67-9473

WILSON, William Dennis, 1940-
A THEORETICAL INVESTIGATION OF SUBSTITUTIONAL Li^+ IN KCl.

The City University of New York, Ph.D., 1967
Physics, solid state

University Microfilms, Inc., Ann Arbor, Michigan

A Theoretical Investigation of Substitutional Li^+ in KCl

by

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A dissertation submitted to the Graduate Faculty in Physics in partial fulfillment of the requirements for the degree of Doctor of Philosophy, The City University of New York.

1967

This manuscript has been read and accepted for the University Committee in Physics in satisfaction of the dissertation requirement for the degree of Doctor of Philosophy.

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Foreword

It is a pleasure to thank my Thesis Director, Prof. Robert D. Hatcher, for his valuable time and constant encouragement, without which this work would not have been possible. I also wish to thank Dr. G. J. Dienes of Brookhaven National Laboratories and Queens College for his many stimulating discussions and contributions to this work and also for his making the facilities of Brookhaven available to me. I am also grateful to Prof. R. Smoluchowski for originally suggesting the problem. Finally, I wish to express my appreciation to Prof. J. Krumhansl for having arranged for me to visit Cornell University and take part in many interesting discussions with the faculty of the Atomic and Solid State Physics Laboratory.

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Chapter I

Introduction

Recent experiments on impurity-doped alkali halide crystals indicate that certain substitutional ions do not lie at regular ion sites but in some off-center position [1-7]. For example, electrocaloric measurements on KCl:Li indicate that this crystal cools upon adiabatic removal of an electric field. From the measured values of the change in temperature and electric field, assuming the specific heat is that of pure KCl, a Langevin dipole moment of 2.54 D is obtained [1]. Low frequency measurements of the complex dielectric constants of KCl:Li indicate the existence of a dipole moment of the order of 1 D and a barrier height between different orientations of the dipole moment of ~.00lev [2]. These facts indicate that the Li^+ does not occupy a normal K^+ site in KCl but lies in some off-center position as first suggested by Lombardo and Pohl [1].

Stimulated by these first experiments, additional measurements have been made. Microwave measurements of the complex dielectric constant yield the tunneling splitting (caused by the multi-well structure of the potential in which the Li^+ sits) directly as the resonant frequency of absorption to be .81 cm^{-1} [3]. Bogardus and Sack have also measured this tunneling splitting to be .15-.81 cm^{-1} by low frequency techniques [4]. Sound velocity and absorption measurements by Byer, Welsh and Sack [5,6] show the Li^+ in KCl to be displaced in the <111> direction. Nolt and Sievers [7] find a low-lying resonant mode at 40 cm^{-1} in KCl:Li; in KBr:Li [6] this resonant mode absorption is at 17.81 cm^{-1} [8].

The KBr:Li crystal exhibits somewhat different properties : no electrocaloric effect has been observed indicating that the Li^+ may be on-site or in such an off-center position that no orientable dipole moment (in the classical sense) exists.

Substitutional anions in the alkali halides have also been shown to exhibit paraelectric cooling. Lombardo and Pohl [1] have observed an electrocaloric effect in NaBr:F but no such effect was found in KCl:F. Although their preliminary measurements were unsure because of the possibility of unwanted impurities (OH^- in NaBr), the existence of the cooling in NaBr:F has since been firmly established [9].

Several theoretical investigations have been made. Matthew [10] first showed that classical crystal forces are compatible with the off-center nature of small substitutional ions. Bowen, Gomez, Krumhansl and Matthew [11,12] have assumed that the Li^+ in KCl moves in a multiple well harmonic oscillator potential with parameters fitted to the observed order of magnitude of the tunneling splitting and resonant mode. With this model, they were able to obtain the correct magnitude and temperature dependence of the dipole moment and a specific heat showing the observed Schottky anomaly in the region of a few degrees Kelvin. Baur and Salzman [13] showed that in the weak field case the dipole moment is not physically of Langevin type but is the result of transition dipole matrix elements between tunneling multiplet states. The classical dipole moment is obtained in the high field limit when the particle is localized in one of its many wells.

In a published article, [14] we determined the equilibrium configuration about the Li^+ ion in KCl with the defect in the <100> direction. This was done principally to establish that the Li^+ is off-center in KCl and is not inconsistent with the experimental work of Byer, Welsh and Sack [5,6] because relative minima along the <100> direction can be accompanied by absolute minima along the <111> direction. In this thesis, we give details concerning the potential which the Li^+ ion sees as it tunnels between equilibrium positions lending support to the model of Bowen, et al. [11,12] Generally, the method developed by Hatcher and Dienes [15] for an interstitial neutral defect in the alkali halides is employed; a description of the method is given in Chapter II. In Chapter III, the observed off-center position and the magnitude of the tunneling splitting of the Li^+ in KCl is used to improve our knowledge of the repulsive potential between ions. The minimum energy configurations with the Li^+ allowed to relax along the <111>,<110>, and<100> directions and also with the Li^+ fixed at its normal lattice site in both KCl and KBr are determined in Chapter IV. In the same chapter the tunneling splitting one should expect is calculated for KCl using the one-dimensional model of Gomez, et al.[12] and for KBr another one-dimensional model is proposed which is consistent with the experimental facts. Finally, the electronic and ionic contributions to the classical dipole moment (strong perturbing field) are evaluated in Chapter IV.

Chapter V contains the results of a fit of the calculated min-

imum energies to a sixth-power polynomial in x, y, and z. The potential thus determined is examined for minima and other characteristics. In Chapter VI, the effect of uniform hydrostatic pressure is considered and the pressure necessary to put the Li^+ back on site in KCl is estimated. In the same Chapter, the stability of KCl:F, NaBr:F and NaCl:Li are investigated to determine if the small impurity ions lie in off-center positions.

An independent method of examining the off-center direction and distance from the origin is suggested in Chapter VII. This method involves the calculation of the nuclear quadrupole interaction of a Li^+ ion in KCl with the field gradient at its nucleus. The equations determining the first order splitting of satellite lines and second order shifts in the central component from the Larmor frequency are developed from fundamental principles. The field gradients due to the displacement of ions surrounding the defect and the electronic dipoles induced on these ions are calculated with the Li^+ in the three minimum energy configurations found in Chapter IV. In this way, the nuclear magnetic resonance (NMR) spectra can be related to the off-center position of the Li^+ in KCl. No experimental NMR work has yet been done but such measurements may lend support to the conclusions of Byer, Welsh and Sack [5,6].

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Chapter II

Method of Calculation

A. General Remarks

In general, the method of calculation developed by Hatcher and Dienes [1] for neutral interstitial defects in the alkali halides is employed. A point polarizable ion model for the crystal is assumed which neglects any effects due to the finite extent of the ions with one qualification - the overlap repulsion between outer election shells is taken to be of the generalized Huggins-Mayer form.

A Li^+ ion is substituted for a K^+ in KCl and the total energy relative to the perfect lattice is expressed as a function of the displaced position of the defect ion and of the displacement parameters assigned to twenty-six ions surrounding the defect. These parameters describe the ionic relaxations due to the substitutional defect in units of the interionic distance. The energy is then minimized with respect to each of these parameters in an iterative procedure until each parameter is determined to within $\frac{1}{2}\%$ of the interionic separation.

The total energy is written as the sum of the electrostatic (monopole-monopole), polarization (monopole-dipole), dipole-dipole, and repulsive energies relative to the perfect lattice:

$$E_{TOTAL}(\rho_1, \rho_2, \ldots \rho_N) = E_{STAT}(\rho_1, \rho_2, \ldots \rho_N) + E_{POL}(\rho_1, \rho_2, \ldots \rho_N)$$
$$+ E_{dip\text{-}dip}(\rho_1, \rho_2, \ldots \rho_N) + E_{rep}(\rho_1, \rho_2, \ldots \rho_N)$$

Details concerning the number and assignment of parameters will be discussed in Chapter IV.

B. Electrostatic Terms

The electrostatic energy of the crystal containing the defect ion relative to the perfect lattice is given by:

$$E_{STAT} = -\frac{1}{2} \sum_{\substack{ij \\ i \neq j}} \frac{e_i e_j}{|\vec{r}'_{ij}|} + \frac{1}{2} \sum_{\substack{ij \\ i \neq j}} \frac{e_i e_j}{|\vec{r}_{ij}|} \qquad \text{II-1}$$

where

$\vec{r}_{ij} = \vec{r}_i - \vec{r}_j$ = vector distance between ions i and j in their normal positions in a perfect lattice.

$\vec{r}'_{ij} = \vec{r}'_i - \vec{r}'_j$ = vector distance between ions i and j in their relaxed positions.

To facilitate the actual computation of equation II-1, we shall refer to ions which are allowed to relax with capital letters, such as L, M, N. Small letters will be used to refer to all the ions in the crystal. When an ion is in its relaxed position, a prime will be placed on the appropriate index. Using this notation, we can write symbolically,

$$E_{STAT} = \sum_{i'j'} - \sum_{ij} \qquad \text{II-2}$$

Equation II-2 can be simplified by writing,

$$\sum_{i'} = \sum_{N'} + \sum_{k} - \sum_{L}$$

with a similar expression for $\sum_{j'}$. Hence

$$\sum_{i'j'} = \left(\sum_{N'} + \sum_{k} - \sum_{L} \right)\left(\sum_{M'} + \sum_{\ell} - \sum_{M} \right)$$

$$= \sum_{N'M'} + \sum_{LN} - 2\sum_{N'N} + 2\sum_{N'\ell} - 2\sum_{kN} + \sum_{k\ell}$$

The electrostatic energy can then be expressed as

$$E_{STAT} = \sum_{N'M'} + \sum_{LN} - 2\sum_{N'N} + 2\sum_{N'\ell} - 2\sum_{kN} \qquad \text{II-3}$$

The last term in equation II-3 is just the Madelung energy, that is, the electrostatic energy of all the ions which are allowed to relax (in their normal lattice positions) due to all other ions in the crystal in their normal positions. This term is therefore well-known. The first three terms are calculated directly on a high-speed computer; the number of ions allowed to relax was chosen to be 27 : those within a cube of side 3 interionic distances surrounding the defect plus the defect itself.

The remaining term in equation II-3 can be calculated using the Ewald [2] method of summation. It requires knowing the electrostatic potential at a relaxed ion site due to all other ions in the crystal. Derivations of this potential are readily available (references 2,3) so that we shall not duplicate it here. The potential, V(x,y,z), near

a negative ion at the origin, (0, 0, 0), due to all other ions in the crystal at their normal lattice sites is given by:

$$\frac{r_0 V}{e} = -\sum_{H_i} \frac{\exp\left[-\frac{\pi}{4}\sum_i (2H_i-1)^2\right]\left\{B\cos[\pi x(2H_1-1)]\cos[\pi y(2H_2-1)]\cos[\pi z(2H_3-1)]\right.}{\frac{\pi}{4}\sum_i (2H_i-1)^2}$$

$$+\frac{\Phi\left(\sqrt{\pi}\sqrt{x^2+y^2+z^2}\right)}{\sqrt{x^2+y^2+z^2}} - \sum_n{}' \frac{G\left(\sqrt{\pi}\left[(n_1-x)^2+(n_2-y)^2+(n_3-z)^2\right]^{1/2}\right)(-1)^{n_1+n_2+n_3}}{\left[(n_1-x)^2+(n_2-y)^2+(n_3-z)^2\right]^{1/2}} \qquad \text{II-4}$$

where

$$\Phi(x) = \frac{2}{\sqrt{\pi}}\int_0^x e^{-t^2}\,dt$$

and

$$G(x) = 1 - \Phi(x)$$

C. Polarization Terms

The polarization energy is made up of the energy of formation of dipoles due to the existence of an electric field at the relaxed positions of the ions and the energy of interaction of these point dipoles with the electric field. It is given by:

$$E_{POL} = -\frac{1}{2}\sum_i \alpha_i \sum_{\substack{j \\ i\neq j}} \sum_{\substack{k \\ i\neq k}} \frac{e_j e_k\, \vec{r}'_{ij}\cdot\vec{r}'_{ik}}{|\vec{r}'_{ij}|^3\,|\vec{r}'_{ik}|^3} \qquad \text{II-5}$$

where α_i is the electronic polarizability of ion i as determined by Tessman, Kahn, and Schockley [4].

In practice this energy is calculated by dividing the vicinity of the defect into three regions. Region I contains the defect and an additional number of ions, N_1, which are allowed to relax; region II begins at the boundary of region I and extends further out from the defect to include an additional number of ions, N_2, which are not allowed to relax. Region III is tacked on to regions I and II and includes all other fixed ions within a cube of side 9 interionic distances (i.e., excluding regions I and II).

The polarization energy, equation II-5, can also be written

$$E_{POL} = -\frac{1}{2} \sum_i \alpha_i \vec{E}_i^2 \qquad II-6$$

where $\vec{E}_i$ is the electric field at ion i in its final relaxed position due to all other ions in the crystal in their relaxed positions; that is,

$$\vec{E}_i = \sum_j \frac{e_j \vec{r}_{ij}}{|\vec{r}_{ij}|^3}$$

We shall divide the calculation into two parts be defining E_{POL}^{I} as the polarization energy of ions in region I (those allowed to relax), and E_{POL}^{II} as the polarization energy of all ions in region II. We are therefore approximating the total polarization energy by the polarization energy of ions within the outer boundary of region II. We have

$$E_{POL} \simeq E_{POL}^{I} + E_{POL}^{II} \qquad II-7$$

The electric field on any ion in region I was determined by summing contributions due to all ions in regions I, II, and III, that is, due to the relaxations of region I ions (not including the ion in question) and also the fixed ions out to a cube of side 9 interionic distances. The electric field at any ion in region II is given by:

$$E_i^{II} = \sum_{\substack{j \\ \text{region I}}} \frac{e_j \vec{r}'_{ij}}{|\vec{r}'_{ij}|^3} + \sum_{\substack{j \neq i \\ \text{all ions not in region I}}} \frac{e_j \vec{r}_{ij}}{|\vec{r}_{ij}|^3} \qquad \text{II-8}$$

Note that there is no prime on $\vec{r}_{ij}$ for ions not in region I because these ions are not allowed to relax. The second term in equation II-8 can be written,

$$\sum_{\substack{j \neq i \\ \text{all ions not in region I}}} \frac{e_j \vec{r}_{ij}}{|\vec{r}_{ij}|^3} = \sum_{\substack{j \neq i \\ \text{all ions including region I ions in fixed positions}}} \frac{e_j \vec{r}_{ij}}{|\vec{r}_{ij}|^3} - \sum_{\substack{j \\ \text{ions in region I in fixed positions}}} \frac{e_j \vec{r}_{ij}}{|\vec{r}_{ij}|^3} \qquad \text{II-9}$$

The sum over all ions in the crystal (including region I ions in their fixed positions) vanishes by symmetry. Hence equation II-8 becomes

$$E_i^{II} = \sum_{\substack{j \\ I}} \frac{e_j \vec{r}'_{ij}}{|\vec{r}'_{ij}|^3} - \sum_{\substack{j \\ I}} \frac{e_i \vec{r}_{ij}}{|\vec{r}_{ij}|^3} \qquad \text{II-10}$$

and the total polarization energy is

$$E_{POL}^{I} + E_{POL}^{II} = -\frac{1}{2} \sum_{\substack{i \\ I}} \alpha_i \left\{ \sum_{j \neq i} \frac{e_j \vec{r}_{ij}'}{|\vec{r}_{ij}'|^3} \right\}^2$$

$$-\frac{1}{2} \sum_{\substack{i \\ II}} \alpha_i \left\{ \sum_{\substack{j \\ I}} \frac{e_j \vec{r}_{ij}'}{|\vec{r}_{ij}'|^3} - \sum_{\substack{j \\ I}} \frac{e_j \vec{r}_{ij}}{|\vec{r}_{ij}|^3} \right\}^2 \qquad \text{II-11}$$

In this way, the energy of ions in the smallest region (I) is calculated by including 729 ions; the energy of ions in region II depends only on the ions in region I.

In practice, 26 ions plus the defect are allowed to relax; 66 additional ions are in region II making a total of 93 ions which contribute to the total polarization energy. The number in region II was determined by trial and error in order to determine the polarization energy to within $\sim$ .0001 ev.

D. Dipole-Dipole Energy

In calculating the electric field at an ion i we have neglected the field due to dipoles on all other ions. This additional field on an ion changes the electronic dipole on the ion which in turn changes the field and dipole on another ion. Hence an iterative procedure is required to calculate exactly the effects of dipoles on all ions. Consider two ions i and j separated by a distance $\vec{r}_{ij}$ directed from i to j and having charges e_i and e_j and polarizabilities α_i and α_j. The field at each ion due to the charge on the other is

$$\vec{E}_i = \frac{e_j \vec{r}_{ij}}{|\vec{r}_{ij}|^3} \quad ; \quad \vec{E}_j = \frac{e_i \vec{r}_{ij}}{|\vec{r}_{ij}|^3}$$

These fields produce dipoles $\alpha_i \vec{E}_i$ and $\alpha_j \vec{E}_j$ on each ion. The field on each ion due to the dipole on the other is given by

$$\vec{E}_i' = \frac{3\vec{r}_{ij} \cdot (\vec{r}_{ij} \cdot \alpha_j \vec{E}_j)}{|\vec{r}_{ij}|^5} - \frac{\alpha_j \vec{E}_j}{|\vec{r}_{ij}|^3} \qquad \text{II-12}$$

with a similar expression for $\vec{E}_j'$. The total field on each ion is then $\vec{E}_i + \vec{E}_i'$ and $\vec{E}_j + \vec{E}_j'$. This new field produces dipoles $\alpha_i(\vec{E}_i + \vec{E}_i')$ and $\alpha_j(\vec{E}_j + \vec{E}_j')$ on each ion which in turn change the fields on each ion. Finally, we can write the field on each ion as

$$\vec{E}_i^{final} = \vec{E}_i + \vec{E}_i' + \vec{E}_i'' + \cdots\cdots$$

$$\vec{E}_j^{final} = \vec{E}_j + \vec{E}_j' + \vec{E}_j'' + \cdots\cdots$$

The polarization energy is then

$$E_{pol} = -\frac{1}{2} \sum_i \alpha_i \left[\vec{E}_i^{final} \right]^2$$

Generalizing to the actual case of a crystal containing many ions, some of which are allowed to relax, we see that equation II-6 includes only the zeroth order terms in E_i^{final}. If we include first order terms also,

$$E_{pol} = -\frac{1}{2} \sum_i \alpha_i (\vec{E}_i + \vec{E}_i')^2 \qquad \text{II-13}$$

or

$$E_{POL} = -\frac{1}{2}\sum_i \alpha_i \vec{E}_i^{\,2} - \frac{1}{2}\sum_i \alpha_i \vec{E}_i'^{\,2} - \sum_i \alpha_i \vec{E}_i \cdot \vec{E}_i'$$

II-14

The first term in equation II-14 we have already calculated. The last term can be written, using equation II-12 summed over all ions j,

$$-\sum_i \alpha_i \vec{E}_i \cdot \vec{E}_i' = \frac{1}{2}\sum_{\substack{i,j \\ i \neq j}} \alpha_i \alpha_j \left\{ \frac{\vec{E}_i \cdot \vec{E}_j}{|\vec{r}_{ij}'|^3} - \frac{3(\vec{r}_{ij}' \cdot \vec{E}_i)(\vec{r}_{ij}' \cdot \vec{E}_j)}{|\vec{r}_{ij}'|^5} \right\}$$

II-15

It is now clear that equation II-15 is the dipole-dipole energy of interaction. That is, including this energy term is equivalent to including the larger part of the first iteration in the calculation of the electric fields due to dipoles on all ions. The second term in II-14 is small and is neglected.

In actual practice, the dipole-dipole energy, equation II-15, is computed for all ions in regions I and II.

E. Repulsive Energy

Because of the difficulties involved in a complete quantum mechanical treatment of a crystal such as KCl, the repulsive interactions have been determined empirically. Phenomenological potentials containing parameters which have been fit to such measured quantities as the lattice constant and compressibility have appeared in the literature [5-9]. Tosi and Fumi [9] have analyzed the various

forms of potentials and suggest the use of the generalized Huggins-Mayer form:

$$V_{ij} = b\, c_{ij}\, e^{(R_i + R_j)/\rho}\, e^{-r_{ij}/\rho}$$

where b is a constant common to all alkali halides, the c_{ij}'s are the Pauling coefficients[5], R_i and R_j are the "basic radii" of the ions, and ρ is a hardness parameter which varies from salt to salt. (In this thesis, σ will denote the hardness parameter when the defect ion is involved.) The parameters were determined by Tosi and Fumi[9] by a least squares fit to the room temperature values of the lattice constant, compressibility and coefficient of linear expansion.

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Chapter III

Determination of Repulsive Parameters

One of the difficulties encountered in the use of a Born-Mayer type repulsive potential is that the fitting of the parameters is made at the equilibrium interionic distance, r_0, so that one cannot be sure of interactions when the ions move any appreciable distance away from their normal sites. Tharmalingam and Lidiard [1] have used the Born-Mayer-Verwey potential [2] in their calculations on the migration of vacancy pairs. This potential takes the Born-Mayer form for interionic distances larger than r_0 and the form $A + B r^{-12}$ for separations less than r_0. The parameters A and B are determined by the continuity of the potential and its derivative at r_0. (This, of course, leaves the second derivative discontinuous.) The increased hardness at small separations proved to agree better with the experimental activation energies for divacancy migration.

Another difficulty with the use of phenomenological potentials occurs in substitutional impurity calculations; the problem is in the choice of interactions involving the defect. Tosi and Doyama [3] in their recent treatment of impurity-vacancy complexes with such impurities as KCl:Na assumed the interactions with the Na^+ to be the same as in NaCl. This neglects effects caused by the different environment of the Na^+; that is, the Na^+ wave function, and hence the Na^+-Cl^- interaction is distorted by the fact that the second nearest neighbors are K^+ ions at a greater distance from the defect than the Na^+-Na^+ second nearest neighbor distance in NaCl. More important is the fact that the Na^+-Cl^-

interaction, which is determined by the usual Huggins-Mayer fitting procedure, is known only at the interionic separation in NaCl (2.820 Å). At the interionic distance in KCl (3.147Å), this interaction is not well known. Despite these complications, the Tosi and Doyama assumption can serve as a useful first approximation.

An additional problem is that the van der Waals coefficients, which were originally calculated by Mayer [4], are not very accurately known: Hajj [5] has recently recalculated them with disagreements by as much as a factor of 4 from Mayer's values.

The evaluation of the repulsive parameters has usually been made using room temperature values of the physical quantities involved. The changes in these parameters at low temperatures is not well known because of a lack of low temperature data on some of the alkali halides. MacDonald [6] has recently calculated the force constant for the Li^+ in KCl using the Born-Mayer form of repulsive interaction. The force constant for KCl and LiCl, in both cases evaluated at the lattice spacing for KCl, was calculated at room temperature and 0° K. It was found that there is a greater softening of the force constant at 0° K than at room temperature.

In the KCl:Li case, we chose the Tosi-Fumi values of the repulsive parameters (reported in their first set of data) for the generalized Huggins-Mayer form for interactions between the ions of the host lattice. As a first approximation, we assumed that interactions involving the defect ion would be as for LiCl. We also included the dipole-dipole and

dipole-quadrupole van der Waals terms, taking the coefficients from Mayer [4]. We then allowed the Li^+ to relax along the <110> and <111> directions and determined the minimum energy configurations using 24 and 18 displacement parameters respectively. It was found that the <110> direction was energetically preferred by .12ev (E(111)= -1.37ev, E (110)= -1.49ev) in disagreement with experiment [8]. Subsequently, we deleted the van der Waals terms because of their uncertainty but this did not appreciably change the result. Indeed, we obtained the same values for the energies in the <111> and <110> directions (to three significant figures) but the values of the displacement parameters were different. In all our further work, we neglected the van der Waals terms.

In keeping with our earlier arguments, we then varied the hardness parameter, σ, for interactions involving the defect from its LiCl value of .342 Å to .317 Å at which value the <111> direction was preferred by .0073ev.

Independent of the value of σ, we found the barrier between the <111> and the <100> configurations to be an order of magnitude higher than that between the <111> and <110>; hence, the barrier for tunneling splitting is across a (110) plane between equivalent <111> directions and, for σ=.317Å is .0073ev. Although we can further vary σ, and therefore the barrier height, we shall find (Chapter IV) that we obtain reasonable agreement with the experimental value of the tunneling splitting if the barrier height is $\sim$.007ev and a one-dimensional model of a

double harmonic oscillator is used. It is to be emphasized, however, that if the three-dimensional model of Bowen, et al [9] is solved using our potential (Chapter V) for the Li^+ in KCl, the value of σ can be further adjusted to obtain agreement with experiment. At this time it is not clear how valuable such a lengthy process of fixing the value of σ exactly would be; the qualitative features of the potential are known and a physical explanation of the experimental results has been given.

It is to be noted that using the Tosi-Fumi potential for the defect ion and the halide, chosen on the basis of a pure crystal (the Tosi and Doyama approximation), puts the Li^+ in an off-center position; varying σ only affects the preferred direction. The change in σ is such as to further soften the repulsive interaction with the defect ion. It is also recognized that this is not a unique potential; varying other parameters may lead to the same result.

For convenience, the repulsive parameters determined by various authors for a generalized Huggins-Mayer form of potential have been listed in Table I along with the adjusted Tosi-Fumi (ATF) potential we finally adopted. The same parameters are used in the appropriate Born-Mayer-Verwey (BMV), Huggins-Mayer-Verwey (HMV), and Tosi-Fumi-Verwey (TFV) potentials. The criterion for stability of the Li^+ at the normal lattice site is the determinant of a matrix W, defined by Hatcher and Dienes [10]. W is the matrix of the second-order coefficients in a Taylor expansion of the energy as a function of the

TABLE I

REPULSIVE PARAMETER	BORN-MAYER BM	HUGGINS-MAYER HM	TOSI-FUMI TF	ADJUSTED TOSI-FUMI ATF
b in 10^{-12} erg/molecule	.229	1.0	.338	.338
R_{Li+} in Å	.78	.475	.816	.816
R_{K+}	1.33	1.185	1.463	1.463
R_{Cl-}	1.81	1.475	1.585	1.585
ρ	.345	.345	.337	.337
σ	.345	.345	.342	.317
r_0	3.137	3.13	3.147	3.147

TABLE II

HOST LATTICE:DEFECT	POTENTIAL EMPLOYED	$\|W\|$
KCl:Li	TFV	6.45×10^5
KCl:Li	HMV	2.56×10^5
KCl:Li	BMV	4.84×10^5
KCl:Li	ATF	-1.65×10^5

displacement parameters. That is,

$$dE = \sum_{i=1}^{N} \frac{\partial E}{\partial p_i} dp_i + \frac{1}{2} \sum_{i,j=1}^{N} \frac{\partial^2 E}{\partial p_i \partial p_j} dp_i dp_j > 0$$

for stability. Since each of the first order derivatives vanishes at an extremum, we are left with a quadratic form in dp_i dp_j . The condition that a quadratic form be positive definite is that the determinant of the matrix of the coefficients, W, as well as all the principal minors, be greater than zero. A positive value of $|W|$ indicates stability, or, in this case, that the Li^+ is on-site (all principal minors were also calculated but are not tabulated).

Table II contains the $|W|$ values for Verwey-type potentials using the Born-Mayer, Huggins-Mayer, and Tosi-Fumi repulsive parameters with the ions surrounding the Li^+ (fixed at the origin) having been allowed to relax to their minimum energy positions. Clearly, regardless of the choice of repulsive parameters, the $A + Br^{-12}$ form for small separations leads to an on-site position for Li^+ in KCl in sharp disagreement with experiment.

Figure I is a plot of some of the repulsive potentials tested: the Tosi-Fumi potential (TF) and the further softening due to our adjustment of σ (ATF). The BMV potential is shown to be considerably harder than the potentials employed. The $K^+ - Cl^-$ interaction is also shown on the same graph for comparison.

For KBr:Li, the hardness parameter was chosen as a first approx-

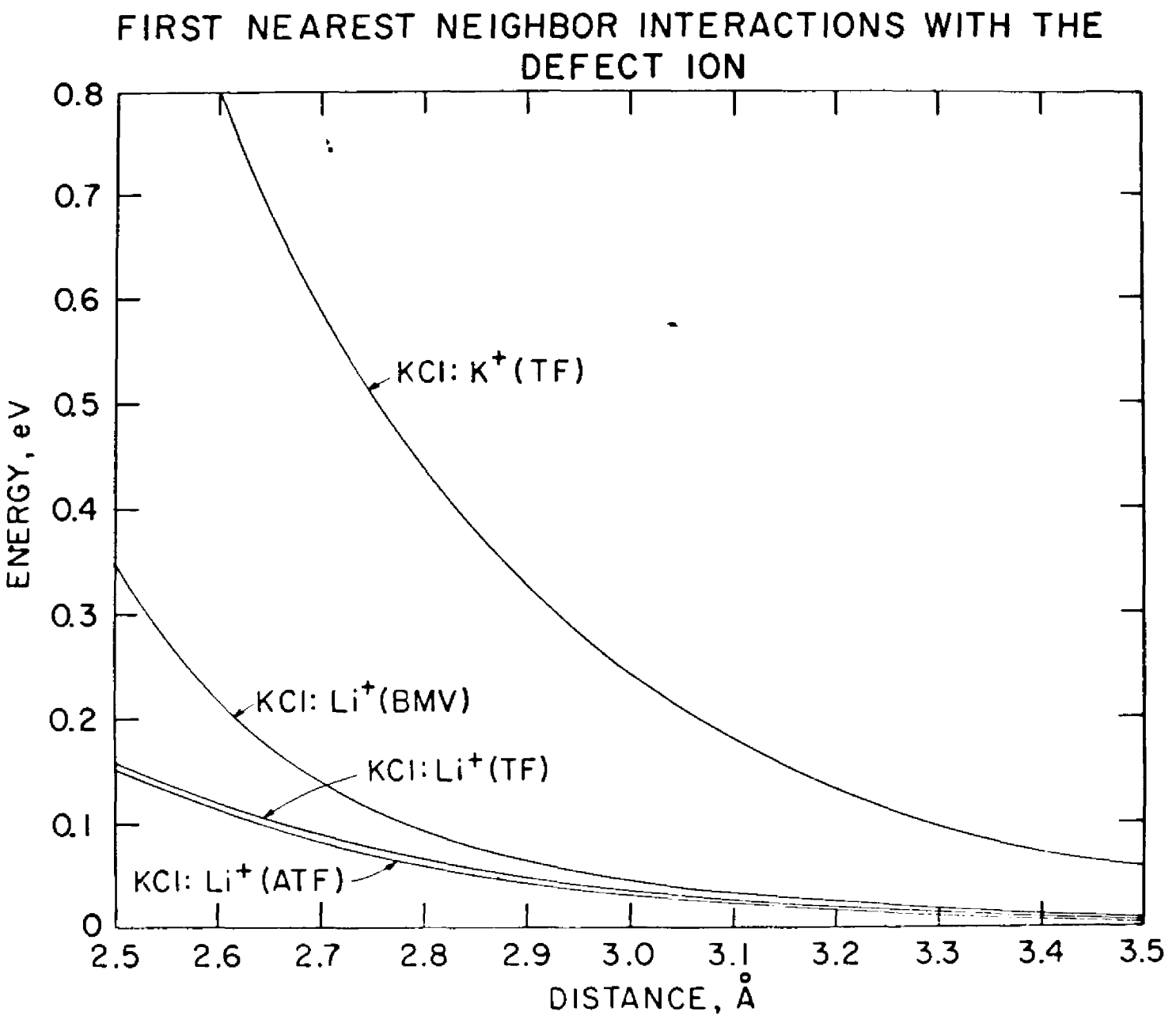
FIRST NEAREST NEIGHBOR INTERACTIONS WITH THE DEFECT ION
ENERGY, eV
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
KCl: K+ (TF)
KCl: Li+ (BMV)
KCl: Li+ (TF)
KCl: Li+ (ATF)
2.5
2.6
2.7
2.8
2.9
3.0
3.1
3.2
3.3
3.4
3.5
DISTANCE, Å

FIG. I

imation, to be lower than the LiBr value by the same percentage as in the KCl:Li case. Hence was given the value .327Å instead of the LiBr value of .353Å.

References - Chapter III

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Chapter IV

Minimum Energy Configurations and Models

A. Assignment of Parameters

It was found that 15, 18 and 24 displacement parameters were required to describe the configurations with the Li^+ allowed to move along the <100>, <111>, and <110> directions, respectively, in order to insure that the calculation is not biased by assumptions of symmetry. Actual calculations showed that further relaxation of the symmetry did not influence the results. Table III contains the details of the actual assignments.

Table IV contains the values of all parameters assigned for the <100>, <111>, and <110> configurations for Li^+ in KCl and KBr and the contributions to the total energy in each case. E_{STAND} in the table refers to the energy necessary to replace the K^+ by an Li^+ ion in the rigid lattice. In all cases, the adjusted Tosi-Fumi potential (ATF) was used.

The <111> configuration has the lowest energy for the KCl:Li case and the minimum position was determined to be (.213,.213,.213) in units of the interionic distance. The positions of the defect ion in the <110> and <100> minimum energy configurations for KCl:Li are (.261,.261,0.) and (.280,0.,0.) respectively. In KBr, the results are very similar except that the <111> and <110> configurations are of almost equal energies. In both cases, the energy of the <100> con-

TABLE III

IONIC COORDINATES IN PERFECT LATTICE	PARAMETERS ASSIGNED to (111) CASE	PARAMETERS ASSIGNED to (110) CASE	PARAMETERS ASSIGNED to (100) CASE
0,0,0	P_1, P_1, P_1	$P_1, P_1, 0$	$P_1, 0, 0$
1,0,0	$-P_2, P_3, P_3$	$-P_2, P_3, 0$	$-P_2, 0, 0$
-1,0,0	P_7, P_8, P_8	$P_4, P_5, 0$	$P_3, 0, 0$
0,1,0	$P_3, -P_2, P_3$	$P_3, -P_2, 0$	$P_4, -P_5, 0$
0,-1,0	P_8, P_7, P_8	$P_5, P_4, 0$	$P_4, P_5, 0$
0,0,1	$P_3, P_3, -P_2$	$P_7, P_7, -P_6$	$P_4, 0, -P_5$
0,0,-1	P_8, P_8, P_7	P_7, P_7, P_6	$P_4, 0, P_5$
1,1,0	$-P_5, -P_5, P_6$	$-P_8, -P_8, 0$	$-P_6, -P_7, 0$
-1,1,0	$P_9, -P_{14}, P_{15}$	$P_9, -P_{16}, 0$	$P_8, -P_9, 0$
1,-1,0	$-P_{14}, P_9, P_{15}$	$-P_{16}, P_9, 0$	$-P_6, P_7, 0$
-1,-1,0	P_{10}, P_{10}, P_{16}	$P_{10}, P_{10}, 0$	$P_8, P_9, 0$
1,0,1	$-P_5, P_6, -P_5$	$-P_{11}, P_{17}, -P_{18}$	$-P_6, 0, -P_7$
-1,0,1	$P_9, P_{15}, -P_{14}$	$P_{12}, P_{19}, -P_{20}$	$P_8, 0, -P_9$
1,0,-1	$-P_{14}, P_{15}, P_9$	$-P_{11}, P_{17}, P_{18}$	$-P_6, 0, P_7$
-1,0,-1	P_{10}, P_{16}, P_{10}	P_{12}, P_{19}, P_{20}	$P_8, 0, P_9$
0,1,1	$P_6, -P_5, -P_5$	$P_{17}, -P_{11}, -P_{18}$	$P_{11}, -P_{10}, -P_{10}$
0,-1,1	$P_{15}, P_9, -P_{14}$	$P_{19}, P_{12}, -P_{20}$	$P_{11}, P_{10}, -P_{10}$
0,1,-1	$P_{15}, -P_{14}, P_9$	$P_{17}, -P_{11}, P_{18}$	$P_{11}, -P_{10}, P_{10}$
0,-1,-1	P_{16}, P_{10}, P_{10}	P_{19}, P_{12}, P_{20}	P_{11}, P_{10}, P_{10}
1,1,1	$-P_4, -P_4, -P_4$	$-P_{13}, -P_{13}, -P_{21}$	$-P_{12}, -P_{13}, -P_{13}$
1,1,-1	$-P_{11}, -P_{11}, P_{18}$	$-P_{13}, -P_{13}, P_{21}$	$-P_{12}, -P_{13}, P_{13}$
1,-1, 1	$-P_{11}, P_{18}, -P_{11}$	$-P_{14}, P_{22}, -P_{23}$	$-P_{12}, P_{13}, -P_{13}$
-1,1,1	$P_{18}, -P_{11}, -P_{11}$	$P_{22}, -P_{14}, -P_{23}$	$P_{14}, -P_{15}, -P_{15}$
1,-1,-1	$-P_{17}, P_{12}, P_{12}$	$-P_{14}, P_{22}, P_{23}$	$-P_{12}, P_{13}, P_{13}$
-1,1,-1	$P_{12}, -P_{17}, P_{12}$	$P_{22}, -P_{14}, P_{23}$	$P_{14}, -P_{15}, P_{15}$
-1,-1,-1	$P_{12}, P_{12}, -P_{17}$	$P_{15}, P_{15}, -P_{24}$	$P_{14}, P_{15}, -P_{15}$
-1,-1,-1	P_{13}, P_{13}, P_{13}	P_{15}, P_{15}, P_{24}	P_{14}, P_{15}, P_{15}

TABLE IV

PARAMETER AND ENERGY IN e.v.	KCℓ:Li (111)	KCℓ:Li (110)	KCℓ:Li (100)	KBr:Li (111)	KBr:Li (110)	KBr:Li (100)
1	.213	.261	.280	.200	.256	.270
2	.099	.109	.120	.094	.094	.110
3	.035	.045	-.025	.024	.040	-.015
4	-.006	-.029	.015	0.0	-.024	.010
5	-.012	.001	.020	-.004	.001	.025
6	-.004	-.009	.025	-.004	.001	.025
7	-.033	.012	-.035	-.022	.012	-.030
8	.005	-.026	.005	.004	-.021	.005
9	-.009	-.025	.020	-.012	-.025	.020
10	.012	.011	.010	.012	.006	.010
11	-.003	.021	-.010	-.004	.021	-.010
12	.008	.010	-.005	.008	.010	-.005
13	0.0	-.005	.005	-.004	-.005	.005
14	.031	-.007	0.0	.028	-.007	0.0
15	-.001	0.0	0.0	0.0	0.0	0.0
16	-.005	.038		-.004	.033	
17	-.007	-.005		-.008	0.0	
18	.004	-.020		.004	-.020	
19		-.009			-.004	
20		.016			.016	
21		0.0			0.0	
22		.007			.007	
23		.008			.003	
24		-.005			-.005	
E_{stat}	-1.1163	-1.2907	-1.0263	-0.8342	-1.0028	-0.7960
$E_{p\emptyset L}$	-0.5203	-0.7486	-0.7232	-0.5528	-0.7645	-0.6900
$E_{dip-dip}$	0.0536	0.0363	-0.0420	0.0774	0.0592	-0.0303
E_{rep}	1.0512	1.4785	1.3589	0.8639	1.2633	1.1404
E_{stand}	-0.8095	-0.8095	-0.8095	-0.7358	-0.7358	-0.7358
E_{tot}	-1.3413	-1.3340	-1.2421	-1.1815	-1.1806	-1.1117

figuration is an order of magnitude higher than that of the <110> position.

It should be mentioned that the <100> case, which we found in our preliminary calculations [1] to require a potential barrier to prevent one of the ions from "running away" to an unreasonable position, no longer required this barrier when the additional displacement parameters were employed. Incidentally, the use of a larger number of parameters only slightly affects the total minimum energy; however it greatly affects the minimum position of the Li^+ along the <100> axis and the constituents of the total energy. As a check on the degree of freedom of the relaxed ions, we calculated the <100> configuration using 45 parameters and obtained a minimum total energy of -1.2383 ev (compared to the 15 parameter calculation of Table IV) with the displacement parameters well behaved. However, we did not perform the last iteration in our minimization procedure and this explains the slightly higher energy of the 45 parameter test case.

B. Tunneling Splitting

For the KCl:Li case, following Gomez, et al. [3], we assumed the simple model of a double harmonic oscillator having a potential

$$V = \begin{cases} V_A = \frac{1}{2} m \omega^2 (x-t)^2 & x > 0 \\ V_B = \frac{1}{2} m \omega^2 (x+t)^2 & x < 0 \end{cases} \qquad \text{IV-1}$$

as shown by the solid lines in diagram I. Here m is

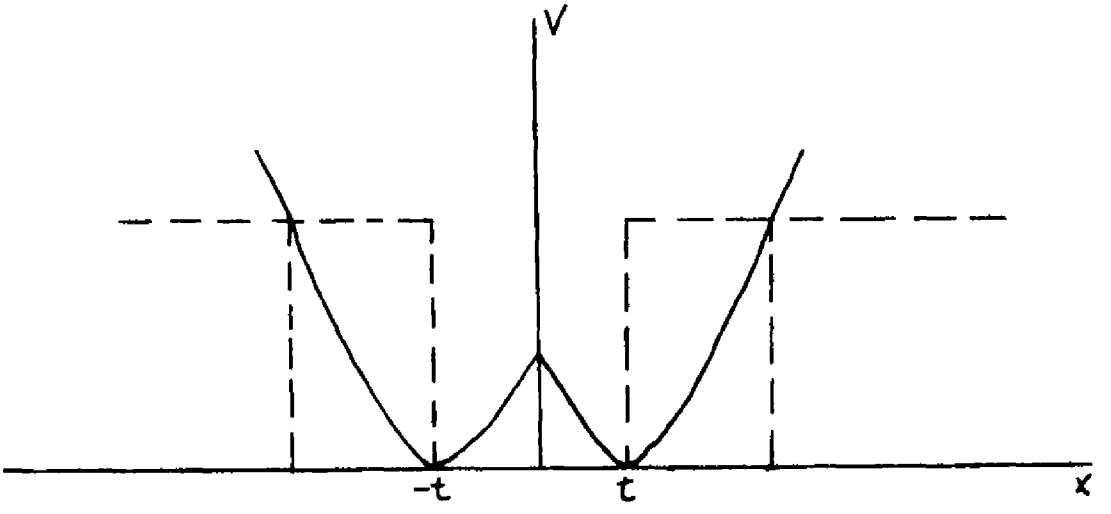

Diagram I

the mass of the defect ion, x is the distance along the path of least potential energy, t is the distance of the absolute minimum, (.213,.213,.213), from the origin (placed at the center of the barrier, (.261,.261,0.)) and ω is determined from the value of the energy at the origin.

The general method of solution of this problem is to take linear combinations of the ground state wave functions for each well, obtained by assuming that the other well does not exist. The variational method is then applied to obtain the energy levels of the system. Let ψ_A and ψ_B be the wave functions of the $x > 0$ and $x < 0$ harmonic oscillators, each obtained by neglecting the other. Then

$$\psi_A(x) = \left(\frac{m\omega}{\pi k}\right)^{1/4} e^{-\frac{m\omega}{2k}(x-t)^2}$$

$$\psi_B(x) = \left(\frac{m\omega}{\pi k}\right)^{1/4} e^{-\frac{m\omega}{2k}(x+t)^2}$$

and the total wave function of the system is written

$$\psi = c_1 \psi_A + c_2 \psi_B$$

The variational theorem states that

$$W = \int_{-\infty}^{\infty} \psi^* \mathcal{H} \psi \, d\chi \geq E$$

where E is the ground state energy. We therefore minimize W with respect to c_1 and c_2. We shall simplify the problem by neglecting kinetic energy terms; since we are interested in the transition energy from the ground to first excited state and the tunnelling-splitting energy, these terms will cancel. Defining

$$E_A \equiv \int_{-\infty}^{\infty} \psi_A V \psi_A \, d\chi = \int_{-\infty}^{\infty} \psi_B V \psi_B \, d\chi$$

$$S = \int_{-\infty}^{\infty} \psi_B^* \psi_A \, d\chi = \int_{-\infty}^{\infty} \psi_A^* \psi_B \, d\chi$$

and using the simplification $\mathcal{H}\psi = V\psi = \varepsilon\psi$, it is a matter of some algebra to show that

$$\frac{\partial W}{\partial c_1} = 2Ec_1 + 2Ec_2 S = 2c_1 E_A + 2c_2 \int_{-\infty}^{\infty} \psi_A V \psi_B \, d\chi$$

$$\frac{\partial W}{\partial c_2} = 2Ec_1 S + 2Ec_2 = 2c_1 \int_{-\infty}^{\infty} \psi_A V \psi_B \, d\chi + 2c_2 E_A$$

or that

$$\begin{vmatrix} E_A - E & \langle \psi_A | V | \psi_B \rangle - ES \\ \langle \psi_A | V | \psi_B \rangle - ES & E_A - E \end{vmatrix} = 0$$

IV-3

Equation IV-3 has two solutions which we shall call E^+ and E^- given by

$$E^{\pm} = \frac{E_A \pm \langle \psi_A | V | \psi_B \rangle}{1 \pm S} \qquad \text{IV-4}$$

The tunneling splitting energy is $\delta = E^- - E^+$. The low-lying resonant absorption is given approximately by $\hbar\omega$ (actually this absorption is somewhat less because the first excited state is somewhat lower than that of the simple harmonic oscillator). The wave functions corresponding to $E^{\pm}$ are

$$\psi^{\pm} = \frac{\psi_A \pm \psi_B}{\sqrt{2(1 \pm S)}} \qquad \text{IV-5}$$

The evaluation of the quantities in equation IV-4 involves no more than straightforward integration and the details will not be given here. The intermediate results are

$$S = e^{-m\omega t^2/\hbar}$$

$$E_A = \frac{\hbar\omega}{4} - \hbar\omega t \left(\frac{m\omega}{\pi\hbar}\right)^{1/2} e^{-\frac{m\omega}{\hbar}t^2} + m\omega^2 t^2 \left\{1 - \Phi\left[\left(\frac{m\omega}{\hbar}\right)^{1/2} t\right]\right\}$$

$$\langle \psi_A | V | \psi_B \rangle = \left\{\frac{\hbar\omega}{4} + \frac{m\omega^2 t^2}{2} - \hbar\omega t \left(\frac{m\omega}{\pi\hbar}\right)^{1/2}\right\} e^{-m\omega t^2/\hbar} \qquad \text{IV-6}$$

where Φ is the error function defined in Chapter II. The tunneling splitting, δ, is given by

$$\delta = \frac{2}{1 - S^2}\left\{S E_A - \langle \psi_A | V | \psi_B \rangle\right\}$$

Substitution of equations IV-6 in the above gives

$$\gamma = \frac{2S}{1-S^2}\left\{\frac{1}{2}m\omega^2t^2 + \hbar\omega t\left(\frac{m\omega}{\pi\hbar}\right)^{1/2}(1-S) - m\omega^2t^2\,\mathrm{erf}\left[\left(\frac{m\omega}{\hbar}\right)^{1/2}t\right]\right\} \qquad \text{IV-7}$$

Using the value $t = .714$ Å determined in the next Chapter of this paper, and a barrier height of .0073 ev from Table IV, we obtained a low-lying mode at 33.1 cm^{-1} and a tunneling splitting of 2.05 cm^{-1} in reasonable agreement with experiment. More realistic three dimensional models have been employed [3,4,5] but only with assumed harmonic oscillator potentials. The potentials developed in this paper have not been used in the three dimensional calculation as yet.

It is clear from Table IV that the Li^+ is off-center in KBr also according to our analysis. The stability of the Li^+ at its normal lattice site is insensitive to the value of the hardness parameter but is quite sensitive to other parameters such as the basic radii of the Li^+ and Br^- ions. The absence of an electrocaloric effect, however, does not necessarily imply that the Li^+ is on site: it may be "frozen in at an off-center position" [2] implying that the barrier between minima is so large that the translational tunneling is negligible and no orientational character of the dipole moment in the Langevin sense exists. Alternatively, if no barrier between minima existed the Li^+ would move freely between <111> configurations and show no tunneling splitting or dipole moment because of the lack of well structure.

We first note that the arbitrary change in hardness parameter which we made causes the minimum energies of the Li^+ in KBr in its $\langle 111 \rangle$ and $\langle 110 \rangle$ configurations to be nearly equal. It is reasonable to assume that a further adjustment of this parameter would make these energies exactly equal in which case no barrier would exist between the $\langle 111 \rangle$ and $\langle 110 \rangle$ configurations. The Li^+ would therefore move freely in a square well type of potential whose depth would be determined by the $\langle 100 \rangle$ configuration energy ($\sim$.069 ev) and whose half-width would be approximately between the distance from the origin (the $\langle 110 \rangle$ configuration) to the (.200,.200,.200) position and the distance from the origin to the (.270,0.,0.) position.

Two square wells were actually chosen, each having a depth of .069 ev (from Table IV), one having a half-width $a = 1.684$ Å, the other having $a = .714$ Å as shown by the dotted lines in Diagram I. The latter parameters are the distances from the $\zeta = 0$ plane to the (.280,0.,0.) and (.213,.213,.213) positions along the path of minima for the KCl host lattice. Slight variations certainly exist in KBr but not having obtained precisely a zero barrier for KBr anyway, we cannot be sure of these distances after further adjustment of the hardness parameter. In any case, we only hope to obtain the upper and lower limits of the low-lying absorption. It was found that the difference in the lowest energies associated with the antisymmetric and symmetric wave functions (of the symmetrical square well) was 33.07 cm^{-1} for $a = .714$ Å and 6.70 cm^{-1} for $a = 1.684$ Å. The experimental value of 17.81 cm^{-1} lies between these limits.

C. Dipole Moment

We now proceed to show how the dipole moment is a quantum-mechanical effect caused by the existence of transition dipole matrix elements between tunneling multiplet states. Again we shall use the one-dimensional model for KCl:Li.

We denote the perturbing electric field by ϵ, the unperturbed energy of the symmetric state E^+, that of the antisymmetric state by E^-, and the distance from the origin to the center of either well by t. The perturbation energy is $e\epsilon x$ where $-e$ is the charge of the Li^+. First order perturbation theory gives no contribution due to the fact that the ψ^+ and ψ^- wave functions are purely symmetric and antisymmetric respectively (see equation IV-15). Second order perturbation theory gives

$$E^{+\prime} = E^+ + \frac{|\langle \psi^+ | e\epsilon x | \psi^- \rangle|^2}{E^+ - E^-}$$

Substituting for ψ^+ and ψ^- yields

$$E^{+\prime} = E^+ + \frac{|\langle \psi_A + \psi_B | e\epsilon x | \psi_A - \psi_B \rangle|^2}{4(1-S^2)^2 (E^+ - E^-)}$$

It is a simple matter to show that

$$\langle \psi_A | e\epsilon x | \psi_A \rangle = e\epsilon t$$

$$\langle \psi_B | e\epsilon x | \psi_B \rangle = -e\epsilon t$$

so that, neglecting the small S^2 terms, $\langle \psi_B | e\epsilon x | \psi_A \rangle = 0$

$$E^{+\prime} = E^+ - (e\epsilon t)^2 / \delta$$

so that, neglecting the small S^- terms,

$$E^{+\prime} = E^+ - (e\epsilon t)^2 / \delta \qquad \text{IV-8a}$$

where $\delta = E^- - E^+$ as before. Similarly,

$$E^{-\prime} = E^- + (e\epsilon t)^2/\delta \qquad \text{IV-8b}$$

First order perturbation theory gives us the perturbed wave functions,

$$\psi^{+\prime} = \psi^+ + \frac{\langle \psi^+ | -e\epsilon x | \psi^- \rangle}{E^+ - E^-} \psi^-$$

$$\psi^{-\prime} = \psi^- + \frac{\langle \psi^- | -e\epsilon x | \psi^+ \rangle}{E^- - E^+} \psi^+$$

which are easily shown to be, neglecting S^2 terms,

$$\psi^{\pm\prime} = \psi^\pm \pm \frac{e\epsilon t}{\delta} \psi^\mp \qquad \text{IV-9}$$

The dipole matrix elements between predominantly symmetric and anti-symmetric states are then given by:

$$\langle p \rangle^{+\prime} = \langle \psi^{+\prime} | ex | \psi^{+\prime} \rangle$$

$$\langle p \rangle^{-} = \langle \psi^{-\prime} | ex | \psi^{-\prime} \rangle$$

Using equations IV-9, remembering that $\langle \psi^+ | ex | \psi^+ \rangle$ and $\langle \psi^- | ex | \psi^- \rangle$ vanish by symmetry, one obtains,

$$\langle p \rangle^{\pm\prime} = \pm \frac{2(et)^2 \epsilon}{\delta} \qquad \text{IV-10}$$

By Boltzmann's theorem, the thermal average of this dipole moment is given by:

$$\overline{\langle p \rangle}^T = \frac{\langle p \rangle^+ e^{-E^+/kT} + \langle p \rangle^- e^{-E^-/kT}}{e^{-E^+/kT} + e^{-E^-/kT}}$$

Letting $\Delta = \frac{2(e\epsilon t)^2}{\delta}$, one obtains,

$$\overline{\langle p \rangle}^T = \frac{2(et)^2}{\delta} \epsilon \left\{ \frac{1 - e^{-(\delta+\Delta)/kT}}{1 + e^{-(\delta+\Delta)/kT}} \right\} \qquad \text{IV-11}$$

In order that the perturbation approach be valid, the perturbing energy $e\epsilon t$ must be less than the tunneling splitting, δ. That is

$$e\epsilon t < \delta$$

or

$$\epsilon < 10^4 \text{ volts/cm}$$

and hence we can neglect Δ. Furthermore, if $\delta/kT < 1$, we can expand IV-11 and obtain

$$\overline{\langle p \rangle}^T = \frac{(et)^2}{kT} \epsilon \qquad \text{IV-12}$$

It is to be emphasized that equation IV-11 applies only in the weak field limit but for all temperatures; equation IV-12 applies only when the thermal energy, kT, is greater than the tunneling splitting ($T > 2°K$).

In the strong field case, the energy splitting due to the tunnel effect is small compared to the energy of the electric field. Thus the field localizes the particle in one well or the other so that

$$\psi^{+} = \psi_A$$

$$\psi^{-} = \psi_B$$

and the resulting dipole moment is

$$\langle p \rangle^{\pm} = \pm e t \qquad \text{IV-13}$$

The thermal average is,

$$\overline{\langle p \rangle}^{T} = e t \tanh\left(\frac{e \epsilon t}{k T}\right) \qquad \text{IV-14}$$

For $kT > e\epsilon t$, the expansion gives

$$\overline{\langle p \rangle}^{T} = \frac{(e t)^2 \epsilon}{k T} \qquad \text{IV-15}$$

which is identical to equation IV-12 obtained in the weak field, high temperature limit.

We therefore obtain a $1/T$ dependence for the dipole moment which can be obtained classically by considerations of an orientable permanent dipole moment (Langevin). Physically, of course, the classical dipole moment can be said to be obtained in the high-field limit when the particle is localized in one of the wells and has a permanent moment given by equation IV-13. However, this neglects the dipoles due to the other ions in the crystal.

In the actual three-dimensional KCl:Li case, the Li^{+} lies along the $\langle 111 \rangle$ direction and the ions surrounding it relax to their minimum energy positions. This distortion of the cubic symmetry of the lattice produces fields at all ion sites which polarize the ions and

hence produce electronic dipole moments on all ions in the lattice. Furthermore, the distortion itself creates ionic dipoles each of which is given by the product of the ionic charge and the displacement of the ion. We have calculated the vector sum of the ionic and electronic contributions separately due to all ions in regions I and II. We find the total ionic dipole moment to be 4.1 D directed along the $\langle 111 \rangle$ axis and the total electronic dipole moment to be 1.1 D directed along the $\langle \bar{1}\bar{1}\bar{1} \rangle$. The electronic and ionic contributions of the defect ion, Li^+, are included. The measurements of Lombardo and Pohl [2] indicate a dipole moment of 2.5 D when the field is along the $\langle 100 \rangle$ axis. The component of our total dipole moment along the $\langle 100 \rangle$ axis is 1.7 D in order of magnitude agreement.

It is interesting to note that using $t = .714\text{Å}$, $\epsilon = 10^4$ volts/cm and $T = 1.37^0$K (Lombardo and Pohl [2]), equation IV-14 gives a value of 1.8 D for the dipole moment. These agreements with experiment may very well be somewhat fortuitous because in one case we are neglecting the fact that the Li^+ moves between equivalent $\langle 111 \rangle$ configurations and therefore the electronic and ionic dipoles change or reorient themselves; in using equation IV-14 we neglect any contribution due to the other ions in the crystal and take into account only the motion of the Li^+.

References - Chapter IV

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2. G. Lombardo and R. O. Pohl, Phys. Rev. Letters 15,291 (1965); Bull, Am. Phys. Soc. 11,212 (1966).

3. M. Gomez-Rodriguez, J. A. Krumhansl and J. A. D. Matthew, AEC Report No. NYO-2391-24, Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, N.Y. (1966).

4. S. P. Bowen, M. Gomez, J. A. Krumhansl and J. A. D. Matthew, Phys. Rev. Letters 16,1105 (1966).

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Chapter V

Determination and Characteristics of the Potential for Li^+ in KCl

It is convenient and useful to describe the potential which the Li^+ sees by a polynomial. A sixth power polynomial, symmetric in x, y, z was fitted to the energies determined by the detailed calculations of Chapter IV. The coefficients of this polynomial were determined by fitting to a) the values of the minimum energies and positions with the Li^+ in KCl constrained to the <100>, <110> and <111> directions as given in Table IV,b) the value of the minimum energy when the Li^+ is fixed at its normal lattice site given in Table V, c) the fact that extrema exist in the three directions tested. The result is:

$$V(x,y,z) = -1.0719 - 4.088(x^2+y^2+z^2) + 21.24(x^2+y^2+z^2)^2$$
$$+41.14(x^2+y^2+z^2)^3 - 14.38(x^2y^2+x^2z^2+y^2z^2)$$
$$-216.2(x^2y^4+x^2z^4+y^2x^4+y^2z^4+z^2x^4+z^2y^4)$$
$$-2.062\,x^2y^2z^2. \qquad \text{V-1}$$

By differentiating this potential with respect to x, y, and z and solving the resulting equations set equal to zero for the z = constant plane, one obtains the condition that two of the position coord-

inates of the defect must be equal at any relative minimum. That is, all minima exist in the x = y, x = z and y = z (equivalent) planes.

The x = y plane was examined in some detail because it contains all the different types of extrema. Figure IIA is an energy contour map of the x = y plane; the curves are separted by .01 ev and the absolute minimum position marked by a +. From the curves it is seen that the < 111 > configuration is the absolute minimum, the origin is a maximum, and the < 100 > and < 110 > configurations are saddle points. There is a broad plateau between the < 111 > and < 110 > configurations and a great density of equipotential lines separating the origin (normal lattice site) from the < 111 > minimum energy configuration. One can also see that the < 100 > configuration is at an appreciably higher energy than the < 110 > . Figure IIB is a similar contour map with equipotential spacings of .001 ev. The path of least potential energy is very nearly circular between the (.213,.213,.213) and the (.261,.261,0.) positions. The radius of this path was determined to be $.369 \pm .002$ Å by minimizing potential V-1 in the x = y plane along the lines $z = \sqrt{2} \times \tan\theta$ for $0^\circ \leq \theta \leq 35.2^\circ$, θ being measured from the z = o plane.

Figure III is a plot of the minima of the potential V-1 along lines in the x = y plane as a function of θ. The Devonshire potential [1], which applies to a diatomic molecule, is also plotted in Figure III for comparison. This latter potential is defined as:

$$V(x,y,z) = .05956\left\{-\frac{3}{2} + \frac{5}{2}\,\frac{x^4+y^4+z^4}{r^4}\right\} - 1.3016 \qquad V\text{-}2$$

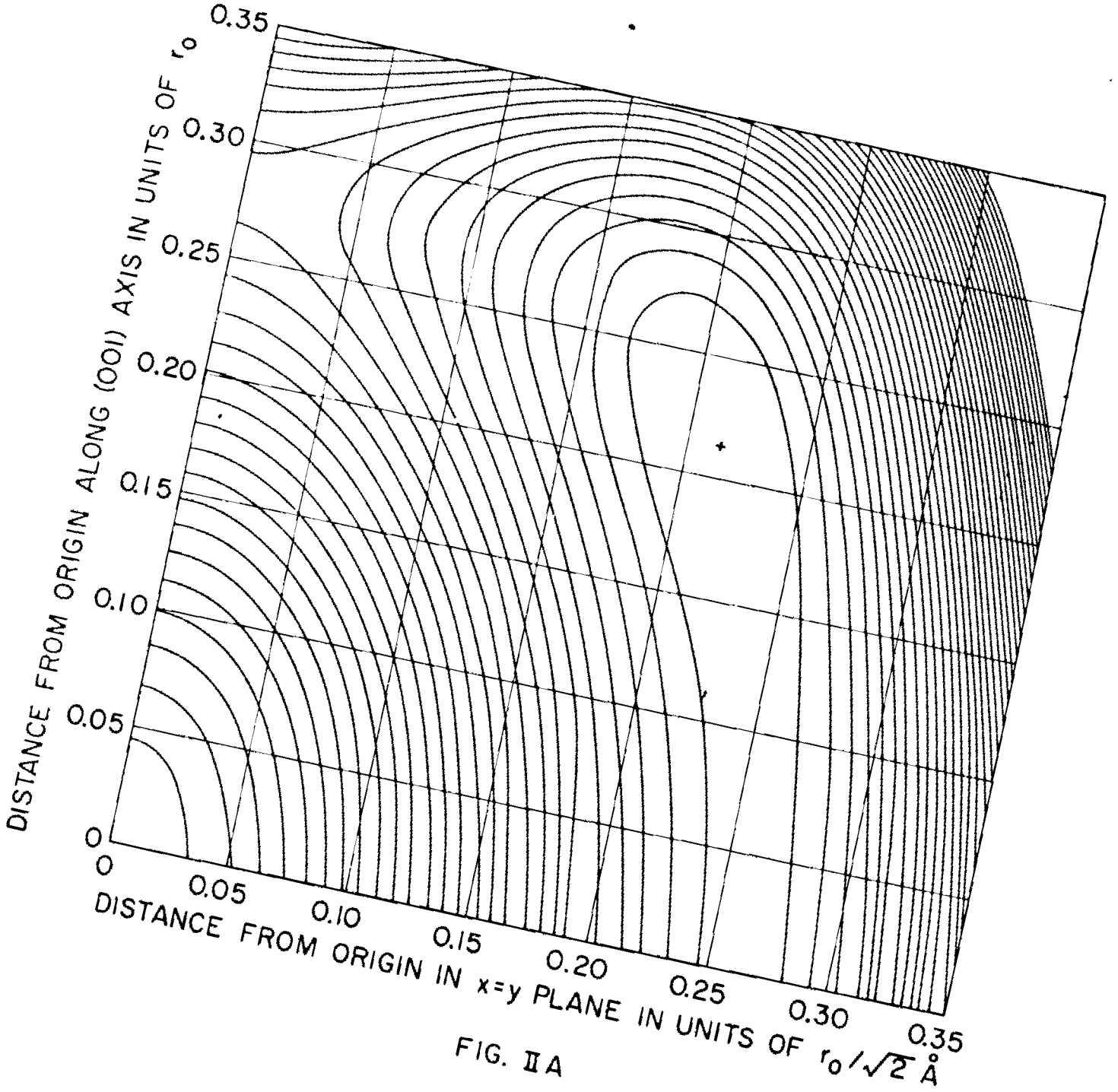
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0
DISTANCE FROM ORIGIN ALONG (001) AXIS IN UNITS OF r_o
0
0.05
0.10
0.15
0.20
0.25
0.30
0.35
DISTANCE FROM ORIGIN IN x=y PLANE IN UNITS OF $r_o/\sqrt{2}$ Å

FIG. II A

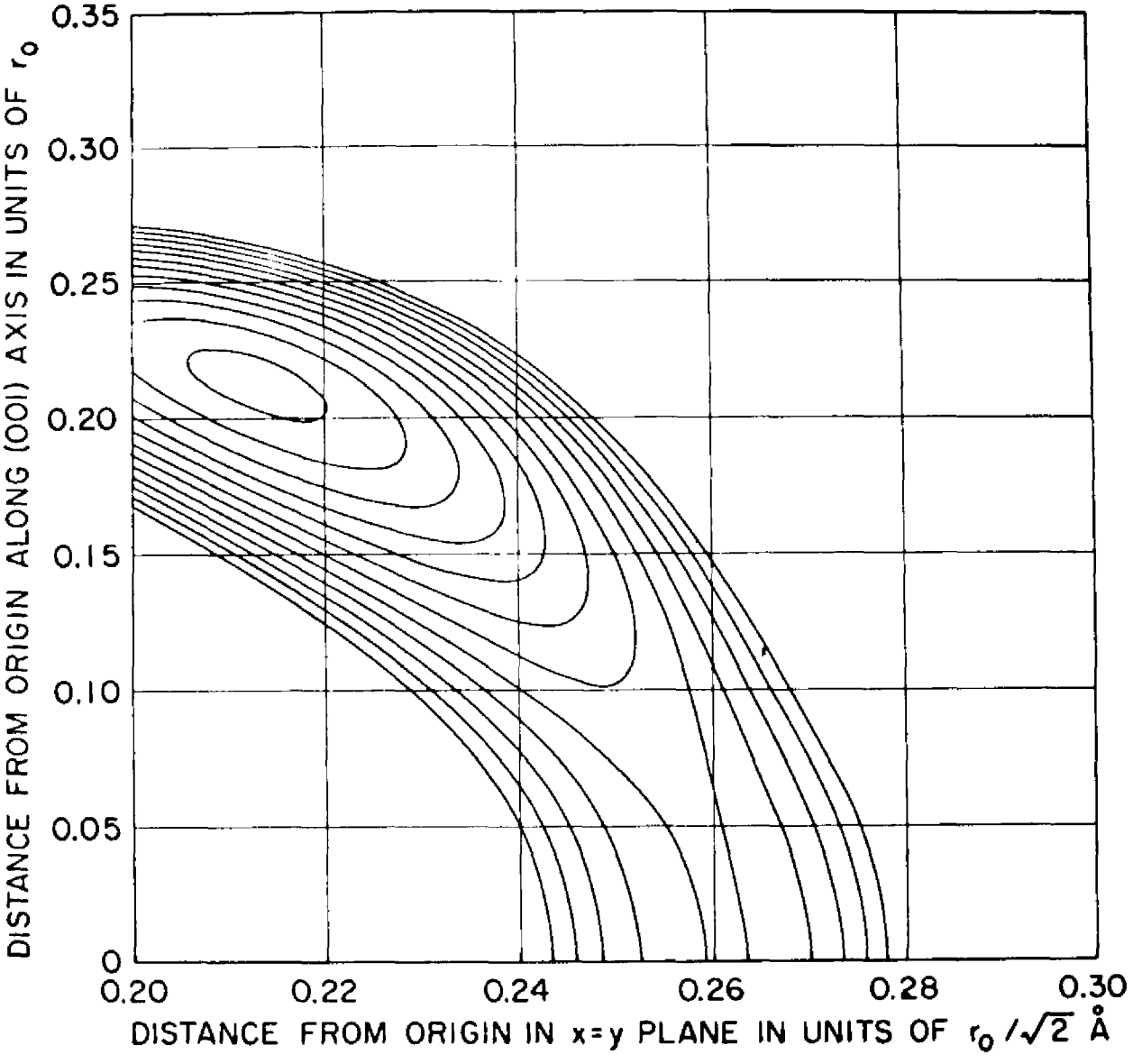
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0
DISTANCE FROM ORIGIN ALONG (001) AXIS IN UNITS OF r_o
0.20
0.22
0.24
0.26
0.28
0.30
DISTANCE FROM ORIGIN IN x=y PLANE IN UNITS OF $r_o/\sqrt{2}$ Å

FIG. II B

where the constants, which are in ev, were fitted to the $\theta = 35.2^{\circ}$ and $\theta = 90^{\circ}$ values of potential V-1 in the x = y plane. If these constants are fitted to the $\theta = 35.2^{\circ}$ and $\theta = 0^{\circ}$ values of potential V-1, one obtains,

$$V(x,y,z) = .01749 \left\{ -\frac{3}{2} + \frac{5}{2} \frac{x^4+y^4+z^4}{r^4} \right\} - 1.3297 \qquad V-3$$

Figure IV is a plot of the potential V-1 as a function of the distance, t, of the Li^+ from the z = 0 plane (its < 110> configuration) along the path of least potential energy. This distance was calculated numerically from $t = \int r d\theta$. From the curve one can obtain the parameter t used in the previous Chapter in the square well approximation for KBr and the double harmonic oscillator approximation for KCl. One notes the considerable flatness of the potential out to $\sim .3$ Å unlike a simple harmonic oscillator potential. Perhaps better quantitative agreement with the experimental tunneling splitting can be obtained by using this potential to calculate the wave functions needed in the treatment given by Bowen, et al.[2]

COMPARISON OF DEVONSHIRE POTENTIAL, V_B, WITH OUR POTENTIAL, V_A, IN THE $x = y$ PLANE

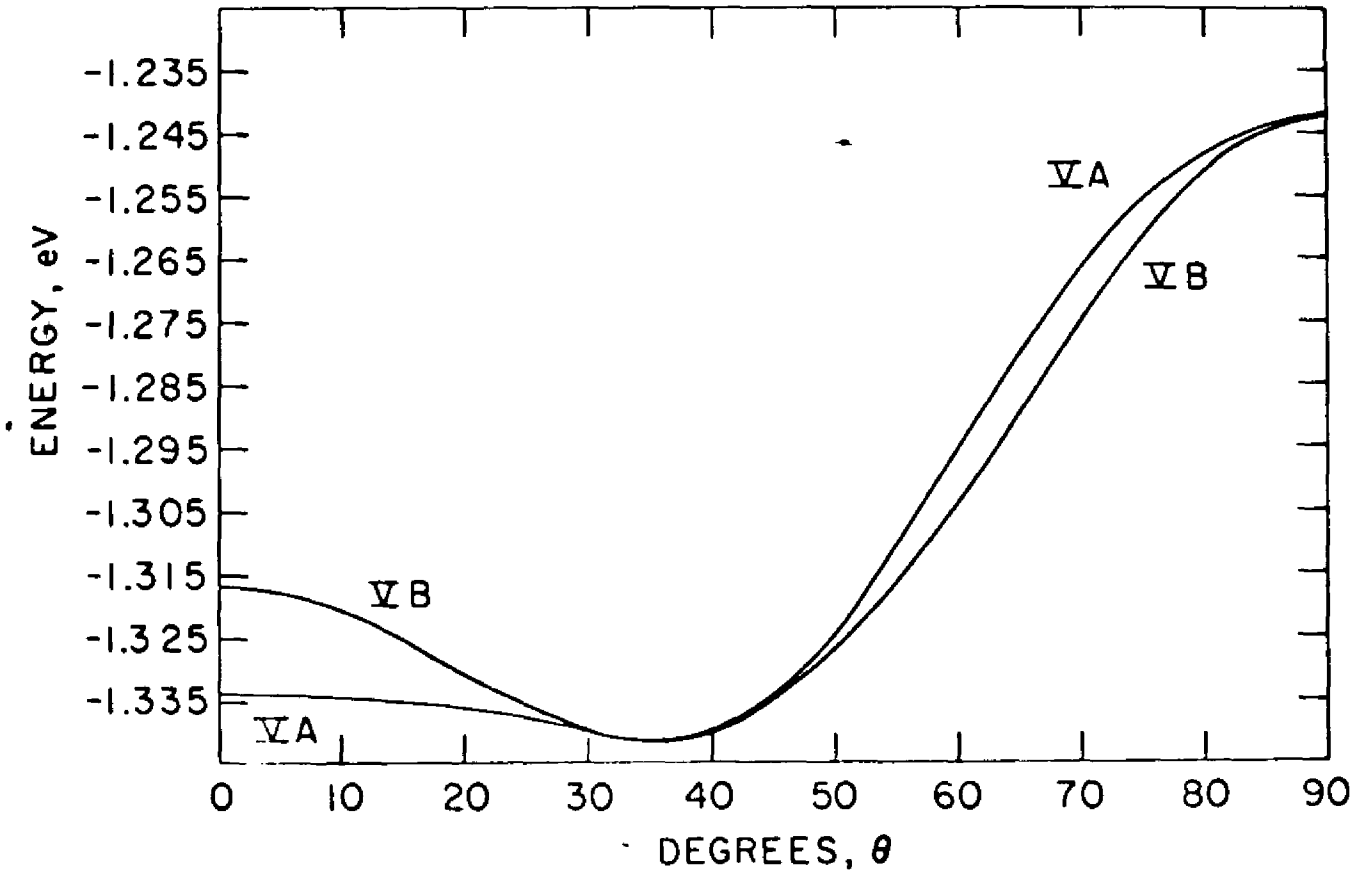

FIG. III

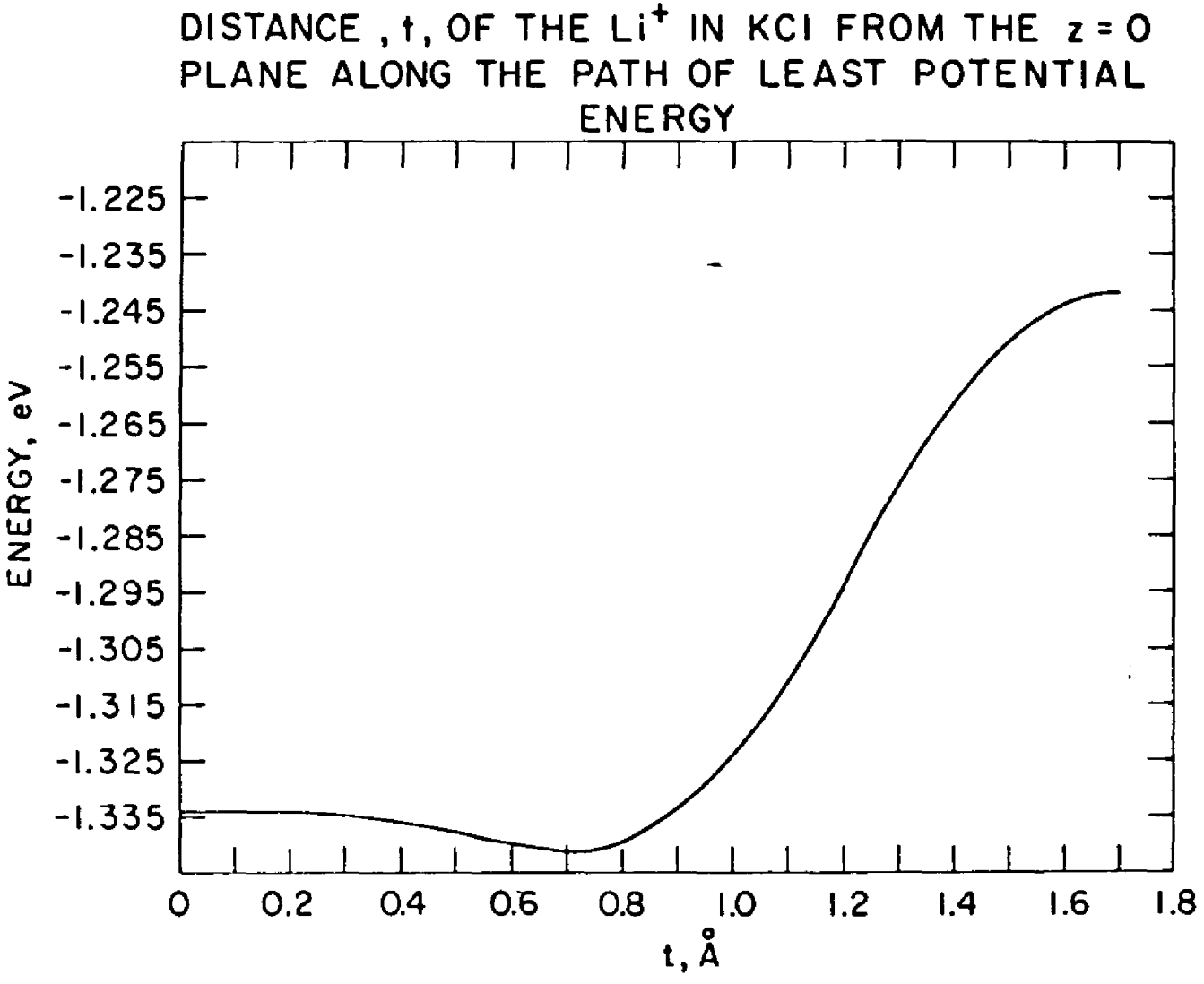
DISTANCE , t, OF THE Li+ IN KCl FROM THE z = 0 PLANE ALONG THE PATH OF LEAST POTENTIAL ENERGY
ENERGY, eV
-1.225
-1.235
-1.245
-1.255
-1.265
-1.275
-1.285
-1.295
-1.305
-1.315
-1.325
-1.335
0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
t, Å

FIG. IV

References - Chapter V

1. A. F. Devonshire, Proc. Royal Soc. (London) A151,601 (1936).

2. S. P. Bowen, M. Gomez, J. A. Krumhansl, and J. A. D. Matthew, Phys. Rev. Letters 16,1105 (1966).

Chapter VI

Other Effects

A. Other Off-Center Ions

A few other small impurity ions in the alkali halides were investigated. In Table V are listed the $|W|$ values (see Chapter III) and the minimum energies obtained when each defect ion is fixed at (.2,.2,.2) in units of the interionic distance and at the origin. For NaBr:F, we find a negative value of $|W|$, indicating instability, and a lower energy in the off-center position. For KCl:F, we find a positive value of $|W|$, and a higher energy in the off-center position. Not having investigated the barrier heights between $\langle 111 \rangle$ and $\langle 110 \rangle$ configurations, we can give no quantitative information about tunneling splitting, etc. These two results, however, are consistent with the findings of Lombardo and Pohl.[1]

Table V also shows that a F^- ion in KBr is stable at a normal Br^- site, and that a Li^+ ion in NaBr or NaCl is unstable. Again, however, we have insufficient information with which to calculate low-lying resonant modes or tunneling splittings. The NaBr:Li and NaCl:Li cases, depending on the potentials which the Li^+ sees, may exhibit paraelectric cooling; the KBr:F case will not according to our findings.

Also in Table V are shown the increasing values of $|W|$ as the size of the impurity ion in KCl increases. This indicates that $|W|$

TABLE V

HOST LATTICE: DEFECT	POTENTIAL EMPLOYED	|W| WITH DISTORTION	ENERGY WITH DEFECT AT ORIGIN e.v.	ENERGY WITH DEFECT AT (.2,.2,.2)[a] e.v.
KCl:Li	ATF	-1.65×10^{5}	-1.0719	-1.3413[c]
KCl:Li	ATFV	-----	-1.0452	-.7668
KCl:Na	TF	4.28×10^{5}	-.7094	-.4136
KCl:K	TF	-----	0.0	.6851
KCl:F	TF	2.45×10^{6}	-.8776	-.7252[b]
KBr:Li	TF	-----	-.9264	-1.1944[b]
KBr:Li	ATF	-2.10×10^{5}	-0.9714	-1.1815[c,b]
KBr:F	TF	2.09×10^{6}	-1.0300	-1.0014
NaBr:Li	TF	-1.88×10^{6}	-.5232	-.5843
NaBr:F	TF	-5.83×10^{6}	-1.2950	-1.4904[b]
NaCl:Li	TF	-1.33×10^{5}	-.6089	-.6382

[a] These values are obtained with six parameters allowed to vary: $P_2, P_3, P_5, P_7, P_{10}, P_{14}$, with $P_1 = .2$ and all others fixed at zero.

[b] See reference 1.

[c] These values are repeated from Table IV.

is a measure of the degree of stability of an ion at a normal site.

B. Effect of Uniform Hydrostatic Pressure

In Table VI are the results of our determination of the uniform hydrostatic pressure necessary to put the Li^+ back on site in KCl. We allowed the defect to move along the < 111 > direction as in Chapter IV but with fewer parameters assigned to the region I ions. Parameters p_1 ,p_2 ,p_3 ,p_5 ,p_7 ,p_{10} , and p_{14} (see Table III) were allowed to vary and all other displacement parameters were fixed at zero. These parameters were chosen because their magnitudes were greater than .01 r_o for the KCl:Li < 111 > case, and hence they have the greatest effect on the minimum energy. An estimate of the error involved in determining the energy in this way was obtained by performing the calculation for all 18 parameters for one case (4% change in lattice parameter) and this error is seen from Table VI to be $\sim$ .01 ev. We estimate that a lattice parameter change of 5-7%, corresponding to a uniform hydrostatic pressure of 25-37 kilobars, is required to drive the Li^+ back on site in KCl.

It is hoped that experimental work will be done in this connection so that still another check of the potential employed in our calculation of KCl:Li can be made.

TABLE VI

$\frac{\Delta r_0}{r_0}$ x 100%	ENERGY WITH Li+ AT ORIGIN	ENERGY WITH Li+ OFF-CENTER[a]
0	-1.0719	-1.3413
3	-1.4242	-1.5021
4	-1.5652	-1.6052 -1.6140[b]
5	-1.7205	-1.7340
6	-1.8891	-1.8845
7	-2.0781	-2.0652
8	-2.2830	-2.2542

[a]These values were determined with seven parameters allowed to vary: $P_1, P_2, P_3, P_5, P_7, P_{10}, P_{14}$.

[b]All 18 parameters allowed to vary.

References - Chapter VI

1. G. Lombardo and R. O. Pohl, Phys. Rev. Letters 15,291 (1965); Bull. Am. Phys. Soc. 11, 212 (1966).

Chapter VII

Nuclear Quadrupole Resonance

A. General Considerations

The Hamiltonian expressing the interaction between the nuclear spin $\underline{I}$ in a static magnetic field $\underline{H}$ is given by [1]

$$\mathcal{H}_M = -\gamma \hbar \underline{H} \cdot \underline{I} \qquad \text{VII-1}$$

where γ is the magnetogyric ratio for the nucleus. If, in addition, the atom or ion is placed in an environment such that a field gradient exists at its nucleus (e.g. in a crystalline field) then a second term, $\mathcal{H}_Q$, must be added to $\mathcal{H}_M$. The field gradient at the nucleus is defined as a symmetric second rank tensor having 9 components

$$V_{ij} = -\frac{\partial^2 \Phi}{\partial x_i \partial x_j}$$

where Φ is the electrostatic potential at the nucleus due to charges and dipoles external to the nucleus. Since the Laplace equation, $\nabla^2 \Phi = 0$, therefore holds, the field gradient tensor is symmetric and traceless.

The quadrupole interaction with the field gradient is given in general by[1]

$$\mathcal{H}_Q = \sum_m Q_2^m \left(\nabla E\right)_2^{-m} \quad , -2 \leq m \leq +2 \qquad \text{VII-2}$$

where

$$Q_2^0 = \frac{eQ}{2I(2I-1)} \left(3 I_z^2 - \underline{I}^2\right)$$

$$Q_2^{\pm 1} = \frac{eQ}{2I(2I-1)} \frac{\sqrt{6}}{2} \left\{ I_z (I_x \pm i I_y) + (I_x \pm i I_y) I_z \right\}$$

$$Q_2^{\pm 2} = \frac{eQ}{4I(2I-1)} \sqrt{6} \, (I_x \pm i I_y)^2$$

$$(\nabla E)_2^0 = \frac{1}{2} V_{zz} \qquad \text{VII-3}$$

$$(\nabla E)_2^{\pm} = -\frac{1}{\sqrt{6}} (V_{xz} \pm i V_{yz})$$

$$(\nabla E)_2^{\pm 2} = \frac{1}{2\sqrt{6}} (V_{xx} - V_{yy} \pm 2 i V_{xy})$$

and the scalar quadrupole moment Q is defined by Casimir[2] as

$$eQ = \int \rho_i \, \vec{r}_i^{\,2} (3 \cos \theta_{iI} - 1) \, d\tau_i$$

where ρ_i is the charge density in volume $d\tau_i$ inside the nucleus at vector distance $\vec{r}_i$ from the center and θ_{iI} is the angle between $\vec{r}_i$ and the nuclear spin axis. Defining

$$I_{\pm} = I_x \pm i I_y$$

$$V_0 = V_{zz} \qquad \text{VII-3A}$$

$$V_{\pm 1} = V_{xz} \pm i V_{yz}$$

$$V_{\pm 2} = \frac{1}{2} (V_{xx} - V_{yy}) \pm i V_{xy}$$

the quadrupole Hamiltonian can be written

$$\mathcal{H}_Q = \frac{eQ}{4I(2I-1)} \left[I_+^2 V_{-2} - (I_z I_+ + I_+ I_z) V_{-1} + (3I_z^2 - I^2) V_0 \right.$$

$$\left. - (I_z I_- + I_- I_z) V_{+1} + I_-^2 V_{+2} \right] \qquad \text{VII-4}$$

The total Hamiltonian for all interactions being considered is given by $\mathcal{H} = \mathcal{H}_M + \mathcal{H}_Q$. It is to be emphasized that the coordinate system used up to now is the actual crystal axis system.

We are interested in solving the Schroedinger equation

$$\mathcal{H} \psi_m = E_m \psi_m \qquad \text{VII-5}$$

where m is the component of the nuclear spin along the direction of the applied Zeeman field, $-I \leq m \leq I$. By multiplying both sides of VII-5 by $\psi^*_{m'}$ and integrating over all space, one transforms the problem into the solution of the secular equation

$$\left| \langle I m' | \mathcal{H} | I m \rangle - E_m \delta_{m',m} \right| = 0 \qquad \text{VII-6}$$

where $\delta_{m',m}$ is the usual Kronecker delta symbol. It is essentially to the evaluation of the matrix elements in VII-6 that we devote the remainder of this chapter.

B. High-Field Case

When the applied $\underline{H}$ field is sufficiently large, the quadrupole Hamiltonian, $\mathcal{H}_Q$, can be treated as a perturbation on the magnetic interaction, $\mathcal{H}_M$. Let us consider the matrix elements $\langle I m' | \mathcal{H}_M | I m \rangle$. Define

$$H_\pm = (H_x \pm i H_y)/\sqrt{2}$$

so that

$$\underline{H} \cdot \underline{I} = H_z I_z + \tfrac{1}{2} (H_+ I_- + H_- I_+)$$

Using the relations,[3] (dropping the I index hereafter)

$$I_\pm |m\rangle = \left[(I \mp m)(I \pm m + 1)\right]^{1/2} |m \pm 1\rangle$$

$$I_z |m\rangle = m |m\rangle \qquad \text{VII-7}$$

$$\underline{I}^2 |m\rangle = I(I+1)|m\rangle$$

one obtains

$$\langle m' | \mathcal{H}_M | m \rangle = -\gamma \hbar \left\{ H_z m \delta_{m'm} + \frac{1}{2} H_+ \left[(I+m)(I-m+1)\right]^{1/2} \delta_{m',m} + \frac{1}{2} H_- \left[(I-m)(I+m+1)\right]^{1/2} \delta_{m',m+1} \right\} \qquad \text{VII-8}$$

In the special case of the $\underline{H}$ field being directed along the z axis of the crystal, H_+ and H_- vanish and the secular equation, VII-6, becomes

$$\left| -\gamma \hbar H_z m \delta_{m'm} - E_m \delta_{m'm} \right| = 0$$

so that

$$E_m^o = -\gamma \hbar m H_z$$

The Bohr frequency condition gives the maximum probability for the transition between the two levels m and $m+1$ (transitions are induced by a radio-frequency field) transverse to $\underline{H}$

$$\nu_L = \frac{E_{m-1} - E_m}{h} = \frac{\gamma H_z}{2\pi} \qquad \text{VII-9}$$

and this frequency of transition, ν_L is known as the Larmor frequency.

Let us, then, impose the condition that the z axis of the crystal is the direction of the large constant magnetic field. The quadrupole effects are then calculated using first and second order perturbation theory to determine

$$E_m = E_m^{o} + E_m^{(1)} + E_m^{(2)}$$

where

$$E_m^{(1)} = \langle m | \mathcal{H}_Q | m \rangle$$

$$E_m^{(2)} = \sum_{\substack{m' \\ m' \neq m}} \frac{|\langle m' | \mathcal{H}_Q | m \rangle|^2}{E_m - E_{m'}} \qquad \text{VII - 10}$$

where $\mathcal{H}_Q$ is given by VII-4. Define

$$A \equiv \frac{eQ}{4I(2I-1)}$$

then

$$\mathcal{H}_Q | m \rangle = A \left\{ V_{-2} I_+^2 | m \rangle + V_{+2} I_-^2 | m \rangle + V_0 (3 I_z^2 - I^2) | m \rangle \right.$$

$$\left. - V_{-1} (I_z I_+ + I_+ I_z) | m \rangle - V_{+1} (I_z I_- + I_- I_z) | m \rangle \right\}$$

Using equations VII-7, it is a simple matter to show that

$$I_\pm^2 | m \rangle = \left[(I \mp m)(I \pm m + 1)(I \mp m - 1)(I \pm m + 2) \right]^{1/2} | m \pm 2 \rangle$$

$$I_z I_\pm + I_\pm I_z = (2m \pm 1) \left[(I \mp m)(I \pm m + 1) \right]^{1/2} | m \pm 1 \rangle \qquad \text{VII - 11}$$

The matrix elements in VII-10 are therefore

$$\langle m | \mathcal{H}_Q | m \rangle = A \left[3m^2 - I(I+1) \right] V_0$$

$$\langle m \pm 1 | \mathcal{H}_Q | m \rangle = A (2m \pm 1) \left[(I \mp m)(I \pm m + 1) \right]^{1/2} V_{\mp 1}$$

$$\langle m \pm 2 | \mathcal{H}_Q | m \rangle = A \left[(I \mp m)(I \pm m + 1)(I \mp m - 1)(I \pm m + 2) \right]^{1/2} V_{\mp 2}$$

Substitution of these matrix elements into the equations VII-10 gives,

after some, manipulation,

$$E_m^{(1)} = A\left[3m^2 - I(I+1)\right] V_0$$

$$E_m^{(2)} = \frac{2A^2 m}{h\nu_L}\left\{\left[4I(I+1) - 8m^2 - 1\right]|V_1|^2 + \left[2m^2 - 2I(I+1) + 1\right]|V_2|^2\right\} \quad \text{VII-13}$$

We now know the shift in any energy level out to second order in the perturbation expansion. In order to determine the shifts in the observed magnetic resonance lines due to the quadupole interaction we must calculate the transition frequencies, $h\nu_m = E_{m-1}^{\text{TOTAL}} - E_m^{\text{TOTAL}}$. Again after some algebraic manipulations, one obtains,

$$\nu_m^{(1)} = -\frac{6A}{h} V_{zz}(m - 1/2)$$

$$\nu_m^{(2)} = \frac{3A^2}{h^2\nu_L}\left\{\frac{2}{3}\left(V_{zx}^2 + V_{zy}^2\right)\left[24m(m-1) - 4I(I+1) + 9\right] - \frac{1}{12}\left[(V_{xx} - V_{yy})^2 + 4V_{xy}^2\right]\left[12m(m-1) - 4I(I+1) + 6\right]\right\} \quad \text{VII-14}$$

Throughout our discussion so far we have neglected the deformation of the electron cloud surrounding the nucleus caused by the field gradient itself. This deformation gives use to an electronic quadrupole moment which either shields or anti-shields the nuclear quadrupole moment. The effect can be taken care of by letting $Q \rightarrow (1 - \gamma_\infty)Q$ where $1 - \gamma_\infty$ is the anti-shielding factor due to Sternheimer.[4] Equivalently, we can define

$$A' = \frac{eQ(1-\gamma_\infty)}{4I(2I-1)} \qquad \text{VII-15}$$

and substitute A' for A in VII-14. We have now completed the derivation of the required relations when the Zeeman field is large and directed along the z axis of the crystal.

C. Quadrupole Effects of Li^+ in KCl in High Field Case

The field gradients at the nucleus of the Li^+ ion are caused by the change in the positions of the charges on neighboring ions as well as by the dipoles induced on all ions by the crystalline field. The field gradients at a position (x_1, x_2, x_3) relative to a point dipole at the origin of magnitude μ and direction cosines (ℓ_1, ℓ_2, ℓ_3) are given by[5]

$$V_{ii} = -\frac{\partial^2 \Xi}{\partial x_i^2} = \frac{3\mu}{r^5}\left[(3\ell_i x_i + \ell_j x_j + \ell_k x_k) - \frac{5x_i^2}{r^5}(\ell_i x_i + \ell_j x_j + \ell_k x_k)\right]$$

$$V_{ij} = -\frac{\partial^2 \Xi}{\partial x_i \partial x_j} = \frac{3\mu}{r^5}\left[(\ell_i x_j + \ell_j x_i) - \frac{5x_i x_j}{r^2}(\ell_i x_i + \ell_j x_j + \ell_k x_k)\right]$$

with

$$r = (x_1^2 + x_2^2 + x_3^2)^{1/2} \qquad \text{VII-16}$$

Das and Dick[5] in their treatment of quadrupole interactions in alkali halide solid solutions (large impurity ions) assumed that the displacements of the ions could be treated as dipoles at the normal lattice

sites and consequently their μ was the sum of the electronic and displacement dipoles placed at a normal lattice site. We have not used this approximation but have calculated directly the field gradients due to the relaxations of the point charges in region I and the electronic dipoles on all ions in regions I and II. Table VII contains the results of our calculating the field gradient at the Li^+ nucleus when the Li^+ is in its minimum energy configurations (.280,0.,0.), (.261, .261,0.), and (.213,.213,.213).

In order to make use of equations VII-14, the $\underline{H}$ field must be parallel to the z axis of the crystal. We would like to determine the quadrupole effects when the $\underline{H}$ field is parallel to the three axes we have allowed the Li^+ to lie along: the $\langle 111 \rangle$, $\langle 110 \rangle$ and $\langle 100 \rangle$. To do this, we re-label the z axis as, e. g., the $\langle 111 \rangle$ axis of the crystal (thereby, we do not have to determine the $\langle m'|\mathcal{H}|m \rangle$ matrix elements again) and transform the field gradient to a new set of axes x' ,y' , z' with z' parallel to the $\langle 111 \rangle$. Let S be the field gradient tensor for the Li^+ along the $\langle 111 \rangle$ direction in the crystal axis system x, y, z, and T be that for the Li^+ along the $\langle 110 \rangle$ direction. Furthermore, let F and G be the matrices which transform S and T into the coordinate system x' ,y' ,z' with z' parallel to the direction of magnetic field. Then

$$S' = F S F^{-1}$$
$$T' = G T G^{-1} \qquad \text{VII} - 17$$

Table VII

Field Gradients for Li^+ in KCl in various positions*

	Position of Li^+ in KCl		
	(.213,.213,.213)	(.261,.261,0.)	(.270,0.,0.)
V_{xx}	0.0	51.94	228.88
V_{xy}	-20.59	-77.9?	0.0
V_{xz}	-20.59	0.0	0.0
V_{yy}	0.0	51.94	-114.44
V_{yz}	-20.59	0.0	0.0
V_{zz}	0.0	-103.88	-114.44

* All field gradients are given in units of e/a^3, e being the electronic charge, and a is the interionic distance. They are all given in the crystal axis system.

define the appropriate similarity transformations with

$$F = \begin{pmatrix} 1/\sqrt{2} & -1/\sqrt{2} & 0 \\ 1/\sqrt{6} & 1/\sqrt{6} & -2/\sqrt{6} \\ 1/\sqrt{3} & 1/\sqrt{3} & 1/\sqrt{3} \end{pmatrix}$$

and

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$$G = \begin{pmatrix} 1/\sqrt{2} & -1/\sqrt{2} & 0 \\ 0 & 0 & -1 \\ 1/\sqrt{2} & 1/\sqrt{2} & 0 \end{pmatrix}$$

We are now in a position to calculate the quadrupole effects with the Li^+ in various positions and the $\underline{H}$ field directed along the three aforementioned axes.

The spin of the Li^+ nucleus is $I = 3/2$ and hence $m = -3/2, -1/2, +1/2, +3/2$; $\nu_m = (E_{m-1} - E_m)/h$ gives the transitions between $\Delta m = \pm 1$ states. The $\pm\frac{3}{2} \leftrightarrow \pm\frac{1}{2}$ transitions are called satellite lines; the $1/2 \leftrightarrow -1/2$ transition is the central component. From equations VII-14 one sees that there is no first-order shift in the central component ($m = 1/2$) and the second order shift in the central component is given by:

$$\nu_m^{(2)} = \frac{3A^2}{h^2 \nu_L} \left\{ -8\left(V_{3x}^2 + V_{3y}^2\right) + \left[(V_{xx} - V_{yy})^2 + 4V_{xy}^2 \right] \right\}$$

VII - 19

Table VIII contains the results of our calculating the first and second order shifts of the $m = -1/2, 1/2$ and $3/2$ lines with the Li^+ in its $\langle 111 \rangle$, $\langle 110 \rangle$ and $\langle 100 \rangle$ configurations and with the $\underline{H}$ field applied along the same three directions in each case. The table shows that if the Li^+ lies in the $\langle 111 \rangle$ direction as the experiments indicate[6], then the first order splitting of the satellite lines increases as the field is rotated from the $\langle 100 \rangle$ to $\langle 111 \rangle$ directions through $\langle 110 \rangle$. Indeed, if the field is directed along $\langle 100 \rangle$, there will be no shifting to first order and only a very small (.01 mc/sec) second order shift. Thus, even if quantitative agreement with experiment is not obtained, the qualitative features such as the off-center direction of the Li^+ should be established.

D. Low-field Case

If the quadrupole interaction is larger than the magnetic interaction, the perturbation method breaks down and an alternative method must be used. We seek solutions to the secular equation, VII-6, with the total Hamiltonian, $\mathcal{H}$, given by the sum of equations VII-1 and VII-4. In this case, we choose a coordinate system, called the principal axis system, in which the field gradient tensor is diagonal. Furthermore, from symmetry considerations the field gradient is axially symmetric so that

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

and hence

$$V_{\pm 1} = V_{\pm 2} = 0$$

Table VIII

COORDINATES OF DEFECT IN r_0	H FIELD ALONG (111)					
	FIRST ORDER			SECOND ORDER		
	$m=-1/2$	$m=+1/2$	$m=+3/2$	$m=-1/2$	$m=+1/2$	$m=+3/2$
(.213, .213, .213)	.718	0.0	-.718	0.0	0.0	0.0
(.261, .261, 0)	.907	0.0	-.907	.017	.050	.017
(.280, 0, 0)	$.087\times10^{-6}$	0.0	$-.087\times10^{-6}$	.321	-.241	.321
	H FIELD ALONG (110)					
	FIRST ORDER			SECOND ORDER		
	$m=-1/2$	$m=+1/2$	$m=+3/2$	$m=-1/2$	$m=+1/2$	$m=+3/2$
(.213, .213, .213)	.359	0.0	-.359	.010	-.0097	.010
(.261, .261, 0)	.454	0.0	-.454	0.0	.083	0.0
(.280, 0, 0)	-.993	0.0	.993	.361	-.316	.361
	H FIELD ALONG (100)					
	FIRST ORDER			SECOND ORDER		
	$m=-1/2$	$m=+1/2$	$m=+3/2$	$m=-1/2$	$m=+1/2$	$m=+3/2$
(.213, .213, .213)	0.0	0.0	0.0	.010	-.0013	.010
(.261, .261, 0)	1.81	0.0	-1.81	0.0	.031	0.0
(.280, 0, 0)	-3.99	0.0	3.99	0.0	0.0	0.0

The only non-vanishing matrix elements of $\mathcal{H}_Q$, from equations VII-12, are then,

$$\langle m'|\mathcal{H}_Q|m\rangle = A' V_0 \left[3m^2 - I(I+1)\right] \delta_{m'm} \qquad \text{VII-20}$$

with A' given by VII-15.

Using equation VII-6, the matrix elements of the total Hamiltonian can be written

$$\langle m'|\mathcal{H}|m\rangle = -\gamma\hbar \Big\{ H_z m \delta_{m'm} + \tfrac{1}{2} H_+ \left[(I+m)(I-m+1)\right]^{1/2} \delta_{m'm-1} + \tfrac{1}{2} H_- \left[(I-m)(I+m+1)\right]^{1/2} \delta_{m'm+1} \Big\} + A' V_0 \left[3m^2 - I(I+1)\right] \delta_{m'm}$$

VII-21

For a spin 3/2 nucleus (Li^7),

$$\langle m'|\mathcal{H}|m\rangle = \left\{ -\gamma\hbar H_z m + A' V_0 \left[3m^2 - 15/4\right] \right\} \delta_{m'm} - \frac{\gamma\hbar}{2} H_+ \left[\left(\tfrac{3}{2}+m\right)\left(\tfrac{5}{2}-m\right)\right]^{1/2} \delta_{m'm-1} - \frac{\gamma\hbar}{2} H_- \left[\left(\tfrac{3}{2}-m\right)\left(\tfrac{5}{2}+m\right)\right]^{1/2} \delta_{m'm+1} \qquad \text{VII-22}$$

From equation VII-22 it is a simple matter to obtain the secular determinant:

$$\begin{vmatrix} \frac{3}{2}\gamma\hbar H_z + 3A'V_0 - E & -\frac{\sqrt{3}}{2}\gamma\hbar H_+ & 0 & 0 \\ -\frac{\sqrt{3}}{2}\gamma\hbar H_- & \frac{1}{2}\gamma\hbar H_z - 3A'V_0 - E & -\gamma\hbar H_+ & 0 \\ 0 & -\gamma\hbar H_- & -\frac{1}{2}\gamma\hbar H_z - 3A'V_0 - E & -\frac{\sqrt{3}}{2}\gamma\hbar H_+ \\ 0 & 0 & -\frac{\sqrt{3}}{2}\gamma\hbar H_- & -\frac{3}{2}\gamma\hbar H_z + 3A'V_0 - E \end{vmatrix} = 0 \qquad \text{VII-23}$$

It is to be emphasized that x, y, z in equation VII-23 refer to the principal axis system in which the field gradient is diagonal. In the special case where the Li^+ is in the $\langle 111 \rangle$ direction (in the crystal axis system), the principal z axis corresponds to the $\langle 111 \rangle$ direction. If the $\underline{H}$ field is directed along $\langle 111 \rangle$, all off-diagonal elements in equation VII-23 vanish. Hence

$$\left(\tfrac{3}{2}\gamma\hbar H_3 + 3A'V_0 - E\right)\left(\tfrac{\gamma}{2}\hbar H_3 - 3A'V_0 - E\right)\left(-\tfrac{\gamma}{2}\hbar H_3 - 3A'V_0 - E\right)\left(-\tfrac{3}{2}\gamma\hbar H_3 + 3A'V_0 - E\right) = 0 \qquad \text{VII-24}$$

Equation VII-24 has four solutions,

$$\begin{aligned} E_1 &= \tfrac{3}{2}\gamma\hbar H_3 + 3A'V_0 \\ E_2 &= \tfrac{\gamma}{2}\hbar H_3 - 3A'V_0 \\ E_3 &= -\tfrac{\gamma}{2}\hbar H_3 - 3A'V_0 \\ E_4 &= -\tfrac{3}{2}\gamma\hbar H_3 + 3A'V_0 \end{aligned} \qquad \text{VII-25}$$

which are the energy levels of a spin 3/2 nucleus. Transitions between these levels are given by $\frac{1}{h}(E_1 - E_2)$, $\frac{1}{h}(E_2 - E_3)$ and $\frac{1}{h}(E_3 - E_4)$ corresponding to $m = -1/2, 1/2, 3/2$ respectively. The central component is therefore

$$\frac{1}{h}(E_2 - E_3) = \frac{\gamma H_3}{2\pi}$$

which is to say that the quadrupole interaction does not shift the central component if the Li^+ is along the $\langle 111 \rangle$ and the $\underline{H}$ field is applied along $\langle 111 \rangle$. This is in agreement with the perturbation calculation of Table VIII. Similar results are obtained for the Li^+ along $\langle 100 \rangle$ and the $\underline{H}$ field along $\langle 100 \rangle$.

Although this method was derived for the low-field case, it holds in general. The perturbation method is useful because the physics of the situation is more clearly visible there. The methods of this section (VIII-D) are presently being used to do a complete study of the NMR problem. Equation VII-23 can be solved for all magnitudes and directions of the magnetic field and for all positions of the Li^+. When experimental work is completed, it is hoped that the position of the Li^+ (not only its direction) relative to the normal lattice site will be well established.

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Chapter VIII

Discussion

Certain improvements in our model for the crystal can be made. For example, we have not included any distortion dipole moment[1] caused by local departures from sphericity of the charge distribution on an ion. The shell model has also been employed[2,3] in some defect calculations. However, Dick[3] has indicated that the displacements and energies are not appreciably affected by deformation of the ions. The results of Chapter VII, however, may be greatly affected by the inclusion of the distortion dipoles.

As was discussed in Chapter II, our inclusion of the dipole-dipole energy is equivalent to taking account of the first iteration in the determination of the electric field due to electronic dipoles on all ions surrounding the defect. The inclusion of the effects of these dipoles is held by some authors[4] to be the same as dividing the field, equation II-11, by the dielectric constant. We feel this is not the case because the dielectric constant is a macroscopic quantity determined by including dipoles due to an applied external field. All dipoles induced in this way are parallel to the field; in the defective crystal, the dipoles are more radial in character and are due to the geometrical rearrangement of charge (and the excess charge in the case of a charged defect such as a vacancy) within the crystal. We are presently working on a method to determine to field due to dipoles on all ions.

A better repulsive potential could possibly be obtained by using low temperature data rather than room temperature measurements to which the Tosi-Fumi potential is fitted. A Heitler-London treatment of, perhaps, first and second neighbors of the Li^+ in KCl would represent a more fundamental approach to the problem.

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Errata

Foreword, line 4:	.... Laboratories ... should be .... Laboratory ....
p. 7, line 5:	.... election ... should be .... electron ....
p. 8, eq. II-1:	$-\frac{1}{2}\sum + \frac{1}{2}\sum$ should be $+\frac{1}{2}\sum - \frac{1}{2}\sum$
p. 9, last line:	.... duplicate ... should be .... derive ....
p. 11, line 1:	.... electionic ... should be .... electronic ....
p. 12, eq. II-10:	in second term, ... e_i ... should be .... e_j.
p. 14, eq. II-12:	$3\vec{r}_{ij} \cdot (\vec{r}_{ij} \cdot \alpha_j \vec{E}_j)$ should be $3\vec{r}_{ij}(\vec{r}_{ij} \cdot \alpha_j \vec{E}_j)$
p. 25, line 2:	.... Hence was given ... should be .... Hence σ was given..
p. 27, line 8:	.... assigned for ... should be .... assigned to ...
p. 35, line 23:	.... 6.70 cm ... should be .... 6.70 cm^{-1} ...
p. 43, line 12:	.... appreciable ... should be .... appreciably ...
p. 60, line 1:	delete comma after the word some.
p. 60, line 4:	.... quadupole ... should be .... quadrupole ....
p. 60, line 8:	.... election ... should be .... electron...
p. 60, line 9:	.... gives use ... should be .... gives rise ...

Wilson, William D. A Theoretical Investigation of Substitutional Li^+ in KCL