>
</tr>
<tr>
<td>6C₂</td>
<td>6</td>
<td>180° rotations about axes through the origin parallel to the cube face diagonals</td>
</tr>
<tr>
<td>6C₄</td>
<td>6</td>
<td>90° rotations about axes through the origin perpendicular to the faces of a cube</td>
</tr>
</tbody>
</table>

The five other classes are products of these classes with the inversion operator, I.

CHARACTER TABLE FOR THE FULL OCTAHEDRAL GROUP

<table>
<thead>
<tr>
<th>IRREDUCIBLE REPRESENTATION</th>
<th>CLASSES</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>E 8C₃ 3C₂ 6C₂ 6C₄ I 8C₃I 3C₂I 6C₂I 6C₄I</td>
</tr>
<tr>
<td>A₁g</td>
<td>1 1 1 1 1 1 1 1 1</td>
</tr>
<tr>
<td>A₂g</td>
<td>1 1 1 -1 -1 1 1 -1 -1</td>
</tr>
<tr>
<td>E₂g</td>
<td>2 -1 2 0 0 2 -1 2 0</td>
</tr>
<tr>
<td>T₁g</td>
<td>3 0 -1 -1 1 3 0 -1 -1 1</td>
</tr>
<tr>
<td>T₂g</td>
<td>3 0 -1 1 -1 3 0 -1 1 -1</td>
</tr>
<tr>
<td>A₁u</td>
<td>1 1 1 1 1 -1 -1 -1 -1</td>
</tr>
<tr>
<td>A₂u</td>
<td>1 1 1 -1 -1 -1 -1 1 1</td>
</tr>
<tr>
<td>E₂u</td>
<td>2 -1 2 0 0 -2 1 -2 0 0</td>
</tr>
<tr>
<td>T₁u</td>
<td>3 0 -1 -1 1 -3 0 1 1 -1</td>
</tr>
<tr>
<td>T₂u</td>
<td>3 0 -1 1 -1 -3 0 1 -1 1</td>
</tr>
</tbody>
</table>
FIGURE 2: SCHEMATIC ARRANGEMENT AND NUMBERING OF THE MINIMA FOR THE EIGHT \(<111>\) AND SIX \(<100>\) DIPOLE SYSTEMS
ZERO FIELD SPLITTING OF THE TUNNELING MULTIPLET

The first step that must be taken is to determine the character of the representation using the dipole orientations as a basis. This is done by observing the effect of an element of a particular class on the system of orientations. As an example, consider the class $3C_2$ of the octahedral group. This class contains a rotation by 180° about the [100] direction. In the six $<100>$ dipole system, this is a rotation about the axis connecting 1 and 4. It can be seen by looking at Figure 2 that this rotation will leave 1 and 4 unchanged, but will change all of the other states. Since the character of a representation is the trace of the matrix for the representation, and 1 and 4 are the only unchanged states, the character for this rotation is 2. This will be the character for the entire class, since all of the other elements of the class can be obtained from this rotation by a unitary transformation, and a unitary transformation leaves the trace of a matrix unchanged. After finding the character of the representation, it is a simple process to determine the splitting of the tunneling multiplet by using the decomposition formula. Both the character and splittings are given in Table 2 for the six $<100>$ and eight $<111>$ dipole systems. These results indicate that the tunneling causes the six $<100>$ dipole system to split into three levels: a singly degenerate, a doubly degenerate, and a triply degenerate level. The eight $<111>$ dipole system splits into four levels: two triply degenerate and two singly degenerate levels.

In order to determine the actual splittings in terms of matrix elements of the tunneling Hamiltonian, it is necessary to determine the eigenfunctions for the problem. These eigenfunctions are linear combinations of the basis functions.
TABLE 2: CHARACTER TABLE AND DECOMPOSITION OF THE REPRESENTATIONS USING DIPOLE ORIENTATIONS ALONG THE SIX <100> AND EIGHT <111> DIRECTIONS

<table>
<thead>
<tr>
<th>REPRESENTATION</th>
<th>E 8C_3 3C_2 6C_2 6C_4 I 8C_3' 3C_2' 6C_2' 6C_4'</th>
</tr>
</thead>
<tbody>
<tr>
<td>Γ &lt;100&gt;</td>
<td>6 0 2 0 2 0 0 4 2 0</td>
</tr>
<tr>
<td>Γ &lt;111&gt;</td>
<td>8 2 0 0 0 0 0 0 4 0</td>
</tr>
</tbody>
</table>

DECOMPOSITION OF THE SIX <100> AND EIGHT <111> DIPOLE REPRESENTATIONS

Γ <100> (6X) = A_{1g} (1X) + E_g (2X) + T_{1u} (3X)

Γ <111> (8X) = A_{1g} (1X) + T_{2g} (3X) + A_{2u} (1X) + T_{1u} (3X)

The numbers in parentheses represent the degeneracy of the irreducible representation.
\[ \psi_x = \sum_i a_{ij} |j_i \rangle \]

In order to determine the \( a_{ij} \)'s, one may use the sample wavefunctions for a particular representation. These are given in most character tables. The technique is then to take an element of the group and let it operate on the sample wavefunctions. Then operate with the same element on \( \psi_x \). The operator must have the same effect on the sample wavefunction as it does on \( \psi_x \). This allows one to determine some of the \( a_{ij} \)'s. It may take the use of several different elements before the eigenfunction is completely determined. The results of this procedure are shown in Tables 3 and 4.

Now that one has the eigenfunctions for the problem, it is a simple matter to determine the actual zero field splitting of the tunneling multiplet in terms of the matrix elements of the Hamiltonian. The symmetry of the system reduces the number of tunneling parameters necessary to describe the system. In the case of the six \( \langle 100 \rangle \) dipole system, there are only two types of tunneling: (1) the tunneling from an orientation to one perpendicular to it, \( \Delta_{90} \), and (2) tunneling from an orientation to one opposite it, \( \Delta_{180} \). In the eight \( \langle 111 \rangle \) dipole system, there are three types of tunneling: (1) tunneling along a cube edge, \( \Delta_E \), (2) tunneling along a cube face, \( \Delta_F \), and (3) tunneling along a cube diagonal, \( \Delta_D \). The splittings of the tunneling multiplet in terms of the tunneling parameters is shown for the six \( \langle 100 \rangle \) and eight \( \langle 111 \rangle \) dipole systems in Tables 3 and 4.

The next step in this calculation is to determine which transitions will occur when an oscillating electric field is applied to the system. The components of the dipole moment transform like \( x \), \( y \), and \( z \). Since \( x \), \( y \), and \( z \) are sample basis functions for the \( T_{1u} \) representation, the components of \( \tilde{\mathcal{U}} \) transform
TABLE 3: EIGENFUNCTIONS AND ENERGIES FOR A SYSTEM USING EIGHT \begin{aligned} \langle 111 \rangle \end{aligned} Dipoles

EIGENFUNCTIONS FOR A SYSTEM USING EIGHT \begin{aligned} \langle 111 \rangle \end{aligned} Dipoles

\begin{align*}
A_{1g} & : \quad \psi = \frac{1}{\sqrt{2}} (|1\rangle - |2\rangle - |3\rangle - |4\rangle - |5\rangle - |6\rangle - |7\rangle - |8\rangle) \\
T_{1u} & : \quad \psi_1 = \frac{1}{\sqrt{2}} (|1\rangle - |5\rangle - |2\rangle + |6\rangle - |3\rangle + |7\rangle + |4\rangle - |8\rangle) \\
& \quad \psi_2 = \frac{1}{\sqrt{2}} (|1\rangle - |5\rangle + |2\rangle - |6\rangle - |3\rangle + |7\rangle - |4\rangle + |8\rangle) \\
& \quad \psi_3 = \frac{1}{\sqrt{2}} (|1\rangle - |5\rangle + |2\rangle - |6\rangle + |3\rangle - |7\rangle + |4\rangle - |8\rangle) \\
T_{2g} & : \quad \psi_1 = \frac{1}{\sqrt{2}} (|1\rangle + |5\rangle + |2\rangle + |6\rangle - |3\rangle - |7\rangle - |4\rangle - |8\rangle) \\
& \quad \psi_2 = \frac{1}{\sqrt{2}} (|1\rangle + |5\rangle - |2\rangle - |6\rangle - |3\rangle - |7\rangle + |4\rangle + |8\rangle) \\
& \quad \psi_3 = \frac{1}{\sqrt{2}} (|1\rangle + |5\rangle - |2\rangle - |6\rangle + |3\rangle + |7\rangle - |4\rangle - |8\rangle) \\
A_{2u} & : \quad \psi = \frac{1}{\sqrt{2}} (|1\rangle - |5\rangle - |2\rangle + |6\rangle + |3\rangle - |7\rangle - |4\rangle + |8\rangle)
\end{align*}

ENERGIES FOR A SYSTEM USING EIGHT \begin{aligned} \langle 111 \rangle \end{aligned} Dipoles

\begin{align*}
E(A_{1g}) & = -3\Delta_E - 3\Delta_F - \Delta_B \\
E(T_{1u}) & = -\Delta_E + \Delta_F + \Delta_B \\
E(T_{2g}) & = +\Delta_E + \Delta_F - \Delta_B \\
E(A_{2u}) & = +3\Delta_E - 3\Delta_F + \Delta_B
\end{align*}

\begin{align*}
\Delta_E & - \text{tunneling along a cube edge} \\
\Delta_F & - \text{tunneling along a cube face diagonal} \\
\Delta_B & - \text{tunneling along a cube body diagonal}
\end{align*}
TABLE 4: EIGENFUNCTIONS AND ENERGIES FOR A SYSTEM USING SIX <100> DIPOLES

EIGENFUNCTIONS FOR A SYSTEM USING SIX <100> DIPOLES

\[ \psi_{1g} = \frac{1}{\sqrt{6}} (11\rangle + 12\rangle + 13\rangle + 14\rangle + 15\rangle + 16\rangle) \]

\[ \psi_{1u} = \frac{1}{\sqrt{2}} (11\rangle - 14\rangle) \]
\[ \psi_{2} = \frac{1}{\sqrt{2}} (12\rangle - 15\rangle) \]
\[ \psi_{3} = \frac{1}{\sqrt{2}} (13\rangle - 16\rangle) \]

\[ E_{g} = \frac{1}{2\sqrt{2}} (11\rangle + 14\rangle + 12\rangle + 15\rangle - 2(13\rangle + 16\rangle) \]
\[ E_{2} = \frac{1}{2} (11\rangle + 14\rangle - 12\rangle - 15\rangle) \]

ENERGIES FOR A SYSTEM USING SIX <100> DIPOLES

\[ E(A_{1g}) = -4\Delta_{90} - \Delta_{180} \]
\[ E(T_{1u}) = +\Delta_{180} \]
\[ E(E_{g}) = +2\Delta_{90} - \Delta_{180} \]

\[ \Delta_{180} - 180^\circ \text{ tunneling} \]
\[ \Delta_{90} - 90^\circ \text{ tunneling} \]
like a $T_{1u}$ representation. Another way of determining the representation for $\vec{\mu}$ is to formulate a transformation matrix for $\vec{\mu}$. The transformation for a rotation of $\phi$ about the z-axis is given by:

$$
\begin{bmatrix}
\mu_x' \\
\mu_y' \\
\mu_z'
\end{bmatrix} =
\begin{bmatrix}
\cos\phi & -\sin\phi & 0 \\
\sin\phi & \cos\phi & 0 \\
0 & 0 & 1
\end{bmatrix}
\begin{bmatrix}
\mu_x \\
\mu_y \\
\mu_z
\end{bmatrix}
$$

Because the z-axis can be oriented in any position, the character is a function only of the angle of rotation.

$$\chi(\phi) = 2\cos\phi - 1$$

The inversion operator, I, operating on $\vec{\mu}$ gives $-\vec{\mu}$, so

$$\chi(\phi, I) = -(2\cos\phi - 1)$$

If one works out the character for the dipole moment using these formulas, it is found to be the same as the character for the $T_{1u}$ representation. By using a multiplication table for the octahedral group, one can determine which transitions are allowed by symmetry. A multiplication table for the octahedral group is presented in Table 5, along with the possible electric field induced transitions.

In order to illustrate what the zero field splitting is like and which transitions will occur in the presence of an oscillating electric field, consider the energy level diagram in Figure 3. In each case, the only tunneling allowed is between nearest neighbor wells. In studying the reorientation of a dipole, it appears that nearest neighbor tunneling should be the easiest, since there is less barrier for the ion to tunnel through. However, it is not necessarily true that this will be the only type of tunneling present in the system. The other tunneling parameters are set equal to zero because it is the simplest situation to analyze, and there does not appear to be a qualitative difference in the results obtained using
### Table 5: Multiplication Table for the Octahedral Group and Possible Electric Dipole Transitions

#### Multiplication Table for the Octahedral Group

<table>
<thead>
<tr>
<th></th>
<th>$A_1$</th>
<th>$A_2$</th>
<th>$E$</th>
<th>$T_1$</th>
<th>$T_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>$A_1$</td>
<td>$A_2$</td>
<td>$E$</td>
<td>$T_1$</td>
<td>$T_2$</td>
</tr>
<tr>
<td>$A_2$</td>
<td>$A_2$</td>
<td>$A_1$</td>
<td>$E$</td>
<td>$T_2$</td>
<td>$T_1$</td>
</tr>
<tr>
<td>$E$</td>
<td>$E$</td>
<td>$E$</td>
<td>$A_1+E_2+E$</td>
<td>$T_1+T_2$</td>
<td>$T_1+T_2$</td>
</tr>
<tr>
<td>$T_1$</td>
<td>$T_1$</td>
<td>$T_2$</td>
<td>$T_1+T_2$</td>
<td>$A_1+E+T_1+T_2$</td>
<td>$A_2+E+T_1+T_2$</td>
</tr>
<tr>
<td>$T_2$</td>
<td>$T_2$</td>
<td>$T_1$</td>
<td>$T_1+T_2$</td>
<td>$A_2+E+T_1+T_2$</td>
<td>$A_1+E+T_1+T_2$</td>
</tr>
</tbody>
</table>

$\gamma_{g} \otimes \gamma_{g} \rightarrow \gamma_{g}$  
$\gamma_{g} \otimes \gamma_{u} \rightarrow \gamma_{u} \otimes \gamma_{g} \rightarrow \gamma_{u}$  
$\gamma_{u} \otimes \gamma_{u} \rightarrow \gamma_{g}$

#### Possible Electric Dipole Transitions

**Six <100> Dipole System:**

- $A_{1g} \rightarrow T_{1u}$
- $E_{g} \rightarrow T_{1u}$

**Eight <111> Dipole System:**

- $A_{1g} \rightarrow T_{1u}$
- $T_{2g} \rightarrow A_{2u}$
- $T_{2g} \rightarrow T_{1u}$
**FIGURE 3:** ENERGY LEVEL SPLITTINGS AND ALLOWED TRANSITIONS FOR THE SIX <100> AND EIGHT <111> DIPOLE SYSTEMS
non-zero tunneling parameters for other than nearest neighbor reorientations. It should be noted that for the six \langle100\rangle dipole system, there are two transitions possible. The one transition is at twice the frequency of the other. In the eight \langle111\rangle dipole system, all transitions are at the same frequency.

**ELECTRIC FIELD INDUCED SPLITTINGS OF THE TUNNELING MULTIPLET**

Now consider the effect of an electric field applied to the system. The electric field reduces the symmetry at the site of the impurity. There is no longer inversion symmetry, and the only allowed rotations are those about axes parallel to the electric field. The point group for an electric field along directions in the (110) plane are given in Table 6. From the reduction in symmetry, one can determine the splittings due to an applied electric field. A schematic representation of this splitting is shown for the eight \langle111\rangle dipole system in Figure 4, and for the six \langle100\rangle dipole system in Figure 5. The experimental apparatus is set up so that the microwave electric field is parallel to the applied field. Therefore, one may use the rule stated in the previous chapter concerning this geometry. The rule is that the only allowed transitions are between states with the same symmetry label.

In order to make calculations of the actual splittings as a function of applied field, it is necessary to determine the Hamiltonian in terms of the zero point vibrational states. The Hamiltonian for the tunneling in the eight \langle111\rangle dipole system is
### TABLE 6: SYMMETRY GROUP CORRESPONDING TO ELECTRIC FIELDS AND STRESSES ALONG DIRECTIONS IN THE (110) PLANE

#### SYMMETRY GROUP CORRESPONDING TO ELECTRIC FIELDS ALONG DIRECTIONS IN THE (110) PLANE

<table>
<thead>
<tr>
<th>DIRECTION</th>
<th>SYMMETRY GROUP</th>
</tr>
</thead>
<tbody>
<tr>
<td>[100]</td>
<td>C&lt;sub&gt;4v&lt;/sub&gt;</td>
</tr>
<tr>
<td>[111]</td>
<td>C&lt;sub&gt;3v&lt;/sub&gt;</td>
</tr>
<tr>
<td>[110]</td>
<td>C&lt;sub&gt;2v&lt;/sub&gt;</td>
</tr>
<tr>
<td>ANY OTHER DIRECTION IN (110) PLANE</td>
<td>C&lt;sub&gt;s&lt;/sub&gt;</td>
</tr>
</tbody>
</table>

#### SYMMETRY GROUP CORRESPONDING TO STRESS FIELDS ALONG DIRECTIONS IN THE (110) PLANE

<table>
<thead>
<tr>
<th>DIRECTION</th>
<th>SYMMETRY GROUP</th>
</tr>
</thead>
<tbody>
<tr>
<td>[100]</td>
<td>D&lt;sub&gt;4h&lt;/sub&gt;</td>
</tr>
<tr>
<td>[111]</td>
<td>D&lt;sub&gt;3d&lt;/sub&gt;</td>
</tr>
<tr>
<td>[110]</td>
<td>D&lt;sub&gt;2h&lt;/sub&gt;</td>
</tr>
<tr>
<td>ANY OTHER DIRECTION IN (110) PLANE</td>
<td>C&lt;sub&gt;2h&lt;/sub&gt;</td>
</tr>
</tbody>
</table>
FIGURE 4: SCHEMATIC REPRESENTATION OF THE ENERGY LEVEL SPLITTINGS FOR THE EIGHT ⟨111⟩ DIPOLE SYSTEM
FIGURE 5: SCHEMATIC REPRESENTATION OF THE ENERGY LEVEL SPLITTINGS FOR THE SIX ⟨100⟩ DIPOLE SYSTEM
\[
\begin{pmatrix}
0 & -\Delta_E & -\Delta_F & -\Delta_E & -\Delta_B & -\Delta_F & -\Delta_E & -\Delta_F \\
-\Delta_E & 0 & -\Delta_E & -\Delta_F & -\Delta_E & -\Delta_B & -\Delta_E & -\Delta_E \\
-\Delta_F & -\Delta_E & 0 & -\Delta_E & -\Delta_F & -\Delta_E & -\Delta_B & -\Delta_E \\
-\Delta_E & -\Delta_F & -\Delta_E & 0 & -\Delta_E & -\Delta_F & -\Delta_E & -\Delta_E \\
-\Delta_B & -\Delta_F & -\Delta_E & -\Delta_E & 0 & -\Delta_E & -\Delta_F & -\Delta_E \\
-\Delta_F & -\Delta_B & -\Delta_F & -\Delta_E & -\Delta_E & 0 & -\Delta_E & -\Delta_E \\
-\Delta_E & -\Delta_F & -\Delta_B & -\Delta_F & -\Delta_E & -\Delta_E & 0 & -\Delta_E \\
-\Delta_F & -\Delta_E & -\Delta_F & -\Delta_B & -\Delta_E & -\Delta_F & -\Delta_E & 0
\end{pmatrix}
\]

For the calculations in this paper, only cube edge tunneling was considered. The cube edge tunneling parameter was called \( \Delta \), and all others were set equal to zero. The tunneling Hamiltonian for a system of this type is given by

\[
\begin{pmatrix}
0 & -\Delta & 0 & -\Delta & 0 & 0 & -\Delta & 0 \\
-\Delta & 0 & -\Delta & 0 & 0 & 0 & 0 & -\Delta \\
0 & -\Delta & 0 & -\Delta & -\Delta & 0 & 0 & 0 \\
-\Delta & 0 & -\Delta & 0 & 0 & -\Delta & 0 & 0 \\
0 & 0 & -\Delta & 0 & 0 & -\Delta & 0 & -\Delta \\
0 & 0 & 0 & -\Delta & -\Delta & 0 & -\Delta & 0 \\
-\Delta & 0 & 0 & 0 & -\Delta & 0 & -\Delta & 0 \\
0 & -\Delta & 0 & 0 & -\Delta & 0 & -\Delta & 0
\end{pmatrix}
\]

The matrix elements of the electric field Hamiltonian are given by

\[
\langle \ell | \mathcal{H}_E | i \rangle = -\hbar \mathcal{E} \cos \left( \theta, \hat{z} \right)
\]

If \( \mathcal{E} \) is expressed in terms of components along the cubic axes,

\[
\mathcal{E} = \mathcal{E} [\alpha \hat{x} + \beta \hat{y} + \gamma \hat{z}]
\]

where \( \alpha, \beta, \) and \( \gamma \) are the direction cosines between \( \mathcal{E} \) and the cubic axes. The diagonal matrix elements for the electric field Hamiltonian are as follows:
\[ H(1,1) = -H(5,5) = -\frac{\mu \xi}{\sqrt{3}} (\alpha + \beta + \gamma) \]
\[ H(2,2) = -H(6,6) = -\frac{\mu \xi}{\sqrt{3}} (-\alpha + \beta + \gamma) \]
\[ H(3,3) = -H(7,7) = -\frac{\mu \xi}{\sqrt{3}} (-\alpha - \beta + \gamma) \]
\[ H(4,4) = -H(8,8) = -\frac{\mu \xi}{\sqrt{3}} (\alpha - \beta + \gamma) \]

Since the microwave electric field is parallel to the applied field, the Hamiltonian for the interaction would be the same as the electric field part of the Hamiltonian, except that \( \xi \) would be replaced by \( \xi \frac{1}{\sqrt{3}} \). In order to make calculations using the digital computer, the Hamiltonian must be made dimensionless. This is done by replacing \( \mu \xi \) by \( \mu \xi / \Delta \), so that everything is determined in terms of the tunneling parameter. The results of computer calculations for this system are shown in Figures 6, 7, and 8. Figure 6 is the energy level splittings as a function of electric field for an applied field along [100], [110], and [111]. The frequency of transition is plotted as a function of electric field in Figure 7, and the intensity of the transitions as a function of frequency in Figure 8.

Two of the features of this system should be noted. There is only one transition present for each of the three directions. For a given frequency, the transition will occur at the lowest field along [100], at the highest field along [111], and at a field between these two values for [110].

Now consider the effect of electric field on the six \langle 100 \rangle dipole system. The zero field Hamiltonian is:
Figure 6: Dependence of the energy level splittings on electric field for the eight \{111\} dipole system.
FIGURE 7: THE FREQUENCY OF TRANSITIONS AS A FUNCTION OF APPLIED ELECTRIC FIELD FOR THE EIGHT (111) DIPOLE SYSTEM
FIGURE 8: INTENSITY OF THE TRANSITIONS AS A FUNCTION OF THE FREQUENCY OF TRANSITION FOR THE EIGHT $\langle 111 \rangle$ DIPOLE SYSTEM
If only 90° tunneling is considered, the tunneling Hamiltonian becomes:

\[
\begin{pmatrix}
0 & -\Delta & -\Delta & 0 & -\Delta & -\Delta \\
-\Delta & 0 & -\Delta & -\Delta & 0 & -\Delta \\
-\Delta & -\Delta & 0 & -\Delta & -\Delta & 0 \\
0 & -\Delta & -\Delta & 0 & -\Delta & -\Delta \\
-\Delta & 0 & -\Delta & -\Delta & 0 & -\Delta \\
0 & -\Delta & 0 & -\Delta & -\Delta & 0
\end{pmatrix}
\]

Expressing the electric field in terms of the direction cosines with respect to the cubic axes, the Hamiltonian for the interaction of the dipole with the electric field has the following matrix elements:

\[
H(1,1) = -H(4,4) = -\mu \, E \, \alpha \\
H(2,2) = -H(5,5) = -\mu \, E \, \beta \\
H(3,3) = -H(6,6) = -\mu \, E \, \gamma
\]

Using this Hamiltonian, it is possible to calculate numerically the energy splittings and transitions which will occur for this system. The results of calculations for this system are shown in Figures 9, 10, 11, and 12. Figures 9, 10, and 11 are calculations of energy level splittings, transitions, and transition intensities for the electric field along [100], [110], and [111]. Figure 12 is the result of a calculation for electric field along \{22.5°, 45°\}. 
FIGURE 9: ENERGY LEVEL SPLITTINGS, TRANSITIONS, AND TRANSITION INTENSITIES FOR $\varepsilon_{||}/\varepsilon_{||}[100]$ IN THE SIX <100> DIPOLE SYSTEM
FIGURE 10: ENERGY LEVEL SPLITTING, TRANSITIONS, AND TRANSITION INTENSITIES FOR $C_{\infty h}/[110]$ IN THE SIX $\{100\}$ DIPOLe SYSTEM.
FIGURE 11: ENERGY LEVEL SPLITTINGS, TRANSITIONS, AND TRANSITION INTENSITIES FOR $\mathbf{E} \parallel \mathbf{E}/[111]$ IN THE SIX $<100>$ DIPOLE SYSTEM
FIGURE 12: ENERGY LEVEL SPLITTINGS, TRANSITIONS, AND TRANSITION INTENSITIES FOR $\hbar \omega / E_{1/2}$ IN THE SIX $\langle 100 \rangle$ DIPOLE SYSTEM
This is an orientation which is 22.5° from the [001] direction in a (110) plane.

In this system, there are two thresholds. One is at 2\(\Delta\) and the other at 4\(\Delta\). The theoretical spectra for a frequency of 3\(\Delta\) is shown in Figure 13. This is a frequency above the 2\(\Delta\) threshold, but below the 4\(\Delta\) threshold. Figure 14 shows the spectra at 5\(\Delta\), which is above both thresholds.

**STRESS INDUCED SPLITTINGS OF THE TUNNELING MULTIPLET**

The effect of stress on the tunneling system is not as easy to determine as the effect of an electric field. Consider, first, the effect of stress on the eight \(\langle111\rangle\) dipole system. There are six components to the elastic dipole moment. Three are uniaxial: \(\gamma_{xx}\), \(\gamma_{yy}\), and \(\gamma_{zz}\). These represent the coupling of uniaxial stresses to the dipole. The \(x\), \(y\), and \(z\) axes are along the cubic axes of the crystal. If the system is compressed with uniaxial stress along a \([100]\)-type direction, all of the dipoles will be affected the same. This means that the uniaxial stress would cause an equal shifting of all the levels. Since this constant shift is disregarded in microwave spectroscopy, one may set \(\gamma_{xx}\), \(\gamma_{yy}\), and \(\gamma_{zz}\) equal to zero for the eight \(\langle111\rangle\) dipole system. Now we are left with only three components: \(\gamma_{xy}\), \(\gamma_{yz}\), and \(\gamma_{zx}\). If we consider the \(\sigma_{xy}\) component of the stress tensor, it can be seen that this component will affect wells 1, 3, 5, and 7 in the same way. Likewise, wells 2, 4, 6, and 8 will be affected in the same way. However, each group of wells will be affected differently. One can use the same arguments for \(\sigma_{yz}\) and \(\sigma_{zx}\), and thus obtain the components of the elastic dipole moment in terms of two variables, \(\gamma_1\) and \(\gamma_2\).
FIGURE 13: PARAELECTRIC RESONANCE SPECTRA FOR THE SIX <100> DIPOLE SYSTEM AT A FREQUENCY OF 3Δ.
FIGURE 14: PARA-ELECTRIC RESONANCE SPECTRA FOR THE SIX ⟨100⟩ DIPOLE SYSTEM AT A FREQUENCY OF 5Δ.
Since the trace of the matrix for each component must be zero, the sum of each row will be zero, or \( \gamma_1 = -\gamma_2 \). The elastic dipole moment is now determined in terms of only one parameter, \( \gamma = \gamma_1 = -\gamma_2 \).

The matrix elements for the stress Hamiltonian, \( H \) are

\[
H(1,1) = H(5,5) = -\gamma \left( \sigma_{xy} + \sigma_{yz} + \sigma_{zx} \right)
\]

\[
H(2,2) = H(6,6) = -\gamma \left( -\sigma_{xy} + \sigma_{yz} - \sigma_{zx} \right)
\]

\[
H(3,3) = H(7,7) = -\gamma \left( \sigma_{xy} - \sigma_{yz} - \sigma_{zx} \right)
\]

\[
H(4,4) = H(8,8) = -\gamma \left( -\sigma_{xy} - \sigma_{yz} + \sigma_{zx} \right)
\]

All of the other components of the stress Hamiltonian are zero.

In order to see how stress splits the tunneling multiplet, consider the effect of uniaxial stress parallel to the [110] and [111] directions. In each case, it is necessary to transform this uniaxial stress into a stress tensor in the coordinate system using the cubic axes. For applied stress, \( \sigma_A \), along [110], \( \sigma_{xy} = \sigma_A / 2 \), and \( \sigma_{yz} = \sigma_{zx} = 0 \). For applied stress along [111], \( \sigma_{xy} = \sigma_{yz} = \sigma_{zx} = \sigma_A / 3 \). The results of calculations using these stress tensors are shown in Figures 15 and 16. It shows that the effect is the same for both negative and positive stresses. The energy levels are symmetric, and the spectrum which would be observed is the same for both signs.
FIGURE 15: STRESS INDUCED ENERGY LEVEL SPLITTINGS FOR UNIAXIAL STRESS PARALLEL TO [110] AND TRANSITIONS INDUCED BY AN OSCILLATING ELECTRIC FIELD PARALLEL TO [110] (EIGHT <111> DIPOLE SYSTEM, $\Delta_E = 1.0$, $\Delta_F = 0.0$)
FIGURE 16: STRESS INDUCED ENERGY LEVEL SPLITTINGS FOR UNIAXIAL STRESS PARALLEL TO [111] AND TRANSITIONS INDUCED BY AN OSCILLATING ELECTRIC FIELD PARALLEL TO [111] (EIGHT <111> DIPOLE SYSTEM, $\Delta_E = 1.0$, $\Delta_F = \Delta_D = 0.0$)
of the stress. Therefore, one need not determine the effect of stress for both signs of the stress. Figures 17 and 18 show the effect of stress on a system with non-cube edge tunneling parameters. The tunneling parameters used are $\Delta_E = 4\Delta_F = \Delta$. In this case, the [110] energy levels are still symmetric, but the spectrum which is observed is no longer symmetric about zero stress. The [111] energy levels are not symmetric. When non-cube edge tunneling is present, the effect of stress on the system must take into account both signs of the stress.

Now consider the effect of stress on the six <100> dipole system. Here one must rely on the cubic symmetry of the system to determine what the components of the elastic dipole moment will be. Consider the elastic dipole moment for the well labeled 1. If we perform a $6C_4$ rotation about $\hat{z}$, then the components of the elastic dipole moment should remain unchanged. Under such a rotation, $\mathcal{R}_{yz}$ becomes $-\mathcal{R}_{yz}$. This means that $\mathcal{R}_{yz} = 0$. If we consider a $3C_2$ rotation about $\hat{x}$, $\mathcal{R}_{xy}$ becomes $-\mathcal{R}_{xy}$ and $\mathcal{R}_{zx}$ becomes $-\mathcal{R}_{zx}$. This implies that $\mathcal{R}_{xy} = \mathcal{R}_{zx} = 0$. There are only three non-zero components of $\mathcal{R}$. They are $\mathcal{R}_{xx}$, $\mathcal{R}_{yy}$, and $\mathcal{R}_{zz}$. The effect of a $6C_4$ rotation is to take $\mathcal{R}_{yy}$ into $\mathcal{R}_{zz}$. This means that $\mathcal{R}_{yy} = \mathcal{R}_{zz}$. In general, the components of $\mathcal{R}$ parallel to the direction of the electric dipole moment will be different from the other two components, but the two perpendicular components will be the same. Because constant shifts in energy are not of interest, the trace of the matrix for each component of the elastic dipole moment must be zero.
FIGURE 17: STRESS INDUCED ENERGY LEVEL SPLITTINGS FOR UNIAXIAL STRESS PARALLEL TO [110] AND TRANSITIONS INDUCED BY AN OSCILLATING ELECTRIC FIELD PARALLEL TO [110] (EIGHT <111> DIPOLE SYSTEM, ΔE = 4ΔF = 1.0, ΔD = 0.0)
FIGURE 18: STRESS INDUCED ENERGY LEVEL SPLITTINGS FOR UNIAXIAL STRESS PARALLEL TO [111] AND TRANSITIONS INDUCED BY AN OSCILLATING ELECTRIC FIELD PARALLEL TO [111] (EIGHT (111) DIPOLE SYSTEM, $\Delta E = 1.0$, $\Delta_0 = 0.0$)
Therefore $2\partial_1 - 4\partial_2 = 0$. This means that $\partial_1 = -2\partial_2$. In terms of a single parameter, $\partial$, the components of the dipole moment are:

\[
\begin{array}{c|cccccc}
\text{Well} & 1 & 2 & 3 & 4 & 5 & 6 \\
\hline
\partial_{xx} & \partial_1 & \partial_1 & \partial_2 & \partial_1 & \partial_2 & \partial_2 \\
\partial_{yy} & \partial_2 & \partial_1 & \partial_2 & \partial_2 & \partial_1 & \partial_2 \\
\partial_{zz} & \partial_2 & \partial_2 & \partial_1 & \partial_2 & \partial_2 & \partial_1 \\
\end{array}
\]

The matrix elements of the Hamiltonian for applied stress, $H$, are:

\[
\begin{align*}
H(1,1) &= H(4,4) = -\partial \langle 2 \sigma_{xx} - \sigma_{yy} - \sigma_{zz} \rangle \\
H(2,2) &= H(5,5) = -\partial \langle -\sigma_{xx} + 2 \sigma_{yy} - \sigma_{zz} \rangle \\
H(3,3) &= H(6,6) = -\partial \langle -\sigma_{xx} - \sigma_{yy} + 2 \sigma_{zz} \rangle \\
\end{align*}
\]

All of the other components of the stress Hamiltonian tensor are zero.

In order to see how stress splits the tunneling multiplet, consider the effect of uniaxial stress along [100] and [110].

The components of the stress tensor for a stress parallel to [100] are: $\sigma_{xx}^\sigma = \sigma$, $\sigma_{yy}^\sigma = \sigma_{zz}^\sigma = 0$. For stress along [110], the components are: $\sigma_{xx}^\sigma = \sigma_{yy}^\sigma = \sigma/2$, $\sigma_{zz}^\sigma = 0$. The results of calculations using these stress tensors are shown in Figures 19 and 20. Since the stress splittings are different for positive and negative stresses, both signs of the stress must be considered in any calculation.

The labeling of the states comes from the representations for the point group of the Hamiltonian with applied stress. The point group for uniaxial stress applied to various directions in the (110) plane are shown in Table 6.
FIGURE 19: ENERGY LEVEL SPLITTINGS INDUCED BY UNIAXIAL STRESS PARALLEL TO [100] IN THE SIX ⟨100⟩ DIPOLE SYSTEM
\( (\Delta_{90} = 1.0, \Delta_{180} = 0.0) \)
FIGURE 20: ENERGY LEVEL SPLITTINGS INDUCED BY UNIAXIAL STRESS PARALLEL TO [110] IN THE SIX <100> DIPOLE SYSTEM 
($\Delta_{90} = 1.0, \Delta_{180} = 0.0$)
One may also make calculations with both stress and electric fields present. In this case, the matrix elements of the stress Hamiltonian are added to the Hamiltonian for the tunneling and applied electric field. This type of calculation will be described in more detail in a later chapter.

It is useful to express the elastic dipole moment in terms of the irreducible representations of the cubic group. It is found (by methods similar to those used for the electric dipole moment) that the elastic dipole can be expressed in terms of three irreducible representations.

\[ \mathcal{C}(\mathcal{N}) = A_{1g}(1X) + E_{g}(2X) + T_{2g}(3X) \]

One may express these in terms of the components of using the cubic axes as a coordinate system.

\[ \mathcal{N}(A_{1g}) = \mathcal{N}_{xx} + \mathcal{N}_{yy} + \mathcal{N}_{zz} \]

This corresponds to a hydrostatic pressure on the system.

\[ \mathcal{N}(E_{g}) = \mathcal{N}_{xx} - \mathcal{N}_{yy} \]
\[ \mathcal{N}(E_{g}) = \sqrt{3}(\mathcal{N}_{xx} + \mathcal{N}_{yy} - 2\mathcal{N}_{zz}) \]

These components correspond to uniaxial stresses.

\[ \mathcal{N}(T_{2g}) = \mathcal{N}_{xy} \]
\[ \mathcal{N}(T_{2g}) = \mathcal{N}_{yz} \]
\[ \mathcal{N}(T_{2g}) = \mathcal{N}_{zx} \]

These correspond to the shear stresses. From this it can be seen that the eight \(<111>\) dipole system will interact only with the \(T_{2g}\) components of a stress, and the six \(<100>\) dipole system interacts only with the \(E_{g}\) components of the stress.
METHODS FOR DETERMINING THE LABELING OF STATES

The states of a system are labeled with their group theoretical designations. In order to determine what the label for a state should be, one has to determine the decomposition of the representation due to the application of a field. Then one can easily label the singly degenerate states. The difficulty comes in labeling the states coming from a doubly or triply degenerate state.

There are two techniques which will help in determining the labeling of the states. The first is the transitions which are possible. If one determines which transitions are allowed between a singly degenerate state and another state coming from a multiply degenerate state, and the calculation shows a transition to one of these states, that state can be labeled. By looking at many of the possible transitions one can build up the labeling system. As an example, consider Figure 6. In all three of these cases, the only allowed transitions are between states belonging to the same representation. For an electric field along [110], the 1A and 3B states were easily labeled, because they come from singly degenerate levels. It is more difficult to label the states coming from the triply degenerate states. The calculation showed a transition between level 1 and one of the states in level 3. Therefore, one of them must be an A representation. In the same way, there is a transition between level 6 and level 4. Therefore, one of these must be a B representation. By a similar checking of the other transitions, the labeling of all of the states can be obtained.

Another method for determining the labeling of a state is to observe the repulsion of the levels. Consider a perturbation
calculation at a given value of the field, with the field being the perturbation to the system. Consider the interaction of only two of the states. The Schrödinger equation for the system of two levels is:

\[
\begin{pmatrix}
(H_{11} - E) & H_{12} \\
H_{21} & (H_{22} - E)
\end{pmatrix}
\begin{pmatrix}
a \\ b
\end{pmatrix} = 0
\]

where \( H_{12} \) is the interaction between the states due to the perturbation.

Making the approximation that the perturbation is small compared to the difference in energy between the two states, the energies for the two states become

\[
E_1 = H_{11} + \frac{|H_{12}|^2}{H_{11} - H_{22}} \quad E_2 = H_{22} + \frac{|H_{12}|^2}{H_{22} - H_{11}}
\]

The difference in energy between the levels is given by

\[
\Delta E = \Delta E_0 + \frac{|H_{12}|^2}{2\Delta E_0}
\]

where \( \Delta E_0 \) is the energy difference in the absence of the perturbation.

Since we are assuming that \( \Delta E_0 \) is positive, if \( \langle 1|H/2\rangle \) is not zero, there will be an increase in the splitting of the states due to the application of more field. Therefore, the states are said to repel each other.

Getting back to paraelectric systems, the only way for \( \langle 1|H/2\rangle \) to be non-zero is if states 1 and 2 are both from the same representation. Even if \( |1\rangle \) and \( |2\rangle \) are from the same representation, the matrix element for the interaction may be zero. However, it is found that this situation very seldom occurs. In general, one can say that states of different representations will not interact with each other. There are many examples of this type of behavior in the figures of this chapter. This technique gives one another method for determining the symmetry of the states and also for checking the results of calculations for consistency.
CHAPTER IV

THE PARAELECTRIC RESONANCE SPECTROMETER

The equipment used to study paraelectric resonance is very similar to a paramagnetic resonance spectrometer. The only real difference is that with a paraelectric resonance spectrometer, an electric field is applied to the sample instead of a magnetic field. The spectrometer used to make the measurements for this paper can be operated in one of two modes. One is straight back reflection and the other is homodyne detection. All of the spectra are taken at about 36 GHz. The spectrometer is capable of producing good spectra on a sample of KCl doped with 100 ppm Li⁺ at incident powers of as low as 0.01 mw. A schematic drawing of the spectrometer is shown in Figure 21.

SAMPLE CAVITY

The sample for which one wishes to determine the spectrum is placed in the center of one of the side walls of the sample cavity. The sample cavity is a rectangular resonant cavity made from brass. The constant electric field is applied across the sample by means of a thin copper electrode which is about 1/8" square. The sample is cut so that two opposite sides are parallel, and the direction along which the field is to be applied is perpendicular to these sides. One of the sides is placed against the wall of the cavity, and the electrode is placed on the other side. The sample is held in place by vacuum grease. This arrangement effectively makes a parallel plate capacitor with the sample in the space between the plates. The wall of the cavity is grounded, and the electrode is set at the desired potential with respect to ground. The actual field applied to the sample is the voltage across the sample
FIGURE 21: PARAELECTRIC RESONANCE SPECTROMETER AND DETECTION SYSTEM
divided by the thickness of the sample. The voltage is applied to the
electrode by means of a small diameter copper wire which is attached
along the edge of the electrode. This wire leads through a teflon feed-
through in the wall of the cavity to the high voltage connection on the
outside of the cavity.

The sample cavity is designed so the oscillating electric field
is perpendicular to the side wall on which the sample is placed. The
microwave electric field is made perpendicular to the side wall so
that the component of the field parallel to the electrode is zero.
If the parallel component were not zero, there would be losses in
the cavity due to currents set up in the electrode. It is also
possible that the microwave field might be distorted in the region of
the electrode. Another restriction on the microwave field is that the
oscillating field must be strongest at the position of the sample in
the center of a side wall.

These restrictions mean that for a $TE_{1mn}$ mode, $l$ and $n$ must be odd,
and $m$ must be zero. With $m$ equal to zero, the oscillating field will be
perpendicular to one pair of parallel side walls. The fact that $l$ and $n$
are odd insures that there will be a maximum in the microwave field at
the center of the side wall.

In light of the foregoing restrictions, and after some experimenta-
tion with different modes, it was determined that the $TE_{303}$ mode was the
best for use in a paraelectric resonance sample cavity. The $TE_{101}$ and
$TE_{103}$ modes are inadequate because the cavity is too small. When the
cavity is loaded with the sample and electrode, the $Q$ of the cavity is
practically destroyed. The $TE_{303}$ cavity is larger, and the $Q$ is not hurt
so much by the introduction of the sample and electrode. There is one
problem which is encountered with a cavity of this size. This is the fact that there are many different modes which can be set up in the same cavity. This makes it difficult to determine which cavity resonance is the proper one. This problem was remedied by designing a cavity so that there was at least 1 GHz between the desired TE$_{303}$ mode and any other mode. This was done by calculating the resonant frequencies of the modes for different proportions of the cavity. Figure 22 shows the mode structure and placement of the sample in the cavity.

**HIGH VOLTAGE SYSTEM**

The constant voltage which is applied across the sample is supplied by a high voltage power supply which is capable of producing voltages from 0 to 20 kilovolts. For a typical sample, this corresponds to electric fields of from 0 to 200 kilovolts per centimeter.

A voltage divider is placed across the output of the power supply. The output of this voltage divider is proportional to the voltage produced by the power supply. The output of this voltage divider is displayed on a voltmeter and is put into the x-axis input of the X-Y recorder. When the system is set up in this way, a one volt output from the voltage divider corresponds to one kilovolt output from the power supply. Since, under ordinary operating conditions, no current is drawn by the circuit beyond this point, this voltage is the actual voltage across the sample. The inaccuracy in this voltage measurement is less than 1%.

One side of the power supply output is grounded, and the other side passes from the voltage divider through a series of ten 10 megohm resistors which serve as protection for the rest of the circuit. Under
$TE_{303}$ MODE STRUCTURE

- ELECTRIC FIELD LINES POINTING UP
- ELECTRIC FIELD LINES POINTING DOWN
- NULL LINES IN MICROWAVE FIELD

FIGURE 22: MODE STRUCTURE AND SAMPLE PLACEMENT IN THE PARAELECTRIC RESONANCE SAMPLE CAVITY
ordinary operating conditions, there is no current through these resistors, and consequently, the voltage drop across them is zero. If, however, there is an electrical breakdown somewhere in the system, a current will flow through the resistors, and the voltage will be dissipated in them. This limits the current in the circuit thus helping to protect the circuit. After going through the limiting resistors, the modulation voltage is applied and then the high voltage goes through a high voltage vacuum feed-through to the sample cavity.

The voltage across the sample is continuously variable by means of a variable speed electric motor which drives a ten-turn potentiometer. This potentiometer substitutes for a similar one-turn potentiometer used to vary the voltage in the high voltage power supply. The rate at which the voltage is changed can be varied continuously by adjusting the speed of the electric motor which drives the potentiometer.

**MICROWAVE SYSTEM**

The oscillating electric field in the cavity is produced by a reflex klystron. With the two klystrons available, any frequency in the range from 28 to 38 GHz can be obtained. The maximum power output at all frequencies is about 200 mw. The power reaching the cavity has a maximum of about 80 to 90 mw.

Microwave power from the klystron goes through an isolator (which acts as a protection against reflected microwaves) to a 20 dB cross-guide directional coupler. The power coming from the side arm goes through a variable attenuator to the H-arm of a magic tee. The attenuator is used to protect the detector diode in this section from too much power. There is a termination on one of the side arms of the magic tee, and a reaction type cavity wavemeter on the other
side arm. The microwaves reflected from the cavity wavemeter are detected by a tunable detector on the E-arm of the magic tee. This portion of the microwave circuit is used to determine the frequency of the microwave power coming from the klystron. With the addition of another tunable detector in place of the termination, this section can be set up as a Pound-type frequency stabilizer, using the cavity wavemeter as a discriminator.

Power in the main waveguide section goes from the 20 dB coupler to a 10 dB multi-hole directional coupler. The power which is taken off at this stage is used as a reference signal for the balanced receiver. The power goes through a simple on-off switch (used in tuning the receiver) to a rotary vane type phase shifter. This phase shifter is used to vary the phase of the reference wave with respect to the signal in the balanced receiver. A rotary vane type phase shifter is used instead of a flap type phase shifter because it offers less variation in attenuation as a function of phase shift and is more accurate. After the phase shifter, the power goes into the reference arm of the balanced receiver. There is also a variable attenuator in this arm to adjust the power reaching the receiver.

After the 10 dB coupler, the power in the main waveguide passes through a direct reading precision variable attenuator which can introduce attenuation from 0 to 50 dB. This attenuator is used to vary the amount of power incident on the sample cavity. From here the power goes through a flap type phase shifter, which is used to help eliminate problems caused by standing waves set up in the waveguide. The power then passes through a 20 dB cross-guide directional coupler. The power which is coupled off goes into a thermistor
detector. The output of the thermistor goes to a power meter which monitors the power reaching the cavity. The power meter reading is 0.01 times the power incident on the sample cavity.

Power in the main waveguide goes from the 20 dB coupler to the low temperature head and a sample cavity. Just before the sample cavity is a tuning device used to couple the proper amount of power into the cavity. This tuner consists of a section of waveguide which is tapered to a width which is less than that required to propagate microwaves at the desired frequency. In this section there is a piece of teflon which allows the microwaves to propagate through the section, because its dielectric constant is larger than that for the waveguide without the teflon. When the teflon is all of the way in, the microwaves will propagate through the section to the iris of the cavity. As the teflon is pulled back from the iris, there will be a section of waveguide where the microwaves are attenuated. This means that less power will reach the cavity. By adjusting the distance from the teflon piece to the iris, the situation can be attained where all of the power reaching the cavity is absorbed, and none is reflected. This is the critical coupling of the cavity. The teflon piece is moved in and out by a lead screw arrangement along the outside of the waveguide.

The power reflected back from the sample cavity is channeled off from the main waveguide by a 3 dB multi-hole directional coupler to a double-pole-double-throw microwave switch. In one position, the power reflected from the cavity goes to the balanced receiver. This is the position used in the phase sensitive detection mode. In the other position, the power reflected from the cavity goes to a tunable
detector. This detector is used in the straight back reflection mode. It is also used to adjust the klystron frequency to the resonant frequency of the sample cavity. When the switch is in this position, the power reflected into the signal arm from the reference arm of the balanced receiver can be monitored by a thermistor. This is used in tuning the receiver so that there is minimum power reflected from the detectors in the balanced receiver.

The balanced receiver consists of a magic tee with a tunable detector on each of the side arms. The signal from the cavity is introduced into the H-arm, and the reference into the E-arm.

**INFORMATION OBTAINABLE WITH A PARAELECTRIC RESONANCE SPECTROMETER**

In a paraelectric resonance experiment, the electric susceptibility, \( \chi_e \), is determined as a function of the electric field in the sample. In order to show that this information can actually be obtained from the spectrometer, let us consider the lumped circuit parameter equivalent of the microwave circuit. The equivalent circuit for the sample cavity would be a series RLC circuit whose impedance is given by

\[
Z = R + i(\omega L - 1/\omega C)
\]

The inductance, \( L \), is not a function of the electric field applied to the system, but the capacitance, \( C \), is affected by changes in the electric susceptibility of the sample due to changes in the electric field. Let us assume that the capacitor in the circuit is a simple parallel plate capacitor with part of the volume between the plates filled with the sample under study. The filling factor, \( \kappa \), is the ratio of the field density integrated over the volume of the sample to the field density integrated over the volume of the cavity. The
capacitance is given by the formula
\[ C = \frac{\varepsilon A}{\Delta} (A - \kappa A) + \frac{\varepsilon A}{\Delta} (1 + 4\pi \chi_e) \kappa A \]
or
\[ C = \frac{\varepsilon A}{\Delta} + \left( \frac{\varepsilon A}{\Delta} \right) 4\pi \chi_e \kappa_e \]

Let the non-resonant capacitance be \( C_0 \), so that
\[ C_0 = \frac{\varepsilon A}{\Delta} \]

This implies that the actual capacitance is
\[ C = C_0 (1 + 4\pi \chi_e \kappa) \]

The impedance of the cavity is then
\[ Z = R + \omega L - \frac{i}{\omega C_0} (1 + 4\pi \chi_e \kappa)^{-1} \]

If we make the assumption that \( 4\pi \chi_e \kappa \ll 1 \), then the impedance becomes
\[ Z = \left[ R + \kappa'' \left( \frac{4\pi \chi_e}{\omega C_0} \right) \right] + i \left[ \omega L - \frac{1}{\omega C_0} \left( 1 - 4\pi \chi_e \kappa' \right) \right] \]

where we have substituted \( \chi' + \chi'' \) for \( \chi_e \). The assumption that \( 4\pi \chi_e \kappa \ll 1 \) is not necessarily valid in all cases. \( \chi_e \) could be fairly large, but the filling factor is usually much less than 1, and so it is usually small enough to compensate for the other factors. If one does not make the assumption that \( 4\pi \chi_e \kappa \ll 1 \), there is a mixing of \( \chi' \) and \( \chi'' \) in the real and imaginary parts of the impedance. The only difference one gets is a denominator for the real and imaginary parts which contains both \( \chi' \) and \( \chi'' \). Therefore, if \( 4\pi \chi_e \kappa \) is not much less than 1, one can not expect to observe either \( \chi' \) or \( \chi'' \) without some mixing of the two.

The real part of the impedance corresponds to an attenuation in the microwave cavity. Therefore, the change in the power reflected from the cavity is a measure of \( \chi'' \), which is called the absorption.

The imaginary part of the impedance is responsible for the resonant frequency of the cavity.
\[ \omega^2 = \frac{1}{LC_0} (1 - 4\pi \chi_e \kappa') \]
and since \( \omega_0^2 = \frac{1}{LC_0} \)
\[ \omega = \omega_0 (1 - 2\pi \kappa' \kappa) \]

The change in the resonant frequency is a measure of \( \kappa' \). Since we are making the assumption that \( 2\pi \kappa \kappa' \ll 1 \), we have that
\[ \omega = \omega_0 (1 - 2\pi \kappa' \kappa') \]

A signal resulting from a change in resonant frequency of the sample cavity is called dispersion.

With the paraelectric resonance spectrometer in the phase sensitive detection mode, we can study either the real or the imaginary part of the power reflected from the sample cavity. This is accomplished by adjusting the phase of the reference wave at the balanced receiver. If the spectrometer is tuned for absorption, shifting the phase by 90° will give dispersion. In the straight back reflection mode, only the absorption part of the reflected power can be studied.

**PHASE SENSITIVE DETECTION SYSTEM**

The balanced receiver is used in the phase sensitive detection mode. Each side arm of the balanced receiver contains a 1N53B microwave detector diode. This detector produces a voltage across itself which is proportional to the microwave electric field incident on it. In one arm, the magnitude of the field is proportional to the sum of the signal and reference. In the other arm, the field is proportional to the difference between the signal and the reference. Therefore, the difference between the voltages across the two detector crystals is proportional to the signal amplitude. Whether the signal is absorption, dispersion, or a combination of the two, is dependent on the phase of the reference wave relative to the signal.
The constant electric field across the sample is modulated at 100 kHz. This modulation voltage comes from the reference channel of the lock-in amplifier. It is amplified and put through two well-insulated transformers, which isolate the modulation from ground. It is then fed into the high voltage system. The modulation used is usually about 30 volts RMS.

When the constant field is near resonance, the modulation will vary the voltage about its constant value. This causes a modulated component in the electric susceptibility. It, in turn, causes the microwaves reflected from the cavity to be modulated. The voltage from the balanced receiver will have a modulated component whose amplitude is proportional to the derivative of the signal. This modulated voltage is sent through a pre-amplifier which amplifies the AC component of the voltage. The pre-amplifier has a low frequency roll off of 3 kHz and a high frequency roll off of 300 kHz. This amplifier eliminates the DC component of the voltage and any noise which is outside the range of the roll offs. The signal is then put into the lock-in amplifier where it goes through a narrow band filter centered on the modulation frequency, and is then compared with the reference used to modulate the constant electric field. The signal is amplified and converted into a DC voltage proportional to the amplitude of the signal by means of phase sensitive detection.

The DC voltage from the lock-in amplifier is then fed into the y-axis input of the X-Y recorder. Therefore, the X-Y recorder produces a graph of the derivative of the signal from the cavity as a function of the constant field applied to the sample.
In order to obtain a spectrum for a sample using the phase sensitive detection mode, the klystron is placed on saw-tooth modulation, so that the complete klystron mode can be observed. The power reflected from the sample cavity is channeled into the tunable detector by the double-pole-double-throw microwave switch. The output of this detector is displayed on the oscilloscope. When the cavity dip is found, the modulation is switched to a 100 kHz sine wave with amplitude of about 1.5 volts RMS. This is used to make the dip symmetric, so that the center frequency is the resonant frequency of the sample cavity. Then the switch is turned to the position which will cause the microwaves to go into the balanced receiver. Then the output of the pre-amplifier is displayed on the oscilloscope. The modulation of the microwave power about the center frequency of the cavity has the same effect as modulation of the resonant frequency of the cavity. This corresponds to a dispersion signal, so if this signal is minimized, by adjusting the phase, the reference is in the proper phase for detecting absorption. After the spectrometer has been tuned, the modulating voltage is removed from the klystron, and a spectrum is taken. In order to obtain the dispersion signal, the phase is changed by 90° from the phase for absorption.

**STRAIGHT BACK REFLECTION DETECTION SYSTEM**

In the straight back reflection mode, the tunable detector used to find the cavity dip in the phase sensitive detection mode is used for the signal detection. The output of the detector goes directly to the y-axis input of the X-Y recorder and the klystron stabilizer. The klystron stabilizer is used in the AC lock mode. A 70 kHz
modulation is put on the reflector voltage, and the sample cavity is used as a discriminator. By using the klystron stabilizer, the klystron frequency is kept the same as the cavity resonant frequency. This eliminates any dispersion signals, since they correspond to changes in the frequency of the sample cavity from the frequency of the klystron. Pure absorption is obtained as a function of applied field. In order to get sufficient sensitivity, the X-Y recorder must be in the most sensitive position (1 mv/cm), and the power must be fairly high (about 5 or 10 mw incident on the cavity). In the straight back reflection mode, the signal is proportional to the square of the microwave electric field, or the microwave power.

**LOW TEMPERATURE SYSTEM**

Since paraelectric resonance spectra must be taken at low temperature, the sample cavity must be immersed in liquid helium. In this way, only the lowest state of the harmonic oscillator will be populated. The helium is contained in a glass dewar. At room temperature, there is approximately one third of an atmosphere of gaseous nitrogen in the jacket of the helium dewar. The helium dewar is placed inside another glass dewar. It has a vacuum in its jacket. Liquid nitrogen is placed in the outer dewar. The gaseous nitrogen in the inner dewar jacket allows heat to be transferred through the jacket from the inner dewar and low temperature head. When the inner dewar has cooled to the temperature of liquid nitrogen, liquid helium is placed in the inner dewar. This causes the gaseous nitrogen in the inner dewar jacket to condense, and makes a hard vacuum in the jacket of the dewar. The helium is then pumped on until it reaches the lowest pressure possible. This pressure is
usually of the order of 1.5 to 2 torr. This corresponds to a temperature of about 1.3\(^\circ\)K. The pressure is measured by a diaphragm-type vacuum gauge located about two feet from the cavities. The helium dewar is usually filled with about 5 liters of helium at the beginning of a run. It takes about 7 liters to get the dewar filled with this amount of helium. About half of the helium is used in getting the temperature below the lambda-point of helium. The helium left when the lowest temperature is obtained is enough for about 6 hrs of running.

**LOW TEMPERATURE HEAD**

Since the amount of data taken for one sample is not very great, a low temperature head was designed so that four samples could be run without taking the low temperature head out of the helium. The low temperature head consists of four separate waveguides with a coupler and cavity on the end of each. Each waveguide has a small section of coin silver waveguide which goes through the base plate. Then there is a long section of thin wall stainless steel waveguide onto which the coupler is attached. The thin wall stainless is used because it has a lower thermal conductivity than the coin silver. It therefore helps to conserve the liquid helium. The coupler is operated by a stainless steel rod which goes through the base plate to the lead screw of the coupler. Along the sections of stainless steel waveguide are four heat shields which help to cut down the radiational heating of the material in the liquid helium. The low temperature head is raised and lowered in and out of the dewar by means of a winch-operated elevator.

**DISCUSSION OF SPECTRA OBTAINED WITH THE PARAELECTRIC RESONANCE SPECTROMETER**

Two types of spectra were taken for each paraelectric system. One type of data is straight back reflection with the klystron locked to the
frequency of the sample cavity. It was necessary to lock the klystron frequency to the frequency of the cavity since there was a strong dispersion signal from the samples. This shifted the cavity frequency significantly as the electric field was swept through the resonance value. The result of this frequency change was a change in the absorption of the cavity due to the dispersion signal. By locking to the cavity, the dispersion signal was eliminated, and the signal was pure absorption. To see the effect of locking to the cavity, Figure 23 shows the spectrum for both applied and microwave fields parallel to [100] in the KCl:Li$^+$ system. One trace is taken with the frequency locked to the cavity resonant frequency, and the other trace is taken without locking the klystron. The spectrum taken with the klystron unlocked is less well resolved and the peak is shifted to a lower field. This is due to the component of the absorption caused by the dispersion.

The second type of spectra were taken with the spectrometer in the phase sensitive detection mode. In this mode, one gets both absorption and dispersion spectra. Since the spectrum is the derivative of the actual signal, any structure which is present will become more prominent using this mode. The main purpose of the phase sensitive detection data is to gain information about the structure of the spectrum. All of the spectra presented in this section of the paper were taken at a frequency of about 36 GHz.

The most important information gained from paraelectric resonance spectra is the number and positions of the lines present. In order to determine the resonant field for a transition, it is necessary to make two measurements: (1) the voltage across the sample at the peak of the resonance, and (2) the distance between the electrode and the side of
$\chi_e$

$\text{KCl:Li}^+(100 \text{ PPM})$
$\text{POWER} = 5 \text{ MW}$
$\text{FREQ.} = 36.43 \text{ GHz}$
$\text{TEMP.} = 1.3^\circ \text{K}$
$\text{E}\parallel\text{E}_{1}[100]$

**FIGURE 23:** STRAIGHT DETECTION SPECTRUM FOR $\text{KC}1: \text{Li}^+$ WITH $\text{E}\parallel\text{E}_{1}[100]$
the cavity. As stated in the section on the high voltage system, the voltage scale on the spectra is accurate to within 1%. If the resonance line is very broad, one may have difficulty determining exactly where the peak of the resonance occurs. One should be able to determine the voltage at the peak to within 5% error.

If the electrode is securely attached to the sample and the sample securely attached to the side of the cavity, then the distance between the electrode and the wall is just the thickness of the sample. However, if the electrode is tilted slightly, the electric field will not be homogeneous, and the electric field value will appear to be larger than it really is. There will also be a broadening of the line due to the tilting of the electrode. The values for resonant fields presented in the next chapters are taken from spectra on which the width does not appear excessively large. Therefore, the values quoted should be within 5% of their actual value unless otherwise noted.
CHAPTER V

PARAELECTRIC RESONANCE SPECTRA FOR KCl:Li$^+$

The KCl samples for which spectra are presented in this chapter were taken from a boule of KCl specially grown by the Harshaw Chemical Company. The boule contained approximately 100 ppm Li$^+$. Samples from another boule which contained approximately 10 ppm Li$^+$ were also run. The results for these samples were not much different from the results for the 100 ppm samples. The only difference was in the intensity of the spectra. The 100 ppm samples gave more intense spectra than the 10 ppm samples.

The samples used for obtaining [100] spectra were cleaved to the proper size. The samples used for other orientations were cut to the proper size with a diamond saw (using the [100] cleavage planes of the crystal to determine the orientation). The usual size of a sample is about 0.08" square by 0.045" thick. Unless otherwise stated, the samples were given no further treatment before they were run.

STRAIGHT DETECTION SPECTRA

The straight detection spectra with the electric field parallel to [100], [110], and [111] are presented in Figures 23, 24, and 25 respectively. In each of the spectra, there appears to be only one intense line present. There is a hint of extra structure present along the [100] and [111] directions, but it is very small in comparison to the intense line. The intense line occurs along [100] at an electric field of 8.98 ±0.40 KV/cm. The full width at half power points is 3.05 KV/cm. With the electric field parallel to [110], the line occurs at 13.10 ±0.70 KV/cm with a half width of 7.16 KV/cm. The intense line
$KCl:Li^+(100PPM)$
POWER = 5 MW
FREQ. = 36.63 GHz
TEMP. = 1.3°K
$\varepsilon_l \parallel [110]$
Figure 25: Straight detection spectrum for KCl:Li$^+$ with E//E$_1$//[111]
for electric field along [111] occurs at $15.77 \pm 0.80$ KV/cm. The width is $8.89$ KV/cm.

More is known about the paraelectric properties of Li$^+$ in KCl than any other paraelectric system. One of the important facts about Li$^+$ is that it is off-center along [111]-type directions. This was shown by the ultrasonic experiments done by Byer and Sack$^8,9$. They studied the effect of Li$^+$ on the velocity of sound in KCl. They found that the velocity of phonons possessing $E_g$ symmetry was not affected by the presence of the Li$^+$ impurity. They did find a dependence on the presence of the Li$^+$ for the velocity of phonons having $T_{2g}$ symmetry. Since, as we have seen, an eight ⟨111⟩ dipole system interacts only with stresses having $T_{2g}$ symmetry (shear stresses), this experiment proves that Li$^+$ is off-center along [111]-type directions. As a further proof, they observed the effect of applied stress on the change in velocity due to the Li$^+$. They found there was no effect from stresses with $E_g$ symmetry, but there was an effect from stresses with $T_{2g}$ symmetry.

Many attempts have been made to determine the form of the zero field splitting of the tunneling multiplet. Lakatos and Sack$^{10}$ observed the temperature dependence of the real part of the dielectric constant at frequencies of 22, 24, and 26 GHz. They found behavior at 22 GHz indicative of a frequency less than the splitting. At 26 GHz the behavior was that of a frequency above the splitting. At 24 GHz, the behavior is closer to that of a frequency equal to the zero field splitting. The results are not completely satisfactory. At the resonant frequency, the real part of the dielectric constant should be independent of the temperature, but experimentally it is not.
However, they come up with a value for the zero field splitting of 0.81 cm\(^{-1}\) (24.3 GHz).

Peressini, Harrison, and Pohl\(^{11}\) have studied the thermal conductivity of KCl doped with Li\(^{+}\). They found a decrease in the thermal conductivity at low temperature as a function of the Li\(^{+}\) concentration. This decrease could be explained by a resonant absorption of phonons at a frequency \(\omega\). For Li\(^{+}\) they determined the splitting which causes the localized mode to be 1.2 cm\(^{-1}\) (36 GHz). Since phonon induced transitions are possible only between states of the same symmetry, this means that the resonant mode is at twice the zero field splitting. The zero field splitting as determined by this experiment is 0.6 cm\(^{-1}\) (18 GHz). Peressini et. al. have a different interpretation. They indicate that the resonant splitting is an averaging between the transitions for the \(A_{1g}-T_{lu}\) and \(A_{2g}-T_{lu}\) splittings. This is done in spite of the fact that the \(A_{1g}-T_{lu}\) transition is not allowed, but is given equal weight in this explanation. They therefore come up with 0.80 cm\(^{-1}\) (24 GHz) as the zero field splitting. They also examined Li\(^{6}\) and found its zero field splitting to be 45% larger than for Li\(^{7}\) (0.9 cm\(^{-1}\) or 27 GHz).

The technique of thermal conductivity does not have very good resolution, since it depends on the whole phonon spectrum to study phonon absorption in a small frequency range. An improvement of the technique was used by Walton\(^{12}\). He used a device which has a much greater resolution. In this technique, phonons in a certain band are removed from the spectrum by the phonon spin interaction of R centers created in KCl. The band removed is around the Larmor frequency of the R center. This band can be changed by an applied
magnetic field. By measuring the change in thermal conductivity as a function of the magnetic field applied, the phonon spectrum can be determined. From this determination, it was shown that resonant scattering occurred at about 1.3 cm\(^{-1}\) (39 GHz). This indicates a zero field splitting of 0.65 cm\(^{-1}\) (19.5 GHz). A similar experiment\(^{13}\) carried out for Li\(^6\) instead of Li\(^7\) indicates a zero field splitting for Li\(^6\) of 0.87 cm\(^{-1}\) (26 GHz) or about 34% greater than for Li\(^7\).

As can be seen from this survey of attempts to measure the zero field splitting for the tunneling multiplet, the results do not appear to be very consistent. One gets values for the zero field splitting of from 0.6 cm\(^{-1}\) (18 GHz) to 0.8 cm\(^{-1}\) (24 GHz). Let us see whether our paraelectric resonance data is consistent with a tunneling splitting in the range from 0.6 cm\(^{-1}\) to 0.8 cm\(^{-1}\). Table 7 shows the calculated spectra for zero field splittings of 18, 20, 22, and 24 GHz, and the deviation of the experimental results from these calculated values. The calculated resonant field values were obtained by fitting the calculated curve to the experimental values. From this fit, one can determine a value for the electric dipole moment. These values are given in the table. (All values for the dipole moment are uncorrected for the difference between the applied electric field and the actual electric field at the site of the impurity. The values are in terms of Debyes. One Debye (D) is \(10^{-18}\) e.s.u.\(^{14}\) or 0.208 e\(^\circ\).) It can be seen that it is impossible to get an accurate value for both the zero field splitting and the electric dipole moment from the measurements taken. If we knew the value of the electric dipole moment, we could determine which value for the zero field splitting fit the results best.
TABLE 7: COMPARISON OF EXPERIMENTAL RESONANT FIELDS WITH THE CALCULATED RESONANT FIELDS FOR KCl:Li⁺

<table>
<thead>
<tr>
<th>DIRECTION</th>
<th>EXPERIMENTAL RESONANT FIELD (KV/cm)</th>
<th>$2\Delta = 18$ GHz FIELD (KV/cm)</th>
<th>ERROR (%)</th>
<th>$2\Delta = 20$ GHz FIELD (KV/cm)</th>
<th>ERROR (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[100]</td>
<td>8.89</td>
<td>9.12</td>
<td>-2.5</td>
<td>9.12</td>
<td>-2.5</td>
</tr>
<tr>
<td>[110]</td>
<td>13.10</td>
<td>12.89</td>
<td>+1.6</td>
<td>12.92</td>
<td>+1.4</td>
</tr>
<tr>
<td>[111]</td>
<td>15.77</td>
<td>15.81</td>
<td>-0.3</td>
<td>15.80</td>
<td>-0.2</td>
</tr>
</tbody>
</table>

ELECTRIC DIPOLE MOMENT (D)  
|              |                                      | 5.86                             | 5.62      |

<table>
<thead>
<tr>
<th>DIRECTION</th>
<th>$2\Delta = 22$ GHz FIELD (KV/cm)</th>
<th>ERROR (%)</th>
<th>$2\Delta = 24$ GHz FIELD (KV/cm)</th>
<th>ERROR (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[100]</td>
<td>9.11</td>
<td>-2.5</td>
<td>9.14</td>
<td>-2.7</td>
</tr>
<tr>
<td>[110]</td>
<td>12.92</td>
<td>+1.4</td>
<td>12.90</td>
<td>+1.6</td>
</tr>
<tr>
<td>[111]</td>
<td>15.80</td>
<td>-0.2</td>
<td>15.78</td>
<td>-0.1</td>
</tr>
</tbody>
</table>

ELECTRIC DIPOLE MOMENT (D)  
|              |                                      | 5.28                             | 5.04      |
In order to determine the electric dipole moment, it is necessary to perform the experiments at frequencies which are much greater than the zero field splitting. This was done by Herendeen and Silsbee, who performed paraelectric resonance experiments at 63 GHz. They get a value for the electric dipole moment of $5.6 \pm 0.2$ D using data around 63 GHz. They also determined that the dipole moment was the same for Li$^6$ as for Li$^7$.

Using far infrared spectroscopy with applied fields, Kirby, Hughes, and Sievers were able to get what should be a very accurate determination of the dipole moment. Using frequencies in the range from 2 cm$^{-1}$ (60 GHz) to 12 cm$^{-1}$ (360 GHz), they determined the dipole moment to be 5.52 D for Li$^7$ and 5.47 D for Li$^6$.

From these two experiments, it appears that the dipole moment for Li$^+$ in KCl is about 5.5 D. We can use this value to get an estimate of the zero field splitting for the system. Looking at Table 7, we see that one obtains a dipole moment of 5.6 D for a zero field splitting of 20 GHz. Therefore, 0.66 cm$^{-1}$ (20 GHz) would be a good estimate of the zero field splitting for Li$^+$ in KCl.

**PHASE SENSITIVE DETECTION SPECTRA**

The phase sensitive detection spectra for electric field parallel to [100], [110], and [111] are presented in Figures 26, 27, and 28. For electric field along [100], there are two structures which do not show up very prominently in the straight detection spectra. The first is a hesitation on the low field side of the intense line. This occurs very close to zero field. The second structure is the high field line which shows up in the straight detection spectra. It occurs at about twice the field for the intense line.
FIGURE 26: PHASE SENSITIVE DETECTION SPECTRUM FOR KCl:Li\(^+\) WITH E//E\(_1//[100]\)

KCl:Li\(^+\) (100 PPM)
POWER = 1 MW
FREQ. = 36.43 GHz
TEMP. = 1.3°K
E//E\(_1//[100]\)
FIGURE 27: PHASE SENSITIVE DETECTION SPECTRUM FOR KCl:Li$^+$
WITH E∥E$_{1}$∥[110]
FIGURE 28: PHASE SENSITIVE DETECTION SPECTRUM FOR KCl:Li\(^+\)
WITH E//E\(_1\) /// [111]
No extra structure occurs for electric field along [110], but there is a rather prominent extra line in the [111] spectra. This line occurs at about 51% of the field for the intense line.

A possible explanation for the structure at lower fields along [100] and [111] is that this is a resonance due to the less prevalent isotope of Lithium, Li$^6$. Since no attempt was made to insure isotopic purity in the samples, there should be 92.6% Li$^7$ and 7.4% Li$^6$ in the samples. Since Li$^6$ differs from Li$^7$ only in the mass, Li$^6$ should have a larger tunneling parameter than Li$^7$, but the same dipole moment. As indicated earlier, Peressini, Harrison, and Pohl$^{11}$ found the tunneling parameter for Li$^6$ to be about 45% larger than for Li$^7$. Hetzler and Walton$^{13}$ found the zero field splitting for Li$^6$ to be about 34% larger than for Li$^7$. Herendeen and Silsbee$^{15}$ also attempted to determine the zero field splitting for Li$^6$. They arrived at a value 45% greater than for Li$^7$.

Using a value for $\Delta$ for Li$^6$ which is 1.45 times the $\Delta$ for Li$^7$, one can determine that the line for Li$^6$ should occur at 0.71 times the field for Li$^7$ in the [111] spectrum. The intensity of the Li$^6$ transition should be 17% of the intensity for the Li$^7$ transition. The position of the Li$^6$ line appears to be at too low a field to be explained in this manner. However, one may have some trouble in determining the position of a line when it is close to an intense broad line such as that for Li$^7$. In our determination, the position of the Li$^6$ line was obtained by taking the difference between the maximum and minimum for the line on the absorption display, and calling this the line position. The position of the intense line was determined by the peak of the dispersion display for that line. Figure 29 shows the effect of an intense line on the position of a
FIGURE 29: EFFECT OF A BROAD INTENSE LINE ON THE APPARENT POSITION OF A SMALL LINE NEAR IT
(DOTTED LINE - ABSORPTION, SOLID LINE - DERIVATIVE)
weak line close to it. The weak line is located at 2.0 and the intense line at 4.0. The intensity of the weak line is 11% of the intensity of the strong line. A gaussian distribution with the same half width is applied to each line. In Figure 29(a) the width is 30% of the spacing between the lines, and the lines appear at their actual position. In Figure 29(b) the width is 60% of the spacing between the lines. In the derivative display (using the usual way for determining the position of a line), the difference between the two lines is increased by about 3%. In Figure 29(c) the width is 90% of the spacing, and the low field line is barely resolved. It appears to have moved out about 25% of the spacing. In Figure 29(d) the width is 120% of the spacing, and the weak line does not show up at all.

From Figure 29(c), it can be seen that the actual position of the weak line is at the minimum for the line rather than between the minimum and the maximum. Going back to the spectra for [111], we have the second line appearing at 58% of the position for the intense line rather than 51%. This indicates that this second line is probably due to Li$^6$.

However, there are some discrepancies. The width of the intense line is 56% of the field position. This is a situation similar to that illustrated in Figure 29(d). In this case, the weak line does not even show up. There are ways of getting around this problem. We have used the same width for both lines. However, if the width were less for the low field line, it would appear to be more intense. As will be discussed later in this paper, random internal strains appear to be responsible for broadening the lines. If Li$^6$ had a different value for its response to stresses (i.e. a different elastic dipole moment), it would have a different width for its line. This
does not appear to be a plausible explanation, since the only difference between the two isotopes is the mass of the nucleus, and this should not affect its interaction with the other ions of the lattice. A more plausible explanation may be that the width of a line is dependent on its frequency as compared to the zero field splitting.

The other difficulty with the explanation is that the line still is at too low a field. It is seen at 58% of the position for the Li$^7$ line instead of 71%. This is not too bad a discrepancy, since the relative position is very dependent on the zero field splitting. If the zero field splitting is taken to be 22 GHz instead of 20 GHz for Li$^7$, and keeping $\delta = 1.45 \, \gamma$, the line will appear at 60% of the position for the intense line instead of 71%. So, even with these reservations, it appears that the second line is due to Li$^6$.

The Li$^6$ line should appear for all orientations. The low field structure in the [100] spectra may be due to the isotope, but it does not appear in the [110] spectra. This would not be too out of the ordinary, since observing the line is very dependent on the width of the intense line, and the [110] line is rather broad. Since a line has been seen by Höcherl and Wolf$^{17}$ in their paraelectric resonance spectra taken at 35 GHz, it appears that conditions must be just right to observe the line in the [110] spectra. Their Li$^6$ line is not very prominent, and amounts to only a change in slope of the derivative display on the low field side of the intense line.

The only other structure which needs to be explained is the high field line seen in spectra for electric field along [100]. Herendeen and Silsbee$^{15}$, using what appears to be a perturbation
argument, say that this high field line is due to a relaxation of the selection rules due to random internal strains. This allows transitions between the $E_1$ and $A_1$ states, and between the $B_1$ and $E_2$ states. Timme, Dischler, and Estle used a non-perturbation method with an approximation to a random stress distribution and obtained a high field line also.

**EFFECT OF HEAT TREATMENT ON KC1:Li$^+$ SPECTRA**

In attempts to observe phonon echoes in KCl at 1 GHz, R. Timme found that heat treatment was necessary to make the echoes appear. He heated the samples for 72 hrs at about 300°C. It was thought that the heat treatment may relieve some of the strains present in the samples. If this were true, then the strain induced broadening of the paraelectric resonance spectra would be reduced by the same technique. When spectra were taken on samples which had been heat treated in this manner, there was no effect on the width or intensity of the spectra. It could be that the heat treatment merely relieved the strains at the polished surfaces of the samples and did not affect the strains in the bulk of the samples.

**SATURATION BEHAVIOR OF KC1:Li$^+$ SPECTRA**

The spectra for KCl:Li$^+$ saturate at powers incident on the cavity between about 2 mw and 10 mw. The power at which saturation occurs varies from sample to sample and run to run, but it always occurs somewhere in this range. The saturation behavior is manifested in a difference in the size of the absorption and dispersion spectra at powers above the saturation point. The dispersion becomes larger than the absorption. This indicates that the dipole system can not relax to the lattice phonons fast enough to maintain a difference in population between the states involved in the transition. The
dispersion is not affected by the relaxation of the dipole system. Figure 30 shows the absorption and dispersion spectra at 10 mw. This can be compared to the spectra seen in Figure 26 for an incident power of 1 mw. At 1 mw, the absorption and dispersion are approximately equal. At 10 mw, the dispersion is appreciably larger than the absorption.
FIGURE 30: EFFECT OF SATURATION ON PHASE SENSITIVE DETECTION SPECTRA FOR KCl:Li⁺
CHAPTER VI

PARAELECTRIC RESONANCE SPECTRA FOR NaCl:OH⁻

The NaCl samples used to obtain spectra came from many sources. All of the spectra shown in this chapter were taken from random cuttings of NaCl obtained from the Harshaw Chemical Company. Spectra were also taken on samples cut from two different NaCl windows and a piece of NaCl of unknown origin. Another set of samples was taken from a boule of NaCl containing 100 ppm Li⁺. All of the samples gave the same spectra with about equal intensity. The spectra were unaffected by heat treatment or additive doping of Li⁺ impurity.

PARAELECTRIC RESONANCE SPECTRA

Paraelectric resonance spectra for NaCl in the phase sensitive detection mode are displayed in Figures 31, 32, 33, and 34 for applied and microwave fields along [100], [110], [111], and {22.5°, 45°} respectively. For the electric field along [100], there is only one line, but for each of the other orientations, there are two lines present: (1) a low field intense line, and (2) a high field weak line. There were two lines present for the orientations {45°, 45°} and {67.5°, 45°}. These spectra appeared to be the same as the rest of the spectra except [100].

In looking at the spectra, one notices something strange about them. In an ordinary derivative display of the absorption signal, the signal should start at zero, reach a positive maximum, pass through zero at the peak of the resonance, reach a negative minimum, and then return to zero. In the phase sensitive dispersion spectra, the signal should start at zero, reach a maximum at the peak of the resonance and
NaCl:OH$^-$
POWER = 1 MW
FREQ. = 36.30 GHz
TEMP. = 1.3°K
E//E$_1$//[100]

**Figure 31:** Phase Sensitive Detection Spectrum for NaCl:OH$^-$
With E//E$_1$//[100]
NaCl:OH⁻
POWER = 1 MW
FREQ. = 36.18 GHz
TEMP. = 1.3°K
E//E₁// [110]

FIGURE 32: PHASE SENSITIVE DETECTION SPECTRUM FOR NaCl:OH⁻
WITH E//E₁// [110]
FIGURE 33: PHASE SENSITIVE DETECTION SPECTRUM FOR NaCl:OH$^-$
WITH $E//E_{1}//[111]$

NaCl:OH$^-$
POWER = 7 MW
FREQ. = 36.39 GHz
TEMP. = 1.3$^\circ$K
$\varepsilon_{111},\varepsilon_{111}^{[111]}$

**DISPERSION**

**ABSORPTION**

$d\chi_e/d\varepsilon$

Electric Field (KV/cm)
NaCl:OH\(^-\)

POWER = 1 MW
FREQ. = 36.31 GHz
TEMP. = 1.3°K
EII E II \& 22.5°, 45°

FIGURE 34: PHASE SENSITIVE DETECTION SPECTRUM FOR NaCl:OH\(^-\)
WITH E//E\(_1\)//{22.5°, 45°}
return to zero. However, in all of the spectra taken, it appears that the absorption and dispersion are interchanged. The traces labeled absorption were taken using the methods outlined in the chapter on the spectrometer for obtaining absorption. This is the same method which gave good absorption signals for the KCl:Li$^+$ system. The dispersion was taken with the phase of the reference shifted by 90° from the value used for absorption. Now, the question arises of whether the absorption is really the absorption or the dispersion, and why, using the same methods, the KCl:Li$^+$ absorption signal appears to have the correct form.

Many attempts were made to eliminate the possibility that the phase was off by 90°. First, the spectra were taken at intermediate phase angles between the phase for absorption and 180° from that phase. The dispersion like absorption signal turned into the absorption like dispersion signal and then into the negative of the original signal as the phase was changed from 90° through 90° to 180°. The signals appeared just as they should except for the 90° discrepancy in the phase angle.

The Q of the cavity was much worse for the NaCl samples than for the KCl samples, and there was some interference due to standing waves set up in the system. An attempt was made to determine if we were not looking at the cavity dip, but rather a standing wave slightly off the resonant frequency of the cavity. A teflon plug was made which could be inserted or removed from the cavity by a lead screw arrangement. In this way, the frequency of the cavity could be varied by about 50 or 60 MHz. This allowed us to shift the cavity resonance with respect to the standing waves. Nothing that was done seemed to change the behavior of the resonance. We still got a dispersion like signal when we should
have gotten absorption. The use of the phase shifter to reduce the effect of the standing waves produced no change in the signal either.

In a final attempt to solve this dilemma, straight detection spectra were taken for electric field along [100]. These spectra did not completely solve the problem, but they did give a little insight into what was going on in the system. Figure 35 shows the straight detection spectrum for NaCl with the klystron locked and unlocked. This can be compared with the straight detection spectra for KCl with the klystron locked and unlocked (Figure 23). Notice in the NaCl spectra that when the cavity is unlocked, the resonance shifts to higher field and becomes more resolved. This is exactly the opposite behavior from that of the KCl samples. In them, the resonance shifts to lower field and is less resolved when the cavity is unlocked. The only insight gained from the straight detection spectra is that the position of the peak is closer to the half way point between the maximum and minimum on the absorption than on the dispersion. Also, the peak of the dispersion is closer to the resonant field than the peak of the absorption. It almost appears that there is a shift in the base line on the absorption signal, but no mechanism can be postulated that would give such an effect.

Because of all the problems inherent in the NaCl spectra, it would be rather useless to try to determine a resonant field for the transitions. Any determination made would be very dependent on the interpretation of the shape of the line. Since, as we saw in the lumped circuit parameter model for a paraelectric resonance experiment, the separating of the real and imaginary parts of the susceptibility is dependent on the size of the susceptibility, one can not say that we are actually only
\text{NaCl:OH}^{-}
\text{POWER} = 5 \text{ MW}
\text{FREQ.} = 36.30 \text{ GHz}
\text{TEMP.} = 1.3^\circ \text{K}
\text{E//}[100]

\text{FIGURE 35: STRAIGHT DETECTION SPECTRUM FOR NaCl:OH}^{-} \text{ WITH } \text{E//E}_{1}/[100]
looking at absorption or dispersion. We might be seeing a combination of the two. The only information we have is the fact that there is an intense, very broad line for each of the directions. The position of the line does not change very much from one orientation to another. There is a second, weak high field line along all directions except [100].

**IDENTIFICATION OF THE PARAELECTRIC IMPURITY**

With this information about the spectra, let us try to determine the symmetry of the paraelectric defect and perhaps identify it. We can eliminate an eight \( \langle 111 \rangle \) dipole system because at any frequency above the threshold frequency, the resonant field for \([110]\) will be \( \sqrt{2} \) times the field for \([110]\), and the resonant field along \([111]\) will be \( \sqrt{3} \) times the field for \([100]\). We do not observe this strong dependence on orientation. In fact, the low field line appears at about the same field for all directions.

The other alternative is a six \( \langle 100 \rangle \) dipole system. The spectra one sees for this system are dependent on the frequency. Figures 13 and 14 show the spectra for frequencies above the \( 2\Delta \) and \( 4\Delta \) thresholds. Notice that at a frequency of \( 3\Delta \), there is only one line along the \([100]\) direction. For the frequency of \( 5\Delta \), there are two strong lines present for the \([100]\) orientation. These lines are far enough apart that they should be fairly well resolved even with a large broadening mechanism active. The experimental spectra show only one line with no other structure for the \([100]\) orientation, so it is likely that the paraelectric impurity we are observing is a six \( \langle 100 \rangle \) dipole system with our frequency somewhere between \( 2\Delta \) and \( 4\Delta \). For the purposes of our analysis, we will assume our frequency to be \( 3\Delta \), although any frequency in the range from \( 2\Delta \) to \( 4\Delta \) would give similar results.
So now we know that our system is a six $<100>$ dipole system with a tunneling parameter between 0.3 cm$^{-1}$ (9 GHz) and 0.6 cm$^{-1}$ (18 GHz). We may rule out all monatomic ions because the theoretical calculations of Wilson, Hatcher, Dienes, and Smoluchowski$^{19}$ indicate that monatomic ions will only be off-center along the [111]-type directions in the alkali halides. Therefore we are left with diatomic ions. The most likely choice is the hydroxyl ion. Kirby, Hughes, and Sievers$^{16}$ have studied the far infrared behavior of NaCl doped with OH$^-$. They found that there is a rather broad absorption at about 2 cm$^{-1}$ (60 GHz) in this system. In looking at the model for our system, the $A_{lg} - T_{lu}$ transition should occur at a frequency of $4\Delta$. Using our estimates for the tunneling parameter, we obtain a frequency for this transition in the range from 1.2 cm$^{-1}$ to 2.4 cm$^{-1}$. Therefore, OH$^-$ is consistent with the information we have obtained about the zero field splitting. Another fact about the system studied by Kirby, et. al. is that the frequency of the absorption increases with the application of an electric field. This indicates that the system is paraelectric. As further evidence that OH$^-$ is the impurity responsible for the resonance, consider the thermal conductivity data of Klein$^{20}$. He measured the thermal conductivity as a function of temperature for NaCl from various sources. He found that NaCl grown in a controlled atmosphere had a higher low temperature thermal conductivity than NaCl grown without special atmospheres. Therefore, he concluded that he was getting phonon absorption due to some impurity which contained oxygen. He found the effect to be particularly prominent in NaCl grown by the Harshaw Chemical Company. This could explain why samples from all sources showed the resonance behavior. All of the boules were probably
grown without a special atmosphere. Water vapor from the atmosphere could get into the melt and perhaps be dissociated and become OH\textsuperscript{−}.

As evidence that the system we are dealing with is a six \langle100\rangle dipole system, one may cite the work of Brugger, Fritz, and Kleinman\textsuperscript{21} on anelastic relaxation of OH\textsuperscript{−} in NaCl. They did acoustic attenuation studies on NaCl obtained from the Harshaw Chemical Company. They found the low temperature ultrasonic attenuation to be independent of temperature for phonons with T\textsubscript{2g} symmetry. There was a temperature dependence for phonons with E\textsubscript{g} symmetry. This indicates that the impurity causing the increase in attenuation has the symmetry of a six \langle100\rangle dipole system.

From the evidence cited, it appears fairly certain that the resonances observed are due to OH\textsuperscript{−}. At any rate, the positive identification of the impurity is immaterial to the discussion of the system. The important thing is that whatever the impurity is, it exhibits the characteristics of a six \langle100\rangle dipole system.

**COMPARISON OF THE EXPERIMENTAL DATA WITH THE SIX \langle100\rangle DIPOLE SYSTEM**

Now that we have suggested that we are dealing with a six 100 dipole system at a frequency between the 2Δ and 4Δ thresholds, let us see how well the model fits the experimental results. Experimentally we observe one intense line along all of the directions tested. The position of this line does not vary much with orientation. If we look at Figure 13, we see that there is one intense line that does not vary much in position. So the intense lines are in agreement with the model.

Now let us consider the extra structure present. For the electric field along [100], the model predicts no extra structure and none is observed. For electric field along [110], there should be a high field
weak line, and one is seen. For electric field along $[22.5^\circ, 45^\circ]$, there should also be a weak high field line. Such a line is seen experimentally.

Now we must consider the [111] spectrum. The theoretical model predicts that only one transition will occur. However, there is a very distinct high field line present in the actual spectra for the [111] orientation. Here we have a rather bad discrepancy between the theoretical prediction of our model and the actual spectra.

It is a situation very similar to that encountered for the [100] spectrum in the KCl:Li$^+$ system. In this case only one line is predicted by the theoretical model for electric field along [100], but a second line is seen. Timme, Dischler, and Estle$^1$ used random internal strains to explain the appearance of the high field line. Therefore, the situation could be similar for the [111] spectra of NaCl:OH$^-$. 

**MODEL FOR EFFECT OF RANDOM INTERNAL STRAINS ON PARAELCTRIC RESONANCE SPECTRA**

The model used is similar to that employed by B. Dischler$^1$ in his calculations of the effect of random strains on the spectra for KCl:Li$^+$. Since we must calculate the spectrum numerically, an approximation must be made to a smooth distribution of strains. We can calculate the spectrum with an applied electric field along a certain direction and an applied stress field along a certain direction. Therefore, we use a discrete set of directions and magnitudes for the stresses as an approximation to the actual random distribution. The more directions and magnitudes we consider, the more nearly we will have a truly smooth random distribution.
In the model used, we say that the dipoles are acted on only by uniaxial stresses along different directions and with various magnitudes for the stress. The directions chosen are the three [100]-type directions, the four [111]-type directions and the six [110]-type directions. These directions were chosen because they were of high symmetry. This meant that in most cases two or more stresses of a given type had the same effect on the spectrum with the electric field in a given direction. For instance, with the electric field along [111], stresses along all three [100]-type directions will have the same effect. This eliminates the necessity of making several calculations, since one calculation can be made for all three directions.

Another feature of these choices of directions is that uniaxial stresses along [111]-type directions will not affect the system. Therefore, the spectra for stresses along [111]-type directions are the same as for the unstressed case. Directions other than these simple directions could be used, but they would greatly increase the number of numerical calculations necessary.

We are assuming that the effect of internal strains on the dipoles can be described by uniaxial stresses along a random distribution of directions. We are approximating this situation with uniaxial stresses along thirteen discrete directions in the crystal. In order to determine how much weight to give to a certain direction, we postulate that the effect of stress along a given direction will approximate the effect of stresses along all of the directions closest to it.

If we draw great circles on a sphere which are equidistant between two directions, we will divide the sphere up into regions. Each point in a region will be closest to the direction for that region. Therefore,
the area of a region will give the weight to be given the direction corresponding to that region. By solid geometry, we can determine the area on the surface of a sphere surrounding a given direction. The area around a <100> direction is 32°56', around a <111> direction 30°54', and around a <110> direction 27°16'. These areas are given in spherical degrees. There are 720 spherical degrees in a sphere. Therefore, the relative weights given to the different directions are:

<100> - 1.00
<111> - 0.94
<110> - 0.83

In order to approximate a distribution of magnitudes, nine magnitudes of the stress were used for each direction. They corresponded to integral values of $\pi/\triangle$ from -4.0 to +4.0. In the calculations, the various magnitudes were weighted in two ways. One way is to give equal weight to all magnitudes of the stress. This we will call the straight distribution. This would make large stresses as important as small stresses. The other weighting system used was a gaussian distribution in the stress centered at zero stress. It has a half width of about 4$\triangle$. This distribution emphasizes the smaller magnitudes of the stress. By looking at the effect of the two weighting functions, one can see the relative effects of small and large strains. Both weighting systems are illustrated in Figure 36.

The method used to determine the effect of our distribution of stresses on the spectrum is relatively simple. For electric field along a given direction, we calculate numerically the spectrum for all directions and magnitudes of the stress. At this point, we have the resonant fields and intensities for each direction and magnitude of the
FIGURE 36: WEIGHTING FUNCTION FOR THE STRAIGHT AND GAUSSIAN DISTRIBUTIONS OF THE MAGNITUDE OF THE STRESS
stress. The intensity is multiplied by the angular weighting function and the magnitude weighting function, and intensities for the same value of electric field are added. This is then the spectrum for electric field along a given direction with a distribution of internal strains.

At this point, we have a number of resonant lines with their intensities. This can be plotted like the spectra in Figure 13. It will appear to be a ragged spectrum. In order to smooth out the rough spots due to the discreteness of the distribution, we replace each line with a gaussian distribution whose height equals the intensity and whose center is at the position of the line. The purpose of using the gaussian distribution instead of the $\delta$-function is to give a smooth curve. It does not correspond to any other broadening mechanism. We adjust the width of the gaussian so that it is as small as possible, but still gives a relatively smooth curve. Spectra calculated in this manner can then be compared with the actual experimental spectra to determine if we see experimentally what we predict theoretically.

**APPLICATION OF THE RANDOM INTERNAL STRAIN MODEL TO THE SIX $\langle 100 \rangle$ DIPOLE SYSTEM**

Let us now consider the effect of random internal stresses on a six $\langle 100 \rangle$ dipole system with cube edge tunneling. The frequency we shall use is $3\Delta$. Figures 37, 38, 39, and 40 show the line spectra for both distributions of the magnitude for electric fields along $[100]$, $[110]$, $[111]$, and $[22.5^\circ, 45^\circ]$. It is rather difficult to interpret these results, but it appears that there is only one line present for the $[100]$ orientation. The $[110]$ spectrum and the $[22.5^\circ, 45^\circ]$ spectra appear to have a weak high field line in addition to the low
FIGURE 37: LINE SPECTRUM FOR E//E_1//[100] WITH A RANDOM DISTRIBUTION OF INTERNAL STRAINS
FIGURE 38: LINE SPECTRUM FOR E/\{E_1/\}//[110] WITH A RANDOM DISTRIBUTION OF INTERNAL STRAINS
FIGURE 39: LINE SPECTRUM FOR $E/E_\perp \parallel [111]$ WITH A RANDOM DISTRIBUTION OF INTERNAL STRAINS
FIGURE 40: LINE SPECTRUM FOR $E//E_{11}, [22.5^\circ, 45^\circ]$ WITH A RANDOM DISTRIBUTION OF INTERNAL STRAINS
field intense line. For electric field along [111], the results are not as easy to interpret. It appears as if there might be a high field line, especially in the gaussian distribution spectrum. In order to smooth the curves, a gaussian was applied to each of the individual lines. The half width of the gaussian used was about 1 electric field unit. The results of this smoothing are shown in Figures 41, 42, 43, and 44.

From these traces, it appears very definite that there is only one line present along [100], and two lines present along [110] and \{22.5^\circ, 45^\circ\}. These results are not too unexpected, since the system has about the same spectra for the unstressed case. However, we see a rather prominent high field structure for the [111] spectrum. This is something which was not predicted by the unstressed Hamiltonian.

We will now try to show that this high field line is not just an effect of the discreetness of our distribution. To try to consider angles which are different from those used would require a great deal of calculation. However, we can take more values for the magnitude of the stress. We have the effect of stress at all integral values of the stress from -4.0 to 4.0. We can interpolate between these values to obtain more values of the magnitude. The magnitude of the stress was broken up into increments of 0.25 for stresses from -4.0 to 4.0. This gives us thirty three values for the stress instead of only nine. The same methods were used to calculate the line spectra. The line spectra for electric field along [111] are shown in Figure 45. Notice that the interpolation makes the high field structure show up even more prominently with respect to the extra structure at high fields. The smoothed curves for the [111] spectrum with the interpolation are
FIGURE 41: SMOOTHED SPECTRUM FOR E//E_1//[100]
FIGURE 42: SMOOTHED SPECTRUM FOR $E//E_1//[110]$
FIGURE 43: SMOOTHED SPECTRUM FOR $E//E_{1}//[111]$
FIGURE 44: SMOOTHED SPECTRUM FOR $E/E_1/[(22.5^\circ, 45^\circ)]$
FIGURE 45: LINE SPECTRUM FOR $E//E_1//[111]$ WITH INTERPOLATION
shown in Figure 46. From this figure it can be seen that interpolation makes the high field line more prominent in comparison with the background.

**DISCUSSION OF RESULTS OBTAINED USING THE RANDOM INTERNAL STRAIN MODEL**

In the previous section we showed the effect of random internal strains on three types of spectra. The first was the [100] spectrum where we had only one line without the stresses. The introduction of the random stresses did not produce a second line. This is in agreement with the experimental data.

The second case was the [110] spectrum. Here we had two lines present without the internal stresses. The introduction of the stresses did not destroy the second line. In these two cases, the introduction of random internal strains did not change what we expected to see.

The third case was the [111] spectrum. Unlike the [100] spectrum, in the [111] spectrum, we had only one line without the stresses, but needed to create a second line by the introduction of the stress distribution. We found this to be the case. A second line was caused by the stresses, and it appeared to be a real phenomena rather than just a consequence of the discreteness of our distribution. This was demonstrated by the fact that improving the approximation by taking more values for the stress made the line appear more prominent.

The approximation we have used to show the effect of random stresses is rather crude. However, the fact that (1) this crude approximation gives the desired results, and (2) an improvement of the approximation makes the desired results appear more prominent,
FIGURE 46: SMOOTHED SPECTRUM FOR $E//E_1$/[111] WITH INTERPOLATION
indicates that the tunneling model with random stresses can describe this system.

Since the gaussian distribution gave results which were closer to the actual spectra than the straight distribution, it appears that the smaller magnitudes of the stress are more important than the larger magnitudes. It is impossible to determine the magnitudes of the strains which would correspond to the values for the stress used. A calculation of this sort would require a knowledge of the elastic dipole moment of the impurity, and this information is not available.

We have learned several things from the paraelectric resonance spectra for this system. We know that it is a six $<100>$ dipole system with a value for the $90^\circ$ tunneling parameter of between $0.3 \text{ cm}^{-1}$ (9 GHz) and $0.6 \text{ cm}^{-1}$ (18 GHz). (We have done our calculation for a tunneling parameter of $0.45 \text{ cm}^{-1}$.)

We have shown that random internal strains are necessary to get all of the structure present in the spectra.

Although we have not been able to positively identify the impurity responsible for the resonance in NaCl, the evidence seems to indicate that it is the hyroxyln ion.
CHAPTER VII

EFFECT OF APPLIED STRESS ON THE PARAELECTRIC RESONANCE SPECTRA

In Chapter V, we indicated that the high field line which appears in the spectrum for KCl:Li⁺ with the electric fields along [100] was caused by the presence of random internal stresses in the host crystal. In Chapter VI, we showed that the high field line present in the [111] spectrum for NaCl:OH⁻ was due to internal stresses. It would appear that stresses have a large effect on paraelectric impurities. As an extension of the work presented in the previous chapters, we will now show both theoretically and experimentally the effect of applied stress on the paraelectric resonance spectra. We will deal only with uniaxial stresses applied parallel to the direction of the electric field.

APPARATUS FOR APPLYING STRESS TO SAMPLES IN THE MICROWAVE CAVITY

The stress is applied to the sample by means of an 1/8" diameter quartz rod which passes through the top of the cavity and presses the sample against the opposite wall. The pressure is applied to the quartz rod by means of a worm gear arrangement. The worm gear is turned by a worm which is attached to a rod passing through the base plate of the low temperature head. It takes fifty turns of the worm to rotate the worm gear one turn. Figure 47 is an exploded view of the stress application device. The force is applied to the quartz rod by means of a screw with tabs on it. The tabs are held in slots on the worm gear holder. They keep the screw from rotating. The hole in the center of the worm gear is threaded so that as the worm gear is turned, the screw will move up or down along the axis of the worm gear. The worm gear is held in place by means of a top plate which is screwed to the worm gear holder. As the worm gear rotates, the screw will apply
FIGURE 47: STRESS APPLICATION DEVICE
stress to the rod. The screw used for applying the stress has 40 threads per inch, so one turn of the worm advances the screw $0.5 \times 10^{-3}$ inches. This means that the device is very sensitive in making small changes in stress. All of the forces are applied along the axis of the device, so the chances of introducing non-uniform stresses are greatly reduced. Another good feature of the device is its compactness. The overall dimensions of the device are 0.60" square by 0.36" high.

In order to measure the stress that was applied, an 1/8" diameter hole was cut in the bottom of the cavity directly below the sample. A brass plunger was placed in the hole. When stress was applied to the sample, it was transmitted through the sample to the plunger. On the outside of the cavity, a wire foil strain gauge was attached to the plunger, so that it measured strain parallel to the axis of the plunger. When the brass was strained, the resistance of the wire foil was changed. A strain gauge meter registered this change in resistance as a change in strain in the brass. The meter reads directly in microinches per inch. As long as the elastic limit of the brass was not exceeded, the stress applied to the sample would be proportional to the strain registered in the brass plunger.

In order for this system to give more than just an arbitrary scale for measuring stresses, the conversion factor between strain in the brass and stress on the sample had to be obtained. This conversion was made by replacing the sample with a piece of single crystal quartz whose cross-section was approximately the same as that of the samples used. The quartz was oriented so that the z-axis was along the direction of the stress. A strain gauge was attached to the quartz piece. As the stress was applied, the strain in the quartz could be obtained as a
function of the strain in the brass. It was found that a strain in the brass of $1.0 \times 10^{-6}$ corresponded to a strain of $4.0 \times 10^{-6}$ in the quartz. Using a value of $10.71 \times 10^{11}$ dyne/cm$^2$ for the elastic modulus along the z-direction of the quartz, it was found that a strain of $1.0 \times 10^{-6}$ in the brass corresponded to a stress on the sample of $4.28 \times 10^6$ dyne/cm$^2$ or 4.28 bars. A pressure of 1 bar is about the same as one atmosphere. On a typical sample (0.080" square), 1 bar corresponds to a force of about $1\frac{1}{2}$ oz.

**EFFECT OF STRESS ON THE [111] SPECTRUM FOR KCl:Li$^+$**

Figure 48 shows the effect of stress on the spectrum for electric field along [111]. (The numbers in parentheses indicate the relative gain used to obtain the spectra.) As the stress was applied, the intensity of the spectrum decreased by a factor of 2. As the stress was increased, the low field line disappeared.

In the discussion of the [111] spectrum for KCl:Li$^+$ in Chapter V, we showed that the second weak line at lower field was due to Li$^6$, while the intense line at higher field was due to Li$^7$. The reason that the Li$^6$ spectrum appears at lower field is the fact that the tunneling parameter for Li$^6$ is about 45% larger than for Li$^7$. In Figure 49, the line spectra for both Li$^6$ and Li$^7$ are presented as a function of stress applied parallel to the electric field. The thick lines represent the Li$^7$ spectra and the thin lines represent the Li$^6$ spectra. The Li$^6$ spectra are drawn so that the zero field line is the same intensity for Li$^6$ as it is for Li$^7$. This was done so that the Li$^6$ lines would show up more prominently. The Li$^6$ lines should actually be 11% of their drawn height.

In the experimental spectra the lines do not change their position, but only their intensity. Let us consider the Li$^7$ line. In the
FIGURE 48: EXPERIMENTAL SPECTRA SHOWING EFFECT OF STRESS ON [111] SPECTRUM FOR KCl:Li$^+$
FIGURE 49: THEORETICAL SPECTRA SHOWING THE EFFECT OF STRESS ON [111] SPECTRUM FOR KCl:Li⁺ (Li⁷ - DARK LINES, Li⁶ - LIGHT LINES)
theoretical spectra, we see that there is one line which remains at the same position as the original line while all of the other lines move across the spectrum. It could be that the weak line we see in the experimental spectra is this residual line. If this is true, then it is necessary to explain why one does not see the other lines move across the spectrum. As a possible explanation, one might consider the effect of random internal stresses on these other lines. The residual line is not affected by stress applied along the [111] direction. It is possible that it would not be affected very strongly by internal stresses along other directions. This means that it would not be broadened as much as some lines. The other lines in the spectrum are affected strongly by the application of the stress along [111]. If they were also affected by the internal stresses along other directions, they might be broadened into a uniform background, with only the residual line showing up strongly. The only way to test this hypothesis is to use the model for random internal stresses and see what happens as the stress is increased. Since this type of calculation must be done numerically for each magnitude of the applied stress, it amounts to a rather large and complicated calculation.

There is one other problem with the spectrum. The Li\textsuperscript{6} line disappears as the stress is increased. Since the Li\textsuperscript{6} line is relatively larger than the Li\textsuperscript{7} line when the stress is applied, it should show up more prominently. The fact that it becomes less prominent is hard to explain. However, we did see in Figure 29 of Chapter V that the prominence of a weak line close to an intense line was strongly dependent on the broadening of the lines. If the lines we see are broadened by the stress, then this might explain the disappearance of the weak line.
EFFECT OF STRESS ON THE [100] SPECTRUM FOR KCl:Li$^+$

Because of the symmetry of the eight $\langle 111 \rangle$ dipole system, stress along the [100] direction should not have any effect on the spectrum. Figures 50, 51, and 52 show the effect of stress on the [100] spectrum. With zero stress, there are two lines. The low field intense line is due to the allowed transition for this direction. The high field line is caused by the presence of random internal stresses in the host crystal. At a stress of 43 bars, the spectrum is unchanged. At 133 bars, something appears to have happened to the spectrum, but really the only thing that has changed is the phase of the signal. This trace represents a dispersion like signal. At 231 bars, the phase is changed by 180° from that of the first two traces. The high field line appears to have broadened slightly, but the spectrum is very little changed from the zero stress spectrum. At 312 bars, there has been a drastic change in the spectrum. The low field line has decreased in intensity, and the high field line has broadened considerably. In the 356 bars trace, the low field line has weakened even more, and the high field line has split into two lines. At 398 bars, the low field line has practically disappeared, and the splitting of the high field line has become more prominent. At 436 bars, the trace shows three lines. It is difficult to tell whether the low field line is the allowed transition with more intensity or an altogether different line.

Everything seems to be in agreement with the theoretical model for stresses below 231 bars. As the stress is increased beyond this value, the intensity of the low field line decreases. Figure 53 shows a plot of the intensity of the low field line as a function of applied stress. For low stresses, the intensities are just about constant. As the
FIGURE 50: EXPERIMENTAL SPECTRA SHOWING THE EFFECT OF STRESS ON [100] SPECTRUM FOR KCl:Li⁺
FIGURE 51: EXPERIMENTAL SPECTRA SHOWING THE EFFECT OF STRESS ON [100] SPECTRUM FOR KCl:Li⁺ (2)
FIGURE 52: EXPERIMENTAL SPECTRA SHOWING THE EFFECT OF STRESS ON [100] SPECTRUM FOR KC1: Li⁺ (3)
FIGURE 53: INTENSITY OF THE ALLOWED TRANSITION AS A FUNCTION OF APPLIED STRESS FOR THE [100] SPECTRUM OF KCl:Li^+
stress gets to larger values, the intensity begins to drop rapidly. The field position of the line does not change as the stress is increased.

This behavior of the spectrum can not be explained in terms of the model as it has been formulated, since the only way the stress can interact with the system is through the elastic dipole moment of the impurity. One must postulate another type of interaction to explain this behavior. A possible explanation is that the stress is changing the potential energy barriers which the impurity encounters as it changes the orientation of its dipole moment. This would make the tunneling parameters a function of the stress applied to the system. Dischler\textsuperscript{23} has formulated a model for the interaction of stress and the cube edge tunneling parameter. Applying this model to stresses along the [100] direction, he finds that the states responsible for the allowed line in the [100] spectrum will split apart as the stress is applied. This means that the position of the allowed line should approach zero electric field as the stress is increased. This type of behavior is not observed. This model considers that cube edge tunneling is the only possibility even when the stress is applied. Perhaps the non-cube edge tunneling becomes more important when the stresses become large. All of these possibilities must be taken into account if the effect of stress on the tunneling parameter is to be calculated. The problem is that when these extra interactions are added, one must introduce more parameters to describe the effect. For the effect of stress on the cube edge tunneling parameter, one must introduce two more parameters. Determining the relative magnitudes of these parameters would be a very difficult task, since the experimental spectra do not give one much information.
EFFECT OF STRESS ON THE [110] SPECTRUM FOR KCl:Li⁺

The most striking effect of stress on the paraelectric resonance spectrum occurs for the [110] spectrum of KCl:Li⁺. The effect for low stresses is shown in Figures 54 and 55. Behavior under the application of large stresses is shown in Figure 56. At the lowest measurable stress, 4.3 bars, the single zero stress line is broadened on the high field side. At 8.6 bars, the line has actually split into two lines. At 12.8 bars, three lines appear in the spectrum. The line at low field is the sharpest. It is at about 70% of the original line position. The other two lines are barely resolved and are very broad. As the stress is increased more, the low field line does not change position, but the two high field lines move off to higher field. For large stresses, there is another line which moves to higher field as the stress is increased. This line is most prominent in the 128 bars spectrum.

The effect of stress on the [110] spectrum using our model is shown in Figure 57. The single line with zero stress splits into two lines as the stress is applied. The lower of the two lines approaches a position 60% of the position for the zero stress line. This line becomes less intense as the stress is increased. This is consistent with the experimental spectra. The higher field line moves out to higher field and a third line appears which also moves toward higher field. This is what we see in the experimental spectra. The experimental spectra are in rather good agreement with the predictions of the model.

Since the experimental and theoretical spectra correlate so well, we can get an estimate of the elastic dipole moment of the impurity from this data. The most prominent feature of the spectra is the appearance of three lines at a stress of 12.8 bars. As an estimate, one might say
FIGURE 54: EXPERIMENTAL SPECTRA SHOWING THE EFFECT OF STRESS ON [110] SPECTRUM FOR KCl:Li⁺
FIGURE 55: EXPERIMENTAL SPECTRA SHOWING THE EFFECT OF STRESS ON [110] SPECTRUM FOR KCl:Li⁺ (2)
FIGURE 56: EXPERIMENTAL SPECTRA SHOWING THE EFFECT OF STRESS ON [110] SPECTRUM FOR KCl:Li⁺ (3)
FIGURE 57: THEORETICAL SPECTRA SHOWING THE EFFECT OF STRESS ON [110] SPECTRUM FOR KCl:Li⁺
that this spectrum is similar to the theoretical spectrum for \( \Delta / \Delta = 6 \). Therefore, the 8.6 bars spectrum would correspond to \( \Delta / \Delta = 4 \). Since both spectra have only two lines, it appears that we are correct so far. The 4.3 bars spectrum would correspond to \( \Delta / \Delta = 2 \). The two lines are well resolved in the theoretical spectrum, but they are not resolved in the experimental trace. This is a minor inconsistency since the lines are so broad. From this evidence, it would appear that \( \Delta / \Delta = 6 \) should correspond to 12.8 bars. If we assume that \( \Delta \) is 1/3 cm\(^{-1}\) (10 GHz), we get a value for \( \gamma \) of \( 3.1 \times 10^{-23} \text{cm}^3 \). Even considering the inaccuracies in our assignment of the experimental spectra to the theoretical spectra, this value should be within 50% of the actual value for the elastic dipole moment.

Byer and Sack\(^9\) were able to get a value for the elastic dipole moment from their anelastic relaxation data. They used a classical model to describe the elastic dipole of the impurity. Expressing their elastic dipole moment in terms of our definitions, they obtained a value for \( \gamma \) of \( 0.14 \times 10^{-23} \text{cm}^3 \). Our value is 22 times greater than this. Such a large discrepancy is hard to rationalize, since both methods measure the same parameter. There have been other measurements of the elastic dipole moment with great discrepancies. Härtel and Lüty\(^24\) measured the elastic dipole moment of OH\(^-\) in KCl by the stress induced dichroism and got a value of \( 0.59 \times 10^{-23} \text{cm}^3 \). Shepherd and Feher\(^25\) measured the elastic dipole moment of the same system using specific heat measurements and came up with a value of \( 3.7 \times 10^{-23} \text{cm}^3 \). This value is 6.3 times as large as the value obtained by Härtel and Lüty. So it seems that large discrepancies are not unusual in the measurement of elastic dipole moments.
In order to gain some physical insight into the problem, let us consider what the elastic dipole moment of the impurity really is. The elastic dipole moment gives the change in energy due to the application of a stress. It is a symmetric tensor whose off-diagonal components are not necessarily zero. We can make it diagonal if we use the principal axis system for the impurity. Since the impurity is symmetric about the [111] direction, the [111] direction will be one of the principal axes of the system. We can choose the other two axes arbitrarily. We shall choose the other two axes to be along [110] and [112]. We therefore have two parameters for the elastic dipole moment: \( n_1 \) along the [111] direction and \( n_2 \) perpendicular to it. We may express our \( n \) in terms of these parameters by a simple rotation of coordinates.

\[
\mathcal{N} = (n_1 - n_2)/3
\]

This means that what we are really observing is the difference between the elastic dipole moment along the [111] direction and that perpendicular to it. We find that

\[
(n_1 - n_2) = 9.3 \times 10^{-23} \text{ cm}^3
\]

We will now treat the crystal and defect as an elastic continuum. (This technique is used by Byer and Sack\textsuperscript{9} and was originally devised by Känzig\textsuperscript{26}.) The nearest neighbors of the impurity are Cl\textsuperscript{−} ions a distance \( a/2 \) out along the [100]-type directions. We approximate the removal of the K\textsuperscript{−} ion by the cutting of a spherical cavity centered on the K\textsuperscript{−} ion with radius \( a/2 \). We approximate the impurity by an ellipsoid. The impurity is placed in the cavity and the surface of the cavity is bonded to the surface of the impurity. Then the system is allowed to reach equilibrium. The Cl\textsuperscript{−} ions are now thought of as being on an ellipsoid rather than on a sphere centered on the original site. Känzig shows that
the energy of the impurity due to the application of a stress is given by

\[ E = -\frac{4\pi}{3} \langle \frac{a}{2} \rangle^2 \sum \langle \Delta \rho_i \rangle \sigma_i \]

where \( \Delta r_i \) is the change in length of the principal axis of the ellipsoid parallel to \( \sigma_i \), or

\[ \Delta r_i = (R_i - \frac{a}{2}) \]

(\( R_i \) is the length of axis of the ellipsoid after it reaches equilibrium.)

We also have an expression for the energy in terms of the elastic dipole moment.

\[ E = -\sum \frac{\sigma_i}{2} \nabla_i \nabla_i \]

From these two expressions for the energy, we find that

\[ \nabla_i = \frac{4\pi}{3} \langle \frac{a}{2} \rangle^2 \langle \Delta \rho_i \rangle \]

Expressing the dipole moment in terms of the difference \( (\nabla_1 - \nabla_2) \)

\[ (\nabla_1 - \nabla_2) = \frac{4\pi}{3} \langle \frac{a}{2} \rangle^2 (R_1 - R_2) \]

Using this formula with \( a = 6.29 \AA \), we get \( (R_1 - R_2) = 2.25 \AA \). Using the value for the elastic dipole moment obtained by Byer and Sack, the difference would be about 0.1 \AA.

Byer and Sack state that their value is in agreement with theoretical calculations for the shift in position of the Cl- ions. It appears that the phenomenon which causes the change in energy we observe is not the same as that responsible for the anelastic relaxation. It is difficult to postulate an interaction between stress and the impurity which would be twenty times more sensitive to stress than the elastic dipole interaction, and which would not be seen in the anelastic relaxation measurements. So we are left with a fundamental inconsistency between our results and those of Byer and Sack.
EFFECT OF STRESS ON THE SPECTRA FOR NaCl:OH⁻

Obtaining good quality data for NaCl:OH⁻ was much more difficult than for KCl:Li⁺. The cavity dip was almost non-existent. It amounted to little more than a flat spot on the klystron mode. Even with these difficulties, spectra were obtained for the [100] direction and the [110] direction. The [111] direction was also tried, but it was impossible to find even a hint of a cavity dip for this orientation. Due to the difficulty involved in obtaining the spectra, one must not put too much faith in the details of the spectra.

The effect of stress on the [100] spectrum is shown in Figure 58. The zero stress line is reduced in intensity as the stress is increased. The position of the line is not changed. The theoretical model predicts that the line should remain in the same position and decrease in intensity as the stress is increased. It appears that the experimental results are in qualitative agreement with the theoretical model.

Figure 59 shows the effect of stress on the [110] spectrum. The high field line does not show up well enough to determine what happens to it, but the intense line remains in the same position and has the same intensity as the stress is increased. The model predicts that the low field line should remain in the same position with the same intensity, and the high field line should disappear.

From these rather sketchy results, it appears that the effect of stress on the [100] and [110] spectra for NaCl:OH⁻ is qualitatively in agreement with the theoretical model. Since nothing remarkable happens in the spectra, it is impossible to even make an estimate of the elastic dipole moment for NaCl:OH⁻.
Figure 58: Experimental spectra showing the effect of stress on [100] spectrum for NaCl:OH⁻
FIGURE 59: EXPERIMENTAL SPECTRA SHOWING THE EFFECT OF STRESS ON [110] SPECTRUM FOR NaCl:OH⁻
CHAPTER VIII

CONCLUDING REMARKS

Let us now determine what information has been obtained by the technique of paraelectric resonance, and whether this technique makes a significant contribution to the understanding of the properties of paraelectric impurities.

One of the most interesting pieces of information we have obtained is the symmetry of the dipole orientations. The fact that the KCl:Li⁺ spectrum as a function of orientation fits so well to the model using eight <111> dipoles made it very evident that this model was correct. In the case of NaCl:OH⁻, the results were not as clear cut. We had a spectrum which provided very little information. There was one line which appeared at about the same field for all orientations tried. This was not in agreement with the eight <111> dipole model. However, it could be explained in terms of the six <100> dipole system at a frequency between the first and second thresholds. For both KCl:Li⁺ and NaCl:OH⁻, it was necessary to make some rather restricting assumptions in order to determine the symmetry of the defect. Further proof of the symmetry of the KCl:Li⁺ system was obtained by the weaker interaction of the spectrum with stress along the [100] direction. Another technique for determining the symmetry of the defect is anelastic relaxation data. This type of data gives conclusive proof of the symmetry of the defect, since one is dealing only with the symmetry of the defect and the elastic wave. Although paraelectric resonance can give one the symmetry of the defect, anelastic relaxation provides a more elegant approach to the problem.
Another fact about the impurity which one would like to obtain using paraelectric resonance is the nature of the tunneling. In the models used to describe the impurity, we have allowed tunneling only between nearest neighbor orientations of the dipole. This model fits the spectra which are observed, but it is quite possible that a model using tunneling other than nearest neighbor tunneling would give an equally good fit. A method for studying the tunneling splitting which should give further information about the tunneling system is the phonon spectrometer of Walton. He does observe evidence of non-cube edge tunneling in the KCl:Li$^+$ system, but it is just on the limit of detectibility, and therefore not to be taken with too much confidence.

Even in the context of our model, one would like to be able to determine a value for the zero field splitting. Since the splitting which we observe is a combination of the zero field splitting and the splitting due to the application of an electric field, one cannot determine the zero field splitting exactly. In the case of NaCl:OH$^-$, the spectra indicate that we are between the first and second thresholds for the impurity, but one cannot narrow it down much further than this. In the case of KCl:Li$^+$, we know only that the threshold is below the frequency at which we are working. It is necessary to use an independent determination of the electric dipole moment (such as that obtained from the far infrared equivalent of paraelectric resonance) in order to get a value for the zero field splitting.

The next piece of information one would like from paraelectric resonance is a value for the electric dipole moment of the impurity. For this it would be necessary to obtain the paraelectric resonance
spectrum as a function of frequency for frequencies which are much higher than the zero field splitting. Therefore, paraelectric resonance at our frequency cannot give a value for the electric dipole moment.

Paraelectric resonance as a function of applied stress allows one to determine the elastic dipole moment of the impurity. Anelastic relaxation can also give one a value for this parameter. Although paraelectric resonance should give a better value for the elastic dipole moment, the fact that the value obtained by anelastic relaxation differs from our value by over twenty times leaves some strong doubts about the method.

As we have shown, paraelectric resonance does not give any information which cannot be obtained by other techniques. However, the other methods are very specialized. They will give only one or two properties of the system. Paraelectric resonance allows one to observe all of the characteristics of the system in perhaps the easiest form.

The reason that it is so difficult to get exact information about the impurity using paraelectric resonance (or any of the other techniques) is that the impurity is very strongly affected by internal stresses in the host crystal. This makes the interpretation of the experimental data rather difficult.

In spite of all the problems, paraelectric resonance is the best method for studying paraelectric impurities. The only obstacle in the use of paraelectric resonance is that it is not observable in very many systems. This makes the technique of only limited use.
IX. REFERENCES


23. B. Dischler, to be published.


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