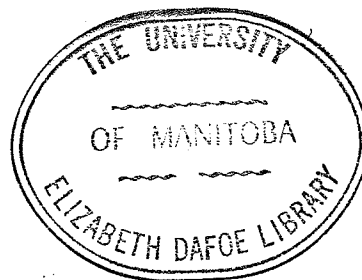THEORETICAL INVESTIGATION

OF

MOSSBAUER QUADRUPOLE SPLITTING

AND

ELECTRIC FIELD GRADIENTS

AT THE SURFACE OF ALKALI HALIDE CRYSTALS

A thesis

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CONTENTS

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ABSTRACT

The calculation of the electric field gradient at four sites in each of six alkali halide crystals, KCl, KBr, KI, RbCl, RbBr, and RbI, is performed on the basis of a model of the surface given by Benson, Freeman, and Dempsey. These four sites correspond to the sites that positive and negative ions would take if they were placed on or in the surface. The Mossbauer quadrupole splitting of I^{129}, assumed to be at the negative ion sites on the surface, is then estimated.

The surface model describes the distortion at the surface in terms of four parameters. These are the displacements of the positive and negative ions from their bulk configurations and the dipole moments which are induced in these ions. The model assumes that the displacements and induced dipole moments are perpendicular to the surface of the crystal.

The results show that because of the indeterminacy in the Sternheimer antishielding factors for surface ions the quadrupole splitting (which is small but measureable) cannot presently be used as a test of the surface model. However, given accurate Sternheimer factors, consideration of the potassium halides may be able to supply such a test since plots of the electric field gradient versus the lattice constant with and without considering the surface distortion have markedly different slopes at the positive ion sites

both in the surface of the crystal and on the surface of
the crystal. Also the electric field gradient at the
positive ion site in the surface of the KI crystal changes
sign because of the distortion. If the direction of the
electric field gradient could be determined experimentally,
this would also serve as a test of the surface model,
independent of the Sternheimer factor.

CHAPTER ONE

INTRODUCTION

With the improvement of experimental techniques[1] it is now possible to produce clean and planar crystal surfaces and hence theoretical discussion of surface experimental data is now feasible. The Mossbauer effect holds promise of being a useful tool in the study of surfaces because of the sharply defined energy of the gamma ray. This investigation estimates the electric field gradient at the surfaces of alkali halide crystals and the quadrupole splitting of the Mossbauer line due to atoms on these surfaces. In order to perform such a calculation it is necessary to consider the configuration of the surface atoms. It is expected that the surface and bulk configurations of the atoms will differ because of the imbalance of forces at the surface. A model of the surface proposed by Benson, Freeman and Dempsey[2] which describes the distortion in terms of four parameters, the displacements of the positive and negative ions and the dipole moments induced in these ions, is used in the calculations. Then by calculating the electric field gradient at the atomic sites it is possible to get the electric field gradient at the nuclear sites by introducing a Sternheimer antishielding factor which gives the contribution of the electronic charge distribution of the Mossbauer atoms to the electric field gradient. Hence the splitting of the

levels of the Mossbauer nuclei due to the interaction
between the nuclear quadrupole moment and the electric
field gradient at the nuclear site can be estimated.

A discussion of the general theory of the Mossbauer
effect and the differences in this effect between surface
and bulk ions is given in chapter II. This chapter also
contains a detailed description of the crystal surface
model used. Chapter III contains a discussion of the electric
field gradient at atomic and nuclear sites. A section on
the Sternheimer antishielding factors is also contained in
this chapter. Chapter IV contains the results of the
calculation of the electric field gradient at four sites
in each of six alkali halide crystals and an estimate of
the quadrupole splitting of the spectra for I^{129} at a
negative ion site on and in the surface of these crystals.
The feasibility of experimentally testing the model of a
crystal surface is discussed on the basis of our detailed
results.

CHAPTER TWO

THE MOSSBAUER EFFECT AND ALKALI HALIDE SURFACES

2.1 INTRODUCTION TO THE MOSSBAUER EFFECT

To understand the Mossbauer effect one must first consider the emission of a gamma ray by a free nucleus. When such a gamma ray is given off, in order to conserve momentum, the nucleus will recoil with momentum $-\vec{P}$ and recoil energy

$$R = \frac{|-\vec{P}|^2}{2M} \tag{1}$$

where $\vec{P} =$ the momentum of the emitted gamma ray and $M =$ the mass of the nucleus after the gamma ray is given off. Thus if E^* is the energy transition of the nucleus, then the energy E of the gamma ray is $E^* - R$. However, if the nucleus under consideration is bound in the crystal one of three possibilities can arise. These possibilities are:[4A]

(1) the free atom recoil energy could be large compared to the binding energy of the atom in the crystal and consequently the atom would be dislodged from its atomic site. This atom can then be treated as a free atom.

(2) the free atom recoil energy could be less than the displacement energy but greater than the maximum phonon energy required to raise the lattice to an excited state (phonon energy). In this case the atom usually dissipates its energy by raising the lattice to an excited state containing many phonons.

(3) the free atom recoil energy could be less than the maximum phonon energy of the crystal. In these last 2 cases the

Mossbauer effect may arise. The probability, however, of it occuring is much greater in case (3).

The recoil energy of a bound nucleus is absorbed by the crystal when a gamma ray is emitted or absorbed. This energy may be absorbed partially in the form of translational energy and partially in the form of internal energy. The translational energy is negligible. This can be seen from the requirement of conservation of momentum $M_1 \vec{V} = \vec{P}$ where $M_1 =$ the mass of the crystal

$\vec{V} =$ the recoil velocity of the crystal

and $\vec{P} =$ momentum of the recoiling nucleus.

Since M_1 is much greater than the mass M of the nucleus, $|\vec{V}|$ will be much smaller than the recoil velocity of the nucleus, and hence the translational energy, $\frac{1}{2} M_1 V^2$, will be negligible from

$$\frac{1}{2} M_1 V^2 = \frac{1}{2} M_1 \frac{P^2}{M_1^2} = \frac{1}{2} \cdot \frac{P^2}{M_1} << \frac{1}{2} \frac{P^2}{M}$$

The recoil energy absorbed in the form of internal energy is received, however, by a quantized system and hence energy can be absorbed only in discrete amounts. In particular there exists a finite probability that no recoil energy is lost to the crystal vibrations when a gamma ray is emitted (or absorbed). As a result the gamma ray which is emitted (or absorbed) has energy $E = E^*$ and the part of the gamma ray spectrum which corresponds to such a gamma ray is the zero-phonon line. This is known as the Mossbauer effect. It

should be noted that momentum is still transferred to the lattice in those events where no recoil energy is transferred to the lattice vibrations. But this momentum is taken up by the crystal as a whole and consequently the corresponding translational velocity is negligible corresponding to the previously mentioned negligible translational energy.

Only a fraction of the gamma rays which are emitted by nuclei bound in a crystal are emitted without recoil energy loss. This fact is elucidated in a sum rule which has been derived by Lipkin.[3] This sum rule states that the average energy transferred to the lattice per event is equal to the energy the nucleus would receive if it were free to recoil. The mathematical statement is

$$\sum_f \left(E_f - E_i\right) P(L_i \rightarrow L_f) = R \qquad (2)$$

where E_f = the energy of the final state of the crystal

E_i = the energy of the initial state of the crystal

and $P(L_i \rightarrow L_f)$ = the probability of the crystal going from its initial state L_i to its final state L_f. It can be seen that this sum rule is consistent with energy conservation. Note that the Mossbauer transitions, that is transitions which transfer no energy to the lattice vibrations (zero phonon transitions) do not contribute to this sum since $E_i = E_f$. Thus if there exists an appreciable probability for energy transfers which are greater than the free atom recoil energy R, there will also be an appreciable probability

for zero energy transfer to the lattice vibrations. That is, if $(E_f - E_i) > R$ for a large number of transitions, then considering these cases alone

$$\underset{f}{\lessapprox} (E_f - E_i) \, P(L_i \rightarrow L_f) \approx R$$

Hence for equation (2) to hold E_i must equal E_f for an appreciable number of transitions. As an illustration[4] of this consider the special case of a nucleus, in a highly localized potential well, which has only one possible bound excited state. Thus if the energy transfer is greater than R, say $E_f - E_i = \frac{3}{2} R$ then from (2), $P(L_i \rightarrow L_f) = \frac{2}{3}$. This means that the probability of recoilless transitions must be $\frac{1}{3}$ from the requirement, which is used in the derivation of this rule, that $\underset{f}{\lessapprox} P(L_i \rightarrow L_f) = 1$.

The importance of the Mossbauer effect lies in the line widths which are associated with the emitted gamma ray. These line widths are equal to the natural (inherent) line widths. The inherent width of the gamma ray is given by the precision with which its energy is defined by the properties of the nucleus. That is, the width arises from the finite time that the nucleus spends in the excited state. The uncertainty principle pertaining to energy and time relates the width Γ of the nuclear state (which also appears as the line width of the gamma ray) to the mean life of the nuclear state. These quantities are related by $\tau \Gamma = \hbar$ or $\Gamma = \dfrac{.609 \hbar}{T_{\frac{1}{2}}}$ where $T_{\frac{1}{2}} =$ the half life of the nuclear state. Thus a

typical $T_{1/2}$ of the order of 10^{-7} seconds corresponds to a line

width of the order of 10^{-9} ev. This is much smaller than the

recoil energy loss which is of the order of 10^{-7} ev. Since

the width of the Mossbauer line is less than the energies of

interaction of the nuclear magnetic dipole and electric

quadrupole moments with the surrounding electronic dis-

tribution, it is in principle possible to study these

interactions by using the Mossbauer effect.

In order to detect the zero-phonon lines it is necessary

to sweep the zero-phonon emission and absorption lines over

one another by means of a Doppler shift. That is, a relative

velocity is imparted between the source and absorber, both

of which contain Mossbauer atoms. Suppose the source is

moved with velocity v and the absorber is maintained at

rest in the lab system. This will result in a Doppler shift

of the emission line by an amount

$$\Delta E = \left(\frac{v}{c}\right) E \tag{3}$$

where c = the velocity of light.

A derivation of this equation for the Doppler shift of the

energy is given in appendix I. This shift of the emission

line results in a reduction in the amount of nuclear

resonance absorption due to less overlap of the emission

and absorption lines (see fig. 1). When the intensity of

radiation at the detector which is placed behind the

absorber is plotted as a function of the velocity of the

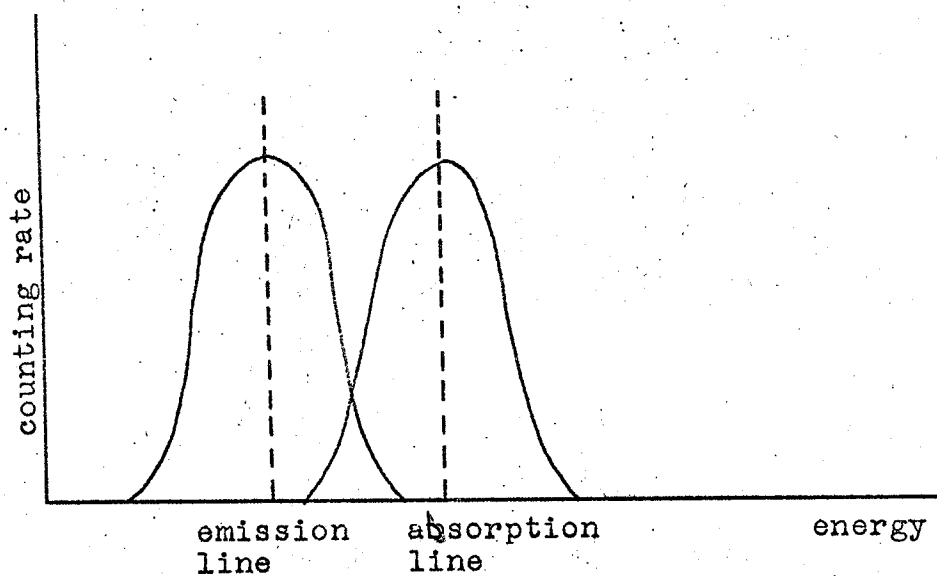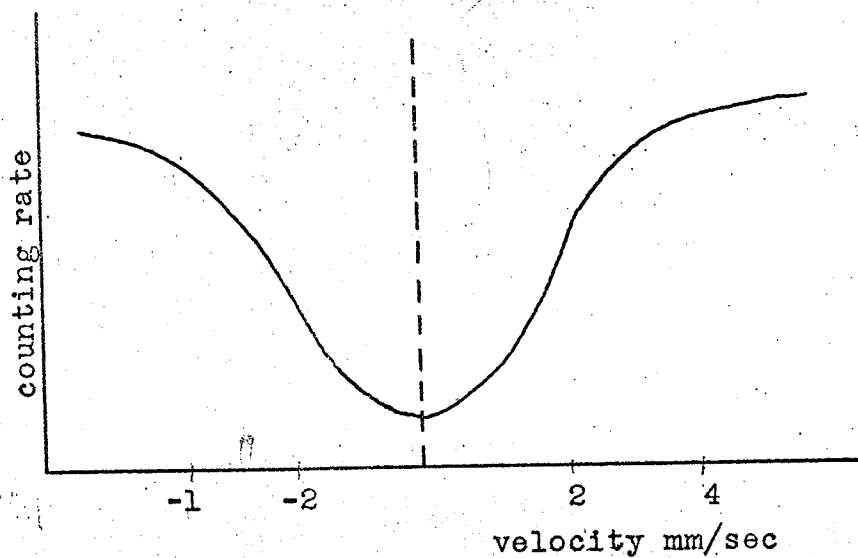FIGURE 1   OVERLAP OF EMISSION AND ABSORPTION LINES

FIGURE 2   MOSSBAUER SPECTRUM

source we get the Mossbauer spectrum (fig. 2). This picture of the emission and absorption lines consisting of very narrow lines holds only if all the emission and absorption processes occur without recoil energy loss. However, in an ordinary crystal only a certain fraction f of the gamma rays are emitted or absorbed without recoil and consequently the line structures are as shown in fig. 3.[4A] The part of the spectrum called the phonon wing corresponds to emission of a gamma ray accompanied by lattice excitation while the sharp line at E corresponds to the recoil free transitions.

The zero-phonon line with which we are concerned in the Mossbauer effect is often split, broadened, and shifted as a result of environment and thermal effects. First, the presence of a magnetic field will produce a splitting of the nuclear levels due to the interaction of this field with the magnetic dipole moment of the nucleus. Consequently a splitting of the zero-phonon line will result.

Second, the nucleus is surrounded and penetrated by a cloud of electronic charge. The nucleus interacts with this charge distribution and the energy of interaction results in a shift of the energy levels of the nucleus, characteristic of the electronic environment, known as the isomer shift. This produces a shift in position of the zero-phonon line of the spectrum.

Third, if the Mossbauer nucleus possesses a quadrupole moment and the symmetry of the crystal is not too high so

FIGURE 3   GAMMA SPECTRUM OF ATOMS

EXHIBITING THE MOSSBAUER EFFECT
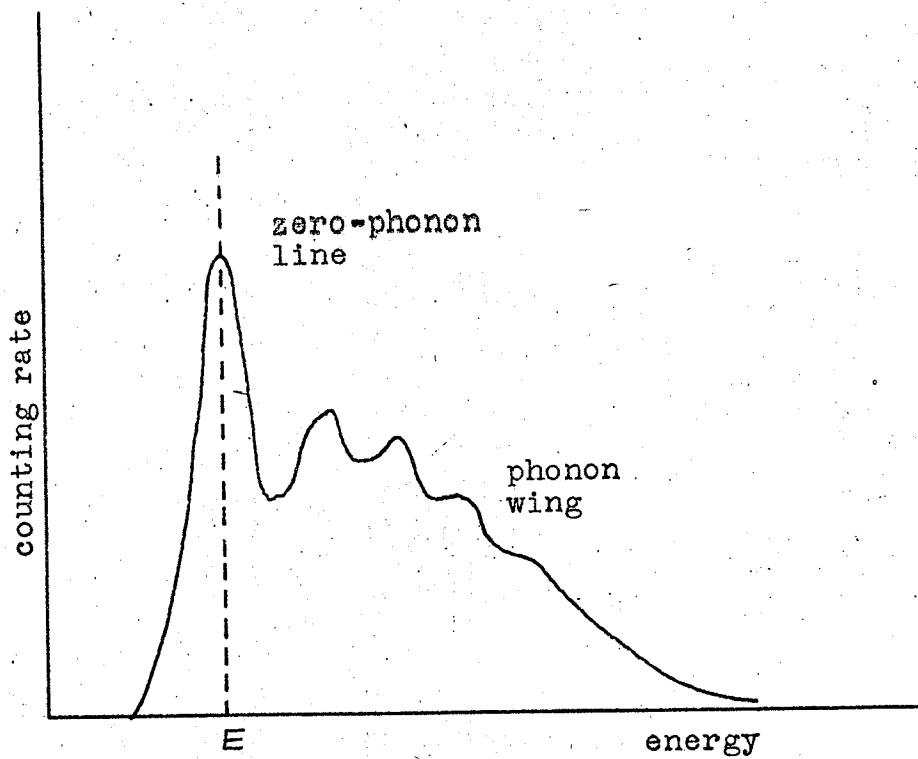
that there is an electric field gradient at the nuclear
site, there will be an interaction between the quadrupole
moment of the nucleus and the electric field gradient. This
will result in a splitting of the nuclear levels and hence
a splitting of the zero-phonon line.

Fourth, thermal effects also produce a change in the
zero-phonon emission and absorption lines. It has been
shown[5] that the Doppler broadening does not have an effect
on the width of the zero-phonon line. However, the second
order Doppler effect does shift this line by[6]

$$\Delta E = \frac{E}{2c^2} \langle v^2 \rangle \qquad (4)$$

Where E = the gamma ray energy

$\langle v^2 \rangle$ = the mean square velocity of the emitting nucleus
and   C = the velocity of light.

If the Mossbauer atoms of a crystal are in different
environments they will experience different electric and
magnetic fields and different electronic distributions
resulting in different interaction energies between these
and the nucleus. This results in different shifts and
splittings of the Mossbauer lines for atoms in different
environments.

A consequence of the splitting and shifting of the
zero-phonon line is that the Mossbauer spectrum may contain
a variety of features. As a simple illustration consider
the Doppler sweeping of an emission line which is split

over an absorption line which is likewise split. If each
of these lines has just two components the resulting
spectrum will have 4 peaks. Hence as the multiplicity of
splitting increases the number of peaks in the Mossbauer
spectrum will increase but not necessarily in a one-to-one
correspondence with the nuclear levels.

2.2   SURFACE MOSSBAUER STUDIES

The application of the Mossbauer effect to the study
of surfaces is in principle straightforward but is ex-
perimentally very difficult.[7] Since the Mossbauer effect
is sensitive to the strength and direction of the lattice
binding forces, the electric and magnetic fields, and the
density of electrons at the nucleus it should be possible
to get information about these quantities for surface atoms
by comparing the Mossbauer spectra for surface atoms
with those for atoms in well-understood bulk configurations.

Before considering how the above quantities affect the
Mossbauer spectrum, consider some of the differences in the
Mossbauer effect between surface and bulk atoms.

The fraction of the gamma rays which are emitted
without recoil is given in general by

$$ f = \sum \left| \langle i | \exp(i \vec{k} \cdot \vec{u}) | i \rangle \right|^2 \qquad (5) $$

where $\vec{k}$ = the wave vector of the emitted gamma ray

$\vec{u}$ = the position vector of the decaying nucleus

and i = the initial (and final) state of the nucleus.

In the harmonic approximation this becomes

$$f = exp\left(-\langle i|(\vec{k}\cdot\vec{u})^2|i\rangle\right) = exp\left(-k^2\langle u_\gamma^2\rangle\right) \qquad (6)$$

where $\langle u_\gamma^2\rangle =$ the thermal mean square displacement of the emitting nucleus along the direction of emission of the gamma ray. Thus if we consider atoms which are in the bulk of the crystal (atom A), on the surface of the crystal (atom B), and in the surface of the crystal (atom C), it is easily seen that f for each of these atoms will be different. Consider figure 4. For atom A, the binding parallel and perpendicular to the surface should be of the same strength in an isotropic crystal, hence $\langle u_\gamma^2\rangle$ and f should be the same in these directions. However, for atoms B and C which are at the surface, f will have different values parallel and perpendicular to the surface. For atom B, $\langle u_\gamma^2\rangle$ will be larger in a direction parallel to the surface if the atom is bound more tightly in a direction into the crystal than along the surface of the crystal. This will result in f being larger in a direction perpendicular to the surface than parallel to the surface. Atom C, on the other hand, is bound on 3 sides by other atoms. Hence it would be expected that $\langle u_\gamma^2\rangle$ out of the crystal is largest and hence f will have its smallest value perpendicular to the surface of the crystal. The strength and direction of the binding of the atoms in the crystal will thus have an effect on $\langle u_\gamma^2\rangle$ and hence will affect f. Also the strength and

FIGURE 4   THREE LOCATIONS OF ATOMS IN A
CRYSTAL UNDERGOING A MOSSBAUER
TRANSITION.
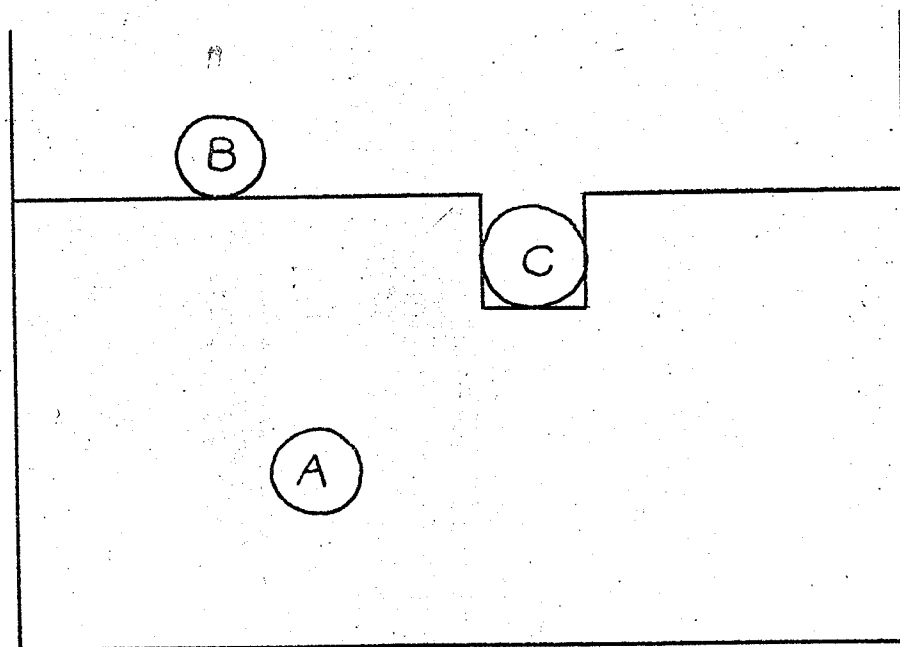
direction of the binding will affect the mean square velocity of the atoms and hence will affect the second order Doppler shift which is given by equation (4).

As mentioned previously a magnetic field will interact with the nuclear dipole moment resulting in a shift of the nuclear levels. Thus by considering the Mossbauer spectra of the surface atoms it should be possible to study the magnetic field at the surface. An electric field in a crystal will distort the electronic charge distribution of the atoms. Thus through a study of isomer shifts the electric field at the surface of the crystal may be found. Associated with the electric field at the surface of the crystal may be an electric field gradient. The interaction between this electric field gradient and the nuclear quadrupole moment will also result in a splitting of the energy levels of the nucleus. As in the case of the electric field, the electric field gradient may be zero inside a crystal of high symmetry (cubic crystal) but due to the break in symmetry at the surface and the distortion of the lattice at the surface a non-zero value for the field may occur there. This investigation is concerned with the electric field gradient at the surface of ionic crystals and with its interaction with the quadrupole moments of Mossbauer atoms on these surfaces.

Although, theoretically surface Mossbauer studies can give useful information about crystal surfaces there are

many experimental difficulties which must be overcome.
First of all, the surfaces under consideration must be
clean and planar since it is difficult enough to interpret
experimental results without the added complication of
impurity atoms and non-planar surfaces. Such inhomogeneous
surroundings would result in different contributions to
the isomeric shifts and line splitting from different
Mossbauer atoms on the surface. Since the Mossbauer
spectrum is formed from the accumulated contributions of
all the Mossbauer atoms in the sample the spectrum would
be broadened and smeared and hence would yield very little
information about the surface.

Godwin[9] has been able to produce relatively clean
surfaces by ultra high vacuum techniques. A high vacuum
is essentual since at a vacuum of 10^{-6} mm of mercury a
monolayer of gas (impurity) can be deposited on a surface
in less than a few seconds and hence the time available
for the experiment is very short. However, at pressures
of 10^{-9} mm of mercury more than 15 minutes is required
for the deposition of a monolayer of impurity gas. Godwin
used pressures as low as 10^{-10} mm of mercury in his
experiments. It should be noted that the attainment and
measurement of such high vacuums is by no means trivial.
During the course of the experiment the temperature of
the surface should be held will below room temperature;
otherwise some of the radioactive Mossbauer atoms will

diffuse to cracks or imperfections in the crystal forming islands. The radioactive atoms which are at these sites will be in a different environment than the other atoms deposited on the crystal surface. Another difficult aspect of these surface experiments is the deposition of the radioactive material on the surface in less than a mono-layer. This difficulty was overcome by Godwin. A further difficulty which arises experimentally is chemical in nature. It has been found that when Fe^{+++} is placed on silica, silica-alumina, and alumina surfaces the same Mossbauer spectra result.[10] This is believed to be due to the fact that the spectra actually arises from finely divided iron oxide rather than isolated Fe^{+++} on the surface. Thus it can be seen that although Mossbauer studies of surfaces hold promise of giving valuable information about the surfaces great difficulties arise in the actual performing of the experiment.

2.3 MODEL OF THE CRYSTAL

At the surface of a crystal the symmetry which is present in the bulk of the crystal is broken. Also it is assumed that the surface atoms are displaced from their regular lattice sites and dipole moments are induced in these atoms. To formulate a model of this distortion imagine a surface created in a crystal without distorting the lattice structure and then allow the surface atoms to relax. Such a model of the distortion of the lattice at

the surface, calculated by Benson, Freeman, and Dempsey,[11] is used in this investigation. (A more restrictive model, which considers the distortion to be confined to the first 2 layers of the crystal, while the present model considers the distortion in the first 5 layers, gave results which were consistent with those of E. G. McRae and C. W. Caldwell Jr.[12]) They considered a sodium chloride type crystal where the energy of interaction between two ions is given by

$$u_{ij} = u_{ij}^o - e_i (\vec{n}_{ij} \cdot \vec{\mu}_i) n_{ij}^{-3} + e_j (\vec{n}_{ij} \cdot \vec{u}_j) n_{ij}^{-3}$$
$$-3 (\vec{n}_{ij} \cdot \vec{\mu}_i)(\vec{n}_{ij} \cdot \vec{u}_j) n_{ij}^{-5} + (\vec{u}_i \cdot \vec{u}_j) n_{ij}^{-3} \tag{7}$$

where $\vec{n}_{ij}$ = the position vector of the jth ion relative to the ith ion and u_{ij}^o = the sum of the Coulomb, dispersive, and repulsive terms and has the form

$$u_{ij}^o = e_i e_j n_{ij}^{-1} - c_{ij} n_{ij}^{-6} - d_{ij} n_{ij}^{-8} + b_{ij} exp(-n_{ij}/\rho)$$

where $e_i e_j n_{ij}^{-1}$ = a Coulomb energy interaction term

$c_{ij} n_{ij}^{-6}$ = a dipole-dipole potential term

$d_{ij} n_{ij}^{-8}$ = a dipole-quadrupole potential term

and $b_{ij} exp(-n_{ij}/\rho)$ = a repulsive term which comes into effect as the ions become close together.

The constants c_{ij} and d_{ij} are van der Waals constants whose values have been calculated by Mayer.[13] He set up a power series in inverse powers of the distance between the ions to represent the potential inside the lattice and then with

the use of assumed absorption curves for the crystals was
able to calculate the van der Waals constants.

The repulsive constant b_{ij} can be written as

$$b_{ij} = b\, f_{ij}\, exp\{(\rho_i + \rho_j)/\rho\} = b\, f_{ij}\, b_i\, b_j$$

where ρ and b are empirically determined constants

ρ_{ij} = the atomic radius

and f_{ij} = the Pauli factors which have values 1.25, 1,
0.75 for $++$, $+-$, and $--$ interactions respectively for all
alkali halides except the lithium halides.[14] Such a form
for the repulsive constant and repulsive term were
assumed[15] and the constants ρ and b were empirically deter-
mined by comparison of calculations using such a potential
to experimental data such as the compressibility of salts.

The other terms in the expression for u_{ij} arise from
a consideration of a dipole in an external electric field.
The potential energy of a dipole $\vec{\mu}$ in an external field $\vec{E}_{ext}$
is given by $-\vec{\mu} \cdot \vec{E}_{ext}$. The electric field produced by a
dipole $\vec{\mu}_j$ is given by the expression

$$3\,\frac{(\vec{n}_{ij} \cdot \vec{\mu}_j)\,\vec{n}_{ij}}{n_{ij}^5} - \frac{\vec{\mu}_j}{n_{ij}^3}$$

Thus the energy of interaction of the dipole moment of the
i^{th} ion with the electric field produced by the dipole
moment of the jth ion is

$$-\vec{u}_i \cdot \vec{E}_{ext}\,(\text{DUE TO } \vec{\mu}_j) = -\frac{3\,(\vec{n}_{ij} \cdot \vec{\mu}_i)(\vec{n}_{ij} \cdot \vec{\mu}_j)}{n_{ij}^5} + \frac{\vec{\mu}_i \cdot \vec{\mu}_j}{n_{ij}^3}$$

Also the field due to the ionic charges is of the form $\dfrac{e_i \vec{n}_{ij}}{n_{ij}^3}$ thus the energy of interaction between the ions with

dipole moments $\vec{\mu}_i$ and $\vec{\mu}_j$ and this field is

$$-\frac{e_i (\vec{n}_{ij} \cdot \vec{\mu}_i)}{n_{ij}^3} + \frac{e_j (\vec{n}_{ij} \cdot \vec{\mu}_j)}{n_{ij}^3} \quad \left(\text{SINCE } \vec{n}_{ij} = -\vec{n}_{ji} \right)$$

This accounts for all the terms, up to and including the

dipole-dipole terms in the expression for the interaction

between 2 ions (equation 7).

In their model Benson, Freeman, and Dempsey (BFD) con-

sidered a semi-infinite crystal where the sites of a

regular NaCl-type crystal were defined by the vector

$\vec{R} = a \left(l \vec{e}_1 + m \vec{e}_2 + n \vec{e}_3 \right)$ where $(\vec{e}_1, \vec{e}_2, \vec{e}_3)$ are the unit vectors

of an orthogonal Cartesian system of axes, a is the distance

between nearest neighbours in the crystal, and (1, m, n) are

a set of integers where

$$-\infty \leq l \leq \infty$$

$$-\infty \leq m \leq \infty$$

$$0 \leq n \leq \infty$$

Successive layers of the crystal are designated by their

n values. Since the lattice deformation at the surface is

assumed to originate because of the imbalance of forces at

the crystal surface BFD assumed that the ions were

displaced only in a direction perpendicular to the surface

of the crystal. They also assumed that a dipole moment was

induced in the surface ions. This distortion was considered

to extend to a distance of 5 atomic layers into the crystal

beyond which the displacement and dipole moment parameters were taken to be zero. The displacements and the induced dipole moments for positive and negative ions in the layer $m = \lambda$ were given by $\Delta_{3\lambda}^{\pm} \vec{\epsilon_3}$ and $\mu_\lambda^{\pm} \vec{\epsilon_3}$ respectively, where $\pm$ refers to ions of charge $\pm \varepsilon$ respectively. To obtain values of $\Delta_{3\lambda}^{\pm}$ and $\mu_\lambda^{\pm}$ corresponding to an equilibrium configuration an expression for the distortion energy was mimimized with respect to these variables. The distortion energy was defined as the difference per ion pair between the energy of the crystal in an arbitrary configuration and the energy in the undistorted configuration. This calculation is described in detail in their paper.[16]

The data obtained from this calculation by BFD was not found to be reliable for all crystals. For one thing no equilibrium configuration could be found for the lithium halides and no explanation was offered why this was so. Furthermore, the data which were calculated for the sodium halide crystals lead to corrections in the surface energy of the crystal which were extremely large and physically unrealistic. The contribution to the surface energy of a crystal from the nth layer of atoms $\Delta\sigma(n)$ was given by

$$\Delta\sigma(m) = \Delta\sigma(\infty) \left[1 - exp(-\gamma m) \right]$$

where γ is a parameter which is an index of the depth of penetration of the relaxation in the surface region. That is, for large γ the surface effects (distortions and

dipole moments) are significant for only a small number of layers from the surface. Since γ is small for the sodium crystals the approximations used in the calculations for these crystals may not be valid. First it was assumed that the distortion of the crystal extended only to the fifth layer into the crystal. However, the induced dipole moments of the ions in the fifth layer of these sodium halides are still quite large and the displacements of the ions are of the same order of magnitude as the displacement of ions in the first layer of other crystals. Also the expression for the distortion energy was arrived at by considering an expansion of the interaction only up to and including dipole-dipole terms. Again this approximation may not be valid because of the large values of the dipole moments which were thus calculated for the sodium halides.

Because of these limitations, we shall consider only the six crystals KCl, KBr, KI, RbCl, RbBr and RbI in our calculations.

CHAPTER THREE

ELECTRIC FIELD GRADIENTS AT ALKALI HALIDE CRYSTAL SURFACES

3.1 INTERACTION ENERGY BETWEEN A NUCLEUS AND ITS SURROUNDINGS

The first term in the expression for the interaction energy between a nucleus in a crystal and its surrounding electronic charge distribution is the isomer shift. This results in a change in position of the nuclear levels.[18] The expression which represents this shift was derived on the assumption of a uniform charge density and a spherical nucleus. When these restrictions are relaxed higher order terms in the interaction energy expression become non-zero. These terms do not shift the nuclear levels but result in a splitting of the levels. To see that this is so first consider the isomer shift. The nucleus is surrounded and penetrated by an electronic charge distribution. The energy of inter- action can be computed classically by considering a uniformly charged spherical nucleus imbedded in a s-electron charge cloud. If there is an electric field present the electron charge density at the nucleus will change and hence there will be an altered Coulomb interaction resulting in a new position of the nuclear level. Thus there is a shift of the level. To see that a splitting results when higher order terms in the interaction energy are considered consider stationary perturbation theory. According to this theory the Hamiltonian describing the system can be expanded as a

power series in a parameter λ

$$H = H_0 + \lambda H_1 + \lambda^2 H_2 + \cdots$$

where H_0 = the unperturbed Hamiltonian

H_1 = the first order perturbation

and H_2 = the second order perturbation

It is assumed that all the eigenvalues and all the eigenstates

of H_0 are known. Also it is assumed that the energy E can

likewise be expanded as a power series in λ. That is

$$E = E_0 + \lambda E_1 + \lambda^2 E_2 + \cdots$$

where E_0 = the energy of the unperturbed system

E_1 = the first order correction to the energy

E_2 = the second order correction to the energy

and E_0, E_1, E_2 are all diagonal matrices.

The following procedure is the standard first order

degenerate perturbation theory.[19] We now arrange the eigen-

values of E_0 so as to bring all the degenerate values

together. Thus E_0 has the form

We now set up a matrix for H_1 with the same basis as that

defining the matrix E_0, mark off H_1 into the same box form

(H_1 need not be zero outside these boxes), and proceed to

diagonalize these boxes. By diagonalizing the sub matrix $H_1^{(n)}$ where

we find its eigenvalues. Thus if $H_1^{(n)}$ was a 3 x 3 matrix there will be 3 eigenvalues (there may still be degeneraries) and hence the level with say $E_0 = c$ may be split into 3 levels.

The second non-vanishing term of the electrostatic interaction of a nucleus with its surrounding electronic charge distribution is the quadrupole coupling (resulting in a splitting of the levels) which is the interaction between the nuclear quadrupole moment and the electric field gradient. This electric field gradient is a 3 x 3 tensor. In an appropriate co-ordinate system this tensor may be reduced to its diagonal form. That is a co-ordinate system is chosen in which there is sufficient symmetry so that cross terms such as $\dfrac{\partial^2 \phi}{\partial x \partial y}$ are zero where ϕ is the scalar potential of the surrounding charge distribution. In such a co-ordinate system the electric field gradient may be specified by 3 components $\dfrac{\partial^2 \phi}{\partial x^2}$, $\dfrac{\partial^2 \phi}{\partial y^2}$ and $\dfrac{\partial^2 \phi}{\partial z^2}$. These 3 components are not unrelated since they must satisfy Laplace's equation in a region of zero charge density.

That is

$$\frac{\partial^2 \phi}{\partial x^2} + \frac{\partial^2 \phi}{\partial y^2} + \frac{\partial^2 \phi}{\partial z^2} = 0$$

Thus there are only 2 independent components of the electric field gradient which are chosen[20] to be

$\frac{\partial^2 \phi}{\partial z^2}$ and N   where $N = \frac{\frac{\partial^2 \phi}{\partial x^2} - \frac{\partial^2 \phi}{\partial y^2}}{\frac{\partial^2 \phi}{\partial z^2}}$ and the components

are chosen so that $\left| \frac{\partial^2 \phi}{\partial z^2} \right| \geqslant \left| \frac{\partial^2 \phi}{\partial x^2} \right| \geqslant \left| \frac{\partial^2 \phi}{\partial y^2} \right|$ and hence $0 \leq \eta \lessgtr 1$

In this study the z-axis is chosen to be perpendicular to the crystal surface and the x and y axes are chosen to be perpendicular to each other and to lie in the surface along the directions to the nearest neighbours. In such a co-ordinate system all the components of the electric field gradient disappear except the diagonal terms because of the symmetry in the x and y directions. Also since we assume that there is distortion of the crystal only in the z direction $\frac{\partial^2 \phi}{\partial x^2} = \frac{\partial^2 \phi}{\partial y^2}$ and consequently $N = 0$. Thus the only component which need be computed to specify the electric field gradient is $\frac{\partial^2 \phi}{\partial z^2}$.

The expression for the interaction energy E_Q between the quadrupole moment of the nucleus and the electric field gradient is given by[21]

$$E_Q = \frac{(eq)Q}{4I(2I-1)} \left[3m_I^2 - I(I+1) \right] \qquad (8)$$

where Q = the nuclear quadrupole moment

    I = the total spin quantum number of the nucleus

    m_I = the quantum number of the projection of the total

        spin in the z direction

and eq = the zz component of the electric field gradient at

the nucleus = $(1 - \gamma_\infty)\dfrac{\partial^2\phi}{\partial_3^2}$ where γ_∞ = the Sternheimer

antishielding factor which will be discussed in the next

section and $\dfrac{\partial^2\phi}{\partial_3^2}$ = the zz component of the electric field

gradient at atomic sites.

In appendix II we have derived an expression for $\dfrac{\partial^2\phi}{\partial_3^2}$

to first order in the small quantities $\Delta_3^{\pm}{}_\lambda$.

$$\frac{\partial^2\phi}{\partial_3^2} = \frac{q}{R^3_{3a}}\left\{-1 + \frac{3n^2}{R^2}\right\} + \frac{3qn\,(\Delta_3)}{R^5_a{}^3}\left\{-3 + \frac{5n^2}{R^2}\right\}$$

$$+ \frac{3np}{R^5_a{}^4}\left\{-3 + \frac{5n^2}{R^2}\right\} + \frac{3p\,(\Delta_3)}{R^5_a{}^4}\left\{3 - \frac{30n^2}{R^2} + \frac{35n^4}{R^4}\right\} \quad (9$$

The two parameters involved in this expression p and Δ_3

are the parameters introduced by BFD[22] to describe the

distortion of the surface atoms' electronic configuration

and their displacement respectively. The induced dipole

moment (p) is not taken to be a first order small quantity

since its value in the sodium halides is of the same order

of magnitude as the dipole moments encountered in free

atoms. However, for the other crystals which were con-

sidered the induced dipole moments may be taken to be first

order small quantities since their values are about an order
of magnitude smaller than the moments induced in the sodium
halides. For other than the sodium halides successive
terms of the series (equation 9) will be as small as or
smaller than the terms which involve both p and (Δz).
However, for the sodium halides, the terms involving both
p and (Δz) may be significant but the calculations for the
sodium halides are not quoted here because it is felt that
the data from BFD for these crystals may be inaccurate (see
the discussion in section 2.3).

3.2 STERNHEIMER ANTISHIELDING FACTORS

A complication arises in the calculation of the electric
field gradient since there are two contributions to it at
the nucleus of the atom under consideration. These two
contributions arise from the charges on distant ions and
from electrons in incompletely filled shells of the atom
itself.

Given a model of point dipole ions as in BFD it is
possible to calculate the electric field gradient at the
atomic sites provided the crystal structure is known. This
is however, not the electric field gradient which acts on
the nucleus. The electric field produced by the ions of
the crystal distort the electronic charge distribution of
the atom under consideration resulting in an additional
contribution to the electric field gradient at the nucleus.

Usually the distortion of the electronic configuration serves
to amplify the electric field gradient due to the distant
charges. As a result a factor $(1-\gamma_{oo})$ known as the
Sternheimer antishielding factor is introduced, where γ_{oo}
is usually negative. These antishielding factors were
first calculated by Sternheimer[23-26] and hence bear his
name. It can be considered that the quadrupole field of
the nucleus induces a quadrupole moment in the electronic
distribution and the combination of this quadrupole moment
and the nuclear quadrupole moment interacts with the
electric field gradient. An equivalent way of viewing this
is to consider that the external electric field distorts the
electronic distribution resulting in an added contribution
to the electric field gradient and it is the combination of
these two contributions to the electric field gradient which
interacts with the quadrupole moment of the nucleus. Das
and Bersohn[27] have shown that these two ways of looking at
the interaction are equivalent.

The antishielding factors were calculated by Sternheimer
in the following manner. First the perturbed wave functions
of the core electrons were calculated. This was done by
solving Schroedinger's equation with an atomic potential and
a perturbation due to the quadrupole moment of the nucleus.
These perturbed wave functions were calculated for the IS,
IP, 2S... etc. closed shells and the quadrupole moment which
is induced in these shells was calculated. Thus by knowing

the total induced quadrupole moment in the electronic
distribution it is possible to calculate the antishielding
factors. The details of such a calculation are given in
reference 24. This procedure corresponds to the first
method described in the preceding paragraph.

A word of caution should be added here. If we consider
an ion inside a crystal, the antishielding factors may not
be those of the free ion. That this could be a large source
of inaccuracy is seen from the fact that the antishielding
factors are critically dependent on the electron distribution
which is liable to change considerably from the free ion to
the crystalline state.

In a review article, Rao[28] suggests that the empirically
calculated antishielding factors for positive ions in alkali
halide crystals are close to the values calculated for free
ions. However, the two values for the negative ions differ
by factors of 2 or 3. Rao also suggests some empirical
values for the antishielding factors for Cl^-, Br^-, and I^-,
which we shall adopt in our estimate of the Mossbauer
quadrupole splitting.

CHAPTER FOUR

CALCULATIONS AND RESULTS

4.1 CALCULATION OF THE ELECTRIC FIELD GRADIENT

The energy of interaction, E_Q, between the nuclear quadrupole moment and the electric field gradient is given by equation 8, with the introduction of the Sternheimer antishielding factor

$$E_Q = (1 - \gamma_\infty)\left(\frac{\partial^2 \phi}{\partial_3^2}\right) Q \left[\frac{3m_I^2 - I(I+1)}{4I(2I-1)} \right] \tag{10}$$

In order to compute the energy of interaction it is necessary to compute the electric field gradient at the surface of the crystal. Because of the particular choice of axes, which were defined earlier, it is necessary to calculate only the zz component of the electric field gradient. This computation was performed with the aid of the IBM 1620 computer at the University of Manitoba at four lattice sites for each of six different crystals. These four sites in the crystal correspond to the position of a positive or negative ion in and on the surface layer of atoms. These lattice sites (A, B, C, and D) are illustrated in figure 5. These sites are offset from the positions the ions would occupy in an infinite crystal since we are considering the surface ions as being displaced by the amounts calculated by BFD.[29]

In order to achieve rapid convergence for $\frac{\partial^2 \phi}{\partial_3^2}$ the summation was carried out by adding the contributions from

FIGURE 5 SITES OF CALCULATION OF ELECTRIC FIELD
         GRADIENT
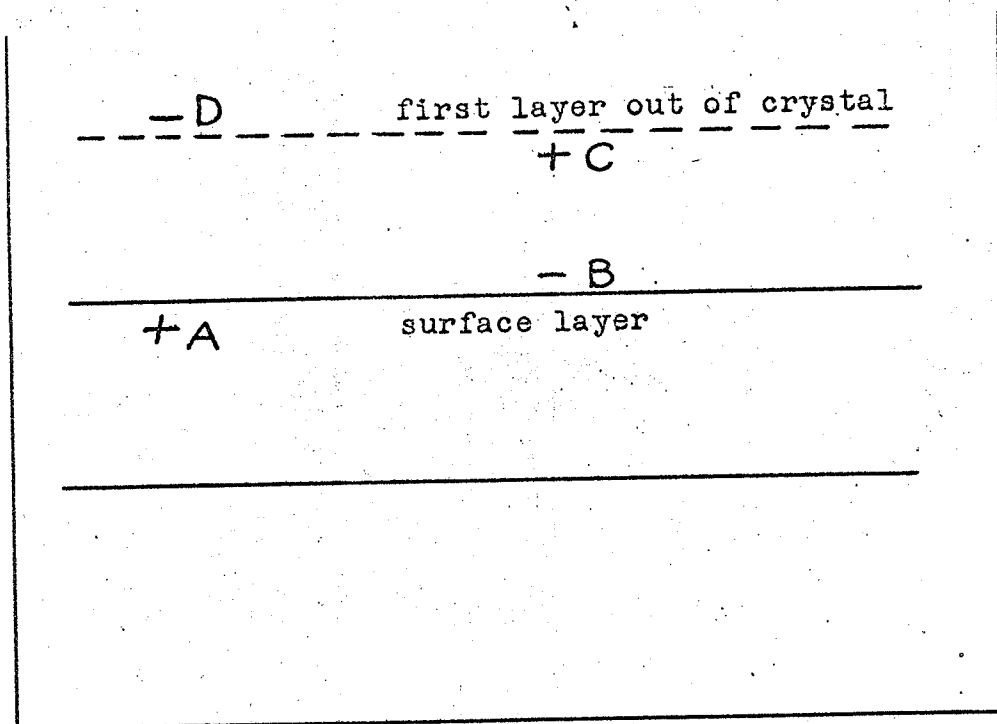
boxes (cubical regions) about the ion in question. This

calculation was taken out to five boxes and it was found

that this was sufficient to give an answer which was accurate

to four significant figures. In fact the main contribution

(88% to 98%) to the electric field gradient was due to the

first box of ions over which the summation was performed.

A program for the evaluation of the electric field gradient

at a negative ion site in the first layer of the crystal

and in the first layer out of the crystal is given in

appendix III.

The contributions to the electric field gradient from

terms depending only on the actual displacement of the ions

and from those depending only on the induced dipole

moments in the ions were calculated separately. The

displacement parameter contribution was given by

$$\frac{3qm\,(\Delta z)}{R^5 a^3}\left\{-3+\frac{5m^2}{R^2}\right\}$$

and the induced dipole moment parameter contribution was

given by

$$\frac{3pm}{R^5 a^4}\left\{-3+\frac{5m^2}{R^2}\right\}$$

The remaining terms of equation 9, except for $\dfrac{-q}{R^3 a^3}$

$+\dfrac{3qm^2}{R^5 a^3}$ which gives the contribution to the

electric field gradient at the surface of an undistorted

crystal, contain both the displacement parameter Δz and

the induced dipole parameter p. But for the six crystals

considered these three terms

$$\frac{3 p^{(\Delta_3)}}{R^5 a^4} \left\{ 3 - \frac{30 m^2}{R^2} + \frac{35 m^4}{R^4} \right\}$$

contribute an amount which only affects the third significant figure.

Table I gives a list of the electric field gradient at the various sites for the six alkali halide crystals, KCl, KBr, KI, RbCl, RbBr, and RbI. This table also includes the contribution to the electric field gradient exclusively from the displacements of the ions and the induced dipole moments. The contribution from terms which depend on both Δz and p are not tabulated, but are included in the final result given in the last column.

4.2 MOSSBAUER QUADRUPOLE SPLITTING

In order to give a measure of the quadrupole splitting it is assumed that the Mossbauer atom I^{129} is placed on the surface of the six crystals considered in this calculation. The reason for choosing I^{129} is that it is the only atom from the group K, Rb, Cl, Br and I which is known to exhibit a sizeable Mossbauer effect. It is reasonable to speculate that the Mossbauer effect may be observed with I^{129} since the fraction of recoilless gamma rays emitted by it is .23 to .29[30] compared to a value[31] of .91 for Fe^{57}, which exhibits the most pronounced Mossbauer effect. Consequently existing detection techniques should suffice in carrying out such an experiment although there would be severe problems

connected with doping the alkali halide surfaces with I^{129}. I^{129} exhibits the Mossbauer effect with the emission of a 26.8 kev. gamma ray.[32] In this transition the total spin quantum number changes from $\frac{5}{2}$ to $\frac{7}{2}$. To get an order of magnitude of the splitting of the Mossbauer line the energy difference between the two levels with total spin quantum number $\frac{5}{2}$ and $m_I = \frac{5}{2}$ and $\frac{3}{2}$ is calculated. From equation 10 we obtain

$$E_Q\left(\frac{5}{2}\right) - E_Q\left(\frac{3}{2}\right) = \left(1-\gamma_\infty\right) Q \frac{\partial^2 \phi}{\partial z^2} \left(\frac{3}{10}\right)$$

The value of 45 is chosen for $\left(1-\gamma_\infty\right)$ [33] and Q is taken to be $\left(-.43 \times 10^{-24}\right)(e)$ cm^2 [34] where e is the electronic charge.

$$\therefore \Delta E_Q = E_Q\left(\frac{5}{2}\right) - E_Q\left(\frac{3}{2}\right) = (45) \frac{\partial^2 \phi}{\partial z^2} \left(-.43 \times 10^{-24}\right)\left(-4.8 \times 10^{-10}\right)\left(\frac{3}{10}\right) \text{ ergs}$$

$$= 17.39 \times 10^{-22} \left(\frac{\partial^2 \phi}{\partial z^2}\right) ev.$$

since 1 erg $= 6.24 \times 10^{11}$ ev.

But since the Mossbauer spectrum is formed by the Doppler sweep of the emission line over the absorption line the splitting is (appendix I)

$$v = c \frac{\Delta f}{f} = c \frac{\Delta E}{E}$$

where E = the energy of the gamma ray

c = the velocity of light

and ΔE = the energy splitting inside the nucleus.

Thus
$$v = \frac{\left(3 \times 10^{10}\right)\left(17.39 \times 10^{-24}\right)}{26.8 \times 10^3} \frac{\partial^2 \phi}{\partial z^2} \frac{cm}{sec}$$

$$= 1.947 \times 10^{-14} \frac{\partial^2 \phi}{\partial z^2} \frac{mm}{sec}$$

TABLE I ELECTRIC FIELD GRADIENT
IN UNITS OF 10^{13} ESU CHARGE/CM^3

crystal (site) in or on surface	undistorted contribution	displacement parameter contribution	dipole parameter contribution	total field gradient
RbCl (−) in	.1.66	−.04	−.08	1.52
(−) out	−1.92	.13	.29	−1.51
(+) in	−1.45	.09	.07	−1.27
(+) out	2.12	−.22	−.26	1.67
RbBr (−) in	1.54	−.04	−.10	1.40
(−) out	−1.59	.09	.29	−1.22
(+) in	−1.17	.14	.08	−0.92
(+) out	1.96	−.24	−.25	1.50
KCl (−) in	1.80	−.06	−.11	1.63
(−) out	−1.93	.12	.31	−1.51
(+) in	−1.36	.17	.08	−1.08
(+) out	2.36	−.32	−.26	1.82
KBr (−) in	1.80	−.06	−.16	1.59
(−) out	−1.75	.11	.36	−1.27
(+) in	−1.07	.30	.12	−0.61
(+) out	2.47	−.47	−.30	1.74
KI (−) in	1.66	−.12	−.20	1.44
(−) out	−1.23	.07	.33	−0.81
(+) in	−0.58	.64	.18	0.32
(+) out	2.29	−.62	−.33	1.39
RbI (−) in	1.37	−.04	−.13	1.24
(−) out	−1.20	.05	.27	−0.87
(+) in	−0.79	.24	.10	−0.41
(+) out	1.78	−.31	−.24	1.25

TABLE II MOSSBAUER QUADRUPOLE SPLITTING

crystal (location on surface)	electric field gradient in units 10^{13} esu ch/cm^3	quadrupole splitting in mm/sec
RbCl (-) in	1.52	.30
(-) out	-1.51	.30
RbBr (-) in	1.40	.27
(-) out	-1.23	.24
KCl (-) in	1.63	.32
(-) out	-1.51	.29
KBr (-) in	1.59	.31
(-) out	-1.27	.25
KI (-) in	1.44	.28
(-) out	-0.81	.16
RbI (-) in	1.24	.24
(-) out	-0.87	.17

On this basis table II gives the estimated splittings of

the Mossbauer spectrum of I^{129} when it is at negative ion

sites in the first layer of the crystal and in the first

layer out of the crystal. $\frac{\partial^2 \phi}{\partial z^2}$ is known at these sites from

table I.

In the future in referring to the different ion sites

at which the electric field gradient is calculated the

following notation shall be used. The location referring

to a positive ion site in the first layer of the crystal

shall be denoted by "(+) in" and the location of a positive

ion site in the first layer out of the crystal shall be

denoted by "(+) out." A similar notation holds for the

negative ions.

4.3 RESULTS

From table I it is seen that the contribution to the

electric field gradient from the dipole parameters and from

the displacement parameters have the same sign, but it is

opposite to the sign of the undistorted contribution.

Consequently, by taking the distortion of the crystal

surface into account the absolute value of the electric

field gradient is decreased from the value calculated

assuming that the surface ions are in bulk configurations.

The correction of the electric field gradient which results

when the distortion associated with the crystal surface is

considered is 8% to 46%. Furthermore, the electric field

gradient at (-) ion sites is positive in the surface

and negative out of the surface. In all except one case, KI, the reverse is true at the (+) ion sites where the electric field gradient is negative in the surface and positive out of the surface. For KI the electric field gradient at both sites is positive. This results from the fact that the undistorted contribution to the electric field gradient is negative and small and as a result the positive contributions from the displacement and dipole parameters are large enough to change the sign of the electric field gradient.

Also it is found that for (-) in and (-) out sites the absolute value of the dipole moment parameter contribution is greater than the absolute value of the displacement parameter contribution by 43% to 80%. However, at the (+) in sites the displacement contribution is greater than the dipole contribution by 20% to 72% while at the (+) out sites the displacement parameter contribution is greater in four cases and less in two cases (RbCl and RbBr).

4.4 DISCUSSION OF RESULTS

A. MOSSBAUER QUADRUPOLE SPLITTING

The quadrupole splittings of the Mossbauer line (.16 to .32 mm/sec), quoted in table II, are small but still measureable. However, an experiment to measure the quadrupole splitting holds little promise of giving information about the BFD model of the surface[35] because of the indeterminacy of the Sternheimer antishielding factors. The value used in this calculation was 45.[36] This estimated value for bulk atoms is considerably smaller than the

value of 138 claculated by Sternheimer[37] for the free iodide
ion. In an actual experiment it is not known to what extent
the surface Mossbauer atoms may be considered free for the
purpose of estimating the Sternheimer factors. Consequently
the Sternheimer factor may be anywhere between 45 and 138.
Because of this large indeterminacy in the Sternheimer
factor the distortion correction to the electric field
gradient is of minor importance because this correction
changes the electric field gradient by 8% to 46% while
the Sternheimer factor is not known to anywhere near this
accuracy.

Such problems involved with the indeterminacy of the
Sternheimer factors are not unique to Mossbauer studies.
Any interaction between an external disturbance and the
nucleus of an atom must consider the perturbation of the
electronic charge distribution of the atom. Nuclear
quadrupole reasonance studies must also consider the
Sternheimer factors of the atoms involved in the
investigation.

Also it may be speculated that a positive Mossbauer
ion such as Fe^{57} may be substituted into one of the
alkali halide crystals considered in this study. Even if
this were possible the splitting would probably not be
detectable since the splittings quoted in table II would be
reduced by a factor of 6 or 7 since the Sternheimer factor
of Fe^{57} is 7.18.[38]

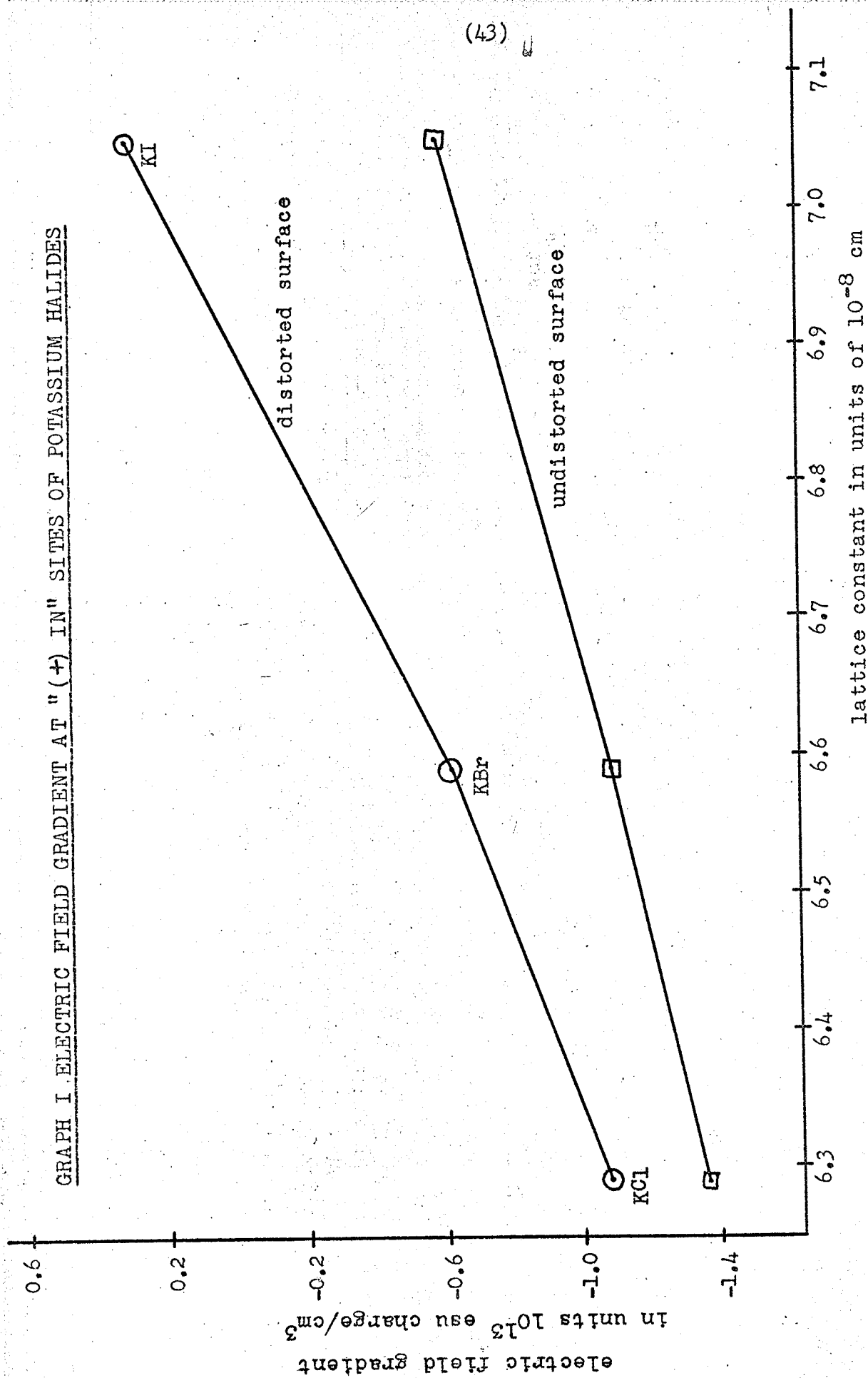## B. ELECTRIC FIELD GRADIENTS (WITHOUT ANTISHIELDING)

It was hoped that a systematic comparison of the electric field gradient taking into account the distortion of the crystal and ignoring the distortion would provide a test of the BFD model[39] of alkali halide surfaces. Consequently plots of G and G_0 versus a were made, where G is the electric field gradient taking into account the distortion of the crystal, G_0 is the electric field gradient ignoring the distortion, and a is the lattice spacing. Values of a were obtained from reference 34. Since $\frac{G - G_0}{G}$ varies from 8% to 46% an experimental test of the BFD model must be able to distinguish between differences in trends which arise from differences in the electric field gradient of less than or equal to 46%. The plots of G vs a and G_0 vs a at the (-) in sites have the same form. The same is true at the (-) out sites. However, these same two plots for the ion sites (+) in and (+) out do show some differences.

When graphs are drawn of G and G_0 versus a for the (-) in, (+) in, and (+) out sites of the rubidium halides it is found that the electric field gradient varies linearly with a and both lines have approximately the same slope. For the (-) out sites, the electric field gradient of the rubidium halides is close but not quite linear in a. On the other hand for the potassium halides the electric field gradient does not vary linearly with a except for the (+) in sites. Here both G and G_0 are close to being linear

with a but the slope in the two cases is different (graph I).
Also at the (+) out sites, although G and G_0 are not linear
with a, least squares lines of G versus a and G_0 versus a
would show a distinct change in slope (graph II). Such a
change in slope of these least squares lines does not show
up when the (-) in and (-) out sites are considered. Thus
it may be possible to test the distortion correction
calculated on the basis of the BFD model by measuring the
electric field gradient at positive ion sites in or on the
surface of rubidium halides, plotting the result against
a, and comparing the slope of the line through these points
to the slopes of the lines in graph I or II.

GRAPH I ELECTRIC FIELD GRADIENT AT "(+) IN" SITES OF POTASSIUM HALIDES

(43)

GRAPH II ELECTRIC FIELD GRADIENT AT "(+) OUT" SITES OF POTASSIUM HALIDES

undistorted surface

KI

KBr

KCl

distorted surface

electric field gradient
in units 10^{13} esu charge/cm^3

lattice constant in units of 10^{-8} cm

(44)
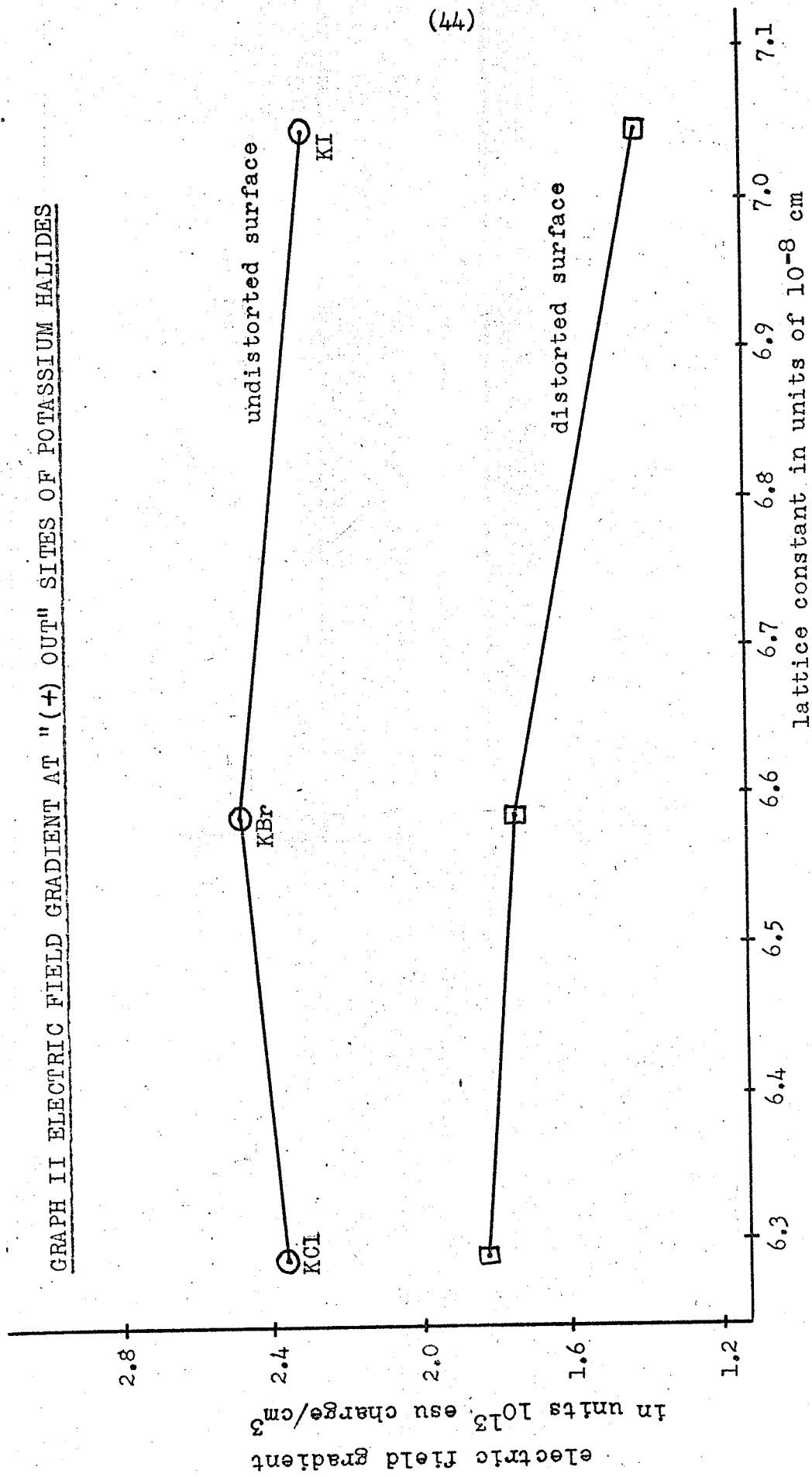
CHAPTER V

CONCLUSIONS

The effect of lattice distortion, displacements and induced dipole moments in the surface ions as calculated by BFD, on the Mossbauer quadrupole splitting at the surface is probably not as large as the effect the surface has on the Sternheimer factors which for I^{129} are known to range from approximately 45 for ions in the bulk of the crystal to 138 for free ions. Thus probably no effective test of the BFD model[40] of alkali halide surfaces can be expected from Mossbauer quadrupole splitting measurements, although the splitting for spectra from I^{129} at (-) in and (-) out sites would be of a measureable magnitude. What would be required would be that the Sternheimer factors for the various sites in the surface be known accurately within limits less than the distortion correction to the electric field gradient so that this distortion correction would be clearly distinguishable in electric field gradient measurements. The same remarks apply to nuclear quadrupole reasonance investigations and to Mossbauer nuclides other than I^{129} which might be used as substitutional probes of the alkali halide surface.

In principle, given accurate Sternheimer factors, it would be possible to test the BFD model of the crystal surface by considering the electric field gradient (efg) at "(+) in" and "(+) out" sites in KCl, KBr, and KI.

Since there is a distinct change in slope of the best fit
straight line plots of G (efg with distortion) versus a
(lattice spacing) and G_0 (efg without distortion) versus
a for these three crystals in both of the above cases,
it may be possible to determine whether the distortion
correction to the electric field gradient is valid by a
comparison of the slope of these theoretical plots with
the slopes of similar experimental plots. Since the
electric field gradient changes sign between in and out
sites we can identify the sites by determining the sign
of the electric field gradient.[41]

The simplest test of the BFD model of alkali halide
surfaces may be given by KI. The distortion contributions
to the electric field gradient due to displacements and
due to induced dipole moments of the ions both have the
same sign, and both tend to reduce the absolute magnitude
of the electric field gradient by amounts varying from
8% to 46%. For the "(+) in" sites of KI this distortion
correction is large enough to change the sign of the electric
field gradient (see table I). This could act as a test of
the BFD model independent of the knowledge of the Sternheimer
factors if a positive ion could be found which when sub-
stituted into the surface of KI produced a measureable
splitting. For if all or most of the Mossbauer probe
nuclei go (or can be placed) into "(+) in" sites in KI,
so that only one split pair of lines is observed, determination

of the direction of the electric field gradient[42] would

give a test of the BFD model of surface distortion.

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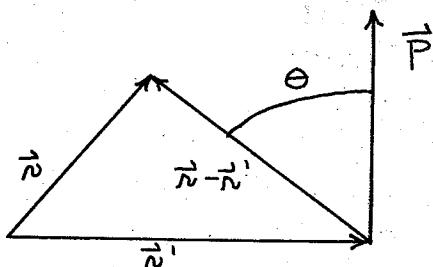   Physics, 25, 441 (1962), p. 496.

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APPENDIX II

ZZ COMPONENT OF ELECTRIC FIELD GRADIENT

The electric field gradient is to be calculated at (a) a positive and negative site in the first layer of the crystal lattice and (b) at a site outside the crystal which corresponds to the position a positive or negative ion would take if it were placed on the crystal surface.

The potential ϕ at these points is given by the sum of two scalar potentials ϕ_1 and ϕ_2 where ϕ_1 is the potential due to point charges and ϕ_2 is the potential due to the dipoles induced in the atoms.

$\phi_1 = \dfrac{q}{|\vec{n}-\vec{n}'|}$ where q = the charge at distance $|\vec{n}-\vec{n}'|$ from the point at which the calculation is being made.

$\phi_2 = \dfrac{\vec{P}\cdot(\vec{n}-\vec{n}')}{|\vec{n}-\vec{n}'|^3}$ where $\vec{P}$ = the dipole moment of the ion and is chosen to be positive in a direction out of the crystal.

$\therefore \phi_2 = \dfrac{|\vec{P}|\cos\theta}{|\vec{n}-\vec{n}'|^2} = \dfrac{(3-3')P}{|\vec{n}-\vec{n}'|^3}$ since $\cos\theta = \dfrac{3-3'}{|\vec{n}-\vec{n}'|}$

(this expression for $\cos\theta$ has the correct sign for all points z^1, either inside or outside the crystal).

$\therefore \phi = \dfrac{q}{|\vec{n}-\vec{n}'|} + \dfrac{P(3-3')}{|\vec{n}-\vec{n}'|^3}$

$$\therefore \frac{\partial \phi}{\partial \mathfrak{z}} = \frac{-q(\mathfrak{z}-\mathfrak{z}')}{|\vec{\pi}-\vec{\pi}'|^3} + \frac{P}{|\vec{\pi}-\vec{\pi}'|^3} - \frac{3P(\mathfrak{z}-\mathfrak{z}')^2}{|\vec{\pi}-\vec{\pi}'|^5}$$

$$\frac{\partial^2 \phi}{\partial \mathfrak{z}^2} = \frac{3q(\mathfrak{z}-\mathfrak{z}')^2}{|\vec{\pi}-\vec{\pi}'|^5} - \frac{q}{|\vec{\pi}-\vec{\pi}'|^3} - \frac{9P(\mathfrak{z}-\mathfrak{z}')}{|\vec{\pi}-\vec{\pi}'|^5} + \frac{15P(\mathfrak{z}-\mathfrak{z}')^3}{|\vec{\pi}-\vec{\pi}'|^7}$$

We will now choose our origin so that $\vec{r} = 0$ $\therefore$ $\vec{\pi} - \vec{\pi}' \rightarrow -\vec{\pi}'$

Also the z-axis is chosen in such a way as to be positive

out of the crystal $\therefore$ $\mathfrak{z}' = -na + (\Delta_{\mathfrak{z}})a$ where a = the lattice

$$-\mathfrak{z}' = na - (\Delta_{\mathfrak{z}})a \qquad \text{spacing}$$

($\Delta_{\mathfrak{z}}$ is chosen positive out of the crystal)

Thus $\dfrac{\partial^2 \phi}{\partial \mathfrak{z}^2} = \dfrac{3q(n-\Delta_{\mathfrak{z}})^2 a^2}{|\vec{\pi}'|^5} - \dfrac{q}{|\vec{\pi}'|^3} - \dfrac{9P(n-\Delta_{\mathfrak{z}})a}{|\vec{\pi}'|^5} + \dfrac{15P(n-\Delta_{\mathfrak{z}})^3 a^3}{|\vec{\pi}'|^7}$

The quantities $|\vec{\pi}'|^{-3}$, $|\vec{\pi}'|^{-5}$ and $|\vec{\pi}'|^{-7}$ can now be expanded in a

power series in (Δz)

$$\vec{\pi}' = la\,\vec{\epsilon}_1 + ma\,\vec{\epsilon}_2 + (-n+\Delta_{\mathfrak{z}})a\,\vec{\epsilon}_3$$

$$= \vec{R}a + (\Delta_{\mathfrak{z}})a\,\vec{\epsilon}_3 \qquad \text{where} \qquad \vec{R} = l\vec{\epsilon}_1 + m\vec{\epsilon}_2 - n\vec{\epsilon}_3$$

and $(\vec{\epsilon}_1, \vec{\epsilon}_2, \vec{\epsilon}_3)$ form an orthogonal set of basis vectors.

Thus
$$|\vec{\pi}'|^{-3} = \left| \vec{R}a + (\Delta_{\mathfrak{z}})a\,\vec{\epsilon}_3 \right|^{-3}$$

$$= \left| R^2 a^2 + 2a^2(\Delta_{\mathfrak{z}})\vec{R}\cdot\vec{\epsilon}_3 + (\Delta_{\mathfrak{z}})^2 a^2 \right|^{-3/2}$$

$$= R^{-3}a^{-3}\left| 1 + \frac{2(\Delta_{\mathfrak{z}})(-n)}{R^2} + \cdots \right|^{-3/2}$$

$$= R^{-3}a^{-3}\left[1 + \frac{3n(\Delta_{\mathfrak{z}})}{R^2} + \cdots \right]$$

Thus to first order in (Δz)

$$|\vec{r}\,'|^{-3} = \frac{1}{R^3 a^3} + \frac{3n(\Delta_3)}{R^5 a^3}$$

Similarly to first order in (Δz)

$$|\vec{r}\,'|^{-5} = \frac{1}{R^5 a^5} + \frac{5n(\Delta_3)}{R^7 a^5}$$

and

$$|\vec{r}\,'|^{-7} = \frac{1}{R^7 a^7} + \frac{7n(\Delta_3)}{R^9 a^7}$$

Thus to first order in (Δz)

$$\frac{\partial^2 \phi}{\partial_3^2} = \frac{g}{R^3 a^3}\left\{-1 + \frac{3n^2}{R^2}\right\} + \frac{3gn(\Delta_3)}{R^5 a^3}\left\{-3 + \frac{5n^2}{R^2}\right\}$$

$$+ \frac{3pn}{R^5 a^4}\left\{-3 + \frac{5n^2}{R^2}\right\} + \frac{3p(\Delta_3)}{R^5 a^4}\left\{3 - \frac{30n^2}{R^2} + \frac{35n^4}{R^4}\right\}$$

The units of p are esu units which are related to debye units, which are quoted in BFD, by 1 debye unit $= 10^{-18}$ esu units.

APPENDIX III

ELECTRIC FIELD GRADIENT AT NEGATIVE ION SITES

```
ZZJOB 5                          1600098 G. RONALD BROWN
ZZFORX52
C          CALCULATION OF ELECTRIC FIELD GRADIENT
C   Z1= DISPLACEMENT OF POSITIVE IONS (+ IS DISPLACEMENT OUT OF CRYSTAL)
C   Z2= DISPLACEMENT OF NEGATIVE IONS (+ IS DISPLACEMENT OUT OF CRYSTAL)
C   P1= MAGNETIC MOMENT OF + IONS (P=+ IF OUT OF CRYSTAL)
C   P2= MAGNETIC MOMENT OF - IONS (P= + IF OUT OF CRYSTAL)
C   SUM4 = CONTRIBUTION DUE TO DISTORTION
C   SUM7 = CONTRIBUTION WITH NO DISTORTION
C   SUM8 = CONTRIBUTION DUE TO POLARIZATION
      DIMENSION Z1(11),P1(11),SUM4(11),Z2(11),P2(11),SUM7(11),SUM8(11)
      DIMENSION SUM11(11)
      DIMENSION SUM20(11)
   62 READ 50,J
   50 FORMAT (I1)
      IF (J-7) 60,61,61
   60 CONTINUE
      READ 30,N2,A,Z1,Z2,P1,P2
   30 FORMAT (I2,E10.4/(10F8.5))
      DO 115 K1=1,2
      SUM =0.0
      TOTAL1=0.0
      TOTAL2=0.0
      TOTAL3=0.0
      IF(K1-2) 101,102,101
  102 DO 105 KT=2,6
      N3=8-KT
      Z1(N3)=Z1(N3-1)
      Z2(N3)=Z2(N3-1)
      P1(N3)=P1(N3-1)
  105 P2(N3)=P2(N3-1)
      Z1(1)=0.0
      Z2(1)=0.0
      P1(1)=0.0
      P2(1)=0.0
  101 CONTINUE
      DO 31 N1=2,N2
      SUM4(N1)=0.0
      SUM7(N1)=0.0
      SUM8(N1)=0.0
```

```
      SUM11(N1)=0.0
      SUM20(N1)=0.0
      DO 21 N=1,N1
      DO 21 L=1,N1
      DO 21 M=1,N1
      AL=L
      AM=M
      AN=N
      IF(N-N1) 19,22,22
  19  IF(L-N1) 20,22,22
  20  IF(M-N1) 21,22,22
  22  IF(K1-2) 106,107,107
 107  IF(N-1) 106,108,106
 108  Q=0.0
      P=0.0
      Z=0.0
      GO TO 12
 106  CONTINUE
      SUM1=AL+AM+AN
      SUM2=SUM1/2.0
      K=SUM2
      AK=K
      IF(AK-SUM2)10,11,11
  10  Q= 4.8022/10.0**10
      Z=Z1(N)
      P=P1(N)
      GO TO 12
  11  Q=-4.8022/10.0**10
      Z=Z2(N)
      P=P2(N)
  12  IF (K1-2) 120,121,121
 120  R2=(AL-1.0)**2+(AM-1.0)**2+((AN-1.0)+Z2(1))**2
      GO TO 122
 121  R2=(AL-1.0)**2+(AM-1.0)**2+((AN-1.0)+Z2(2))**2
 122  CONTINUE
      R= SQRTF(R2)
      AN1= AN-1.0
      PS1= 3.0*Q*AN1**2/(R**5*A**3)
      PS2= 15.0*Q*AN1**3*Z/(R**7*A**3)
      PS3= -9.0*AN1*Z*Q/(R**5*A**3)
      PS4= -Q/(R**3*A**3)
      PS5= 15.0*AN1**3*P/(R**7*10.0**18*A**4)
      PS6= -9.0*AN1*P/(R**5*10.0**18*A**4)
      PS7=-90.0*P*AN1**2*Z/(R**7*10.0**18*A**4)
      PS8= 105.0*P*AN1**4*Z/(R**9*10.0**18*A**4)
```

```
      PS9= 9.0*P*Z/(R**5*10.0**18*A**4)
      SUM3= PS2 + PS3
      SUM6 = PS1 + PS4
      SUM5= PS5 + PS6
      SUM12 = PS7 + PS8 + PS9
      IF(L-1) 13,13,14
   13 IF(M-1) 15,15,16
   14 IF(M-1) 16,16,17
   16 SUM3=2.0*SUM3
      SUM6= 2.0*SUM6
      SUM12 = 2.0*SUM12
      SUM5= 2.0*SUM5
       GO TO 15
   17 SUM3=4.0*SUM3
      SUM6=4.0*SUM6
      SUM5=4.0*SUM5
      SUM12 = 4.0*SUM12
   15 SUM4(N1)= SUM4(N1) + SUM3
      SUM7(N1)=SUM7(N1) +SUM6
      SUM8(N1)=SUM8(N1) +SUM5
      SUM11(N1) = SUM11(N1) + SUM12
   21 CONTINUE
      SUM20(N1)=SUM20(N1)+SUM4(N1)+SUM7(N1)+SUM8(N1)+SUM11(N1)
      SUM= SUM + SUM4(N1)
      TOTAL1=TOTAL1 +SUM7(N1)
      TOTAL2=TOTAL2 + SUM8(N1)
      TOTAL3 = TOTAL3 + SUM11(N1)
      N11= N1-1
      PUNCH 40,N11,SUM4(N1),SUM7(N1),SUM8(N1),SUM11(N1),SUM20(N1)
   40 FORMAT (23H CONTRIBUTION FROM BOX(,I2,3H)= ,E12.6/(28XE12.6))
   31 CONTINUE
      GRANDT=SUM+TOTAL1+TOTAL2+TOTAL3
      PUNCH 41,SUM,TOTAL1,TOTAL2,TOTAL3,GRANDT
   41 FORMAT (22H TOTAL CONTRIBUTION = ,E12.6/(22XE12.6))
  115 CONTINUE
      GO TO 62
   61 CONTINUE
      CALL EXIT
      END
ZZZZ
```