A Molecular Model for the Emission Process of $F_A(II)$ Centres in Alkali Halides

A Thesis
submitted in partial fulfilment of
the requirement for the degree of
Master of Science
at
The University of Manitoba
by
Andrew Yum Sing Kung
August, 1976.

"A MOLECULAR MODEL FOR THE EMISSION PROCESS OF F_A(II) CENTRES IN ALKALI HALIDES"

by

ANDREW YUM SING KUNG

A dissertation submitted to the Faculty of Graduate Studies of the University of Manitoba in partial fulfillment of the requirements of the degree of

MASTER OF SCIENCE

ACKNOWLEDGEMENTS

I would like to acknowledge gratefully Prof. J.M.Vail, my thesis supervisor, for his advice and assistance throughout the course of the work.

I would also like to thank Dr. A.M.Stoneham of the Theoretical Physics Division, A.E.R.E., Harwell, Oxon., England, where the following work was performed, for the generous allowance of computing time.

My thanks is also due to the kind hospitality of Prof. R.Evrard of the E.S.I.S., International Centre of Theoretical Solid State Physics, Institute of Physics, University of Liège, Belgium, where the final manuscript of the work was written up.

ABSTRACT

A variational calculation is carried out to estimate the emission energies of $F_A(II)$ centres in alkali halides. The $F_A(II)$ centre is treated as a hypothetical molecule immersed in a dielectric continuum. The hypothetical molecule consists of a single electron moving in the field of two unit positive charges and a central anion of effective charge Z different from unity. The ground and first excited states of such a molecule are evaluated as a function of interionic separation and effective charge from which the emission energies of $F_A(II)$ centres are deduced through a semi-empirical scheme.

Lattice relaxation is treated in the point-ion model with Coulomb and nearest neighbour Born-Mayer interaction. Only the zeroth order displacement of the saddle point ion and its two nearest neighbours are considered. The excess electron's charge is represented by point charges of $-\frac{1}{2}e$ at the centre of each potential well in determining these displacements. The set of displacements then determine Z, which forms a single-parameter characterization of each individual centre. Surveying the list of these values of Z reveals that there are three outstanding candidates as new type II centres beside the four experimentally known ones. These potential $F_A(II)$ centres are NaF:Li, RbF:Li and RbF:Na. Their emission energies are estimated by using the molecule to be 0.915, 0.513 and 0.591 eV. respectively.

LIST OF DEFINED SYMBOLS

a : lattice spacing.

a_o : Bohr radius.

(B,ρ) : Born-Mayer repulsive parameters.

c : constant determined from $c = r_{ab}/\sqrt{2}\, a$

$C_{g,u}$: coefficient of central orbital of the electronic wavefunction.

(d_1,d_2,d_3) : displacements of Saddle-Point anion, nearest host cation and impurity cation.

(D/d_-) : misfit parameter.

e : electronic charge.

eV : electron volt.

E : energy of model molecule immersed in dielectric medium.

E' : energy of model molecule in free space.

h : Planck's constant.

k : Boltzmann constant.

k_o : high frequency dielectric constant.

$N_{g,u}$: normalization constants.

R : interionic separation of model molecule in free space.

r_a, r_b : distances of electron from positive charges at sites A and B respectively.

r : distance of electron from central charge.

r_{ab} : effective separation of two-well potential.

V_c : potential from a cation vacancy along (110) direction in NaCl-type lattice.

V_p : potential due to a perfect NaCl-type lattice.

Z : effective charge of Saddle-Point anion.

α : localization parameter of electron.

α_M : Madelung's constant.

CONTENTS

Chapter 4 Evaluation of the Effective Charge Z.

Chapter 5 The Intrepretation and Discussion of the Magnitude of Z.

Chapter 6 Ground and First Excited State Energies of the Hypothetical Molecule - Numerical Results.

Chapter 7 Estimated Emission Energies of the New Type II Centres.

CHAPTER 1

F_A- CENTRES IN ALKALI HALIDES

1.1. Introduction

Colour Centres has been one of the major reseach themes in Solid State Physics during this century. The terminology is derived from the early observation that certain ionic crystals become coloured when exposed to cathode rays, each with its own colouration. Subsequent investigations have revealed that the phenomenon is due to selective absorption of light by defects present within the crystal lattices. A thorough review of the early work is the two articles written by Seitz$^{(1)}$. Of the numerous defect centres that have been identified, the F-centre in alkali halides, which consists of an electron trapped in an anion vacancy, has attracted particular attention because of the simplicity of the structures of both the defect and the host lattice.

The standard methods of creating F - centres in the laboratory is by irradiating the ionic crystal with X-rays, or heating it in an excess of alkali vapour. The X-ray frees electrons from the ionic cores into the conduction band, which are then trapped by the anion vacancies already present in the lattice at temperatures higher than absolute zero. Application of alkali vapour causes alkali ions to adhere to the surface of the crystal, which then draw halide ions from the interior of the crystal, creating anion vacancies to trap electrons. The optical absorption bands, known commonly as the F-bands, are invariably bell-shaped and lie in the visible part of the spectrum. With increasing temperature, the half-width of the band is increased and its peak is shifted to the low energy side. The emission band, which is due to the radiative transition of the excited F-electron to the ground state, has similar characteristics, and is on the low energy side of the absorption band. The shift between absorption and emission energies is known as the Stoke's Shift.

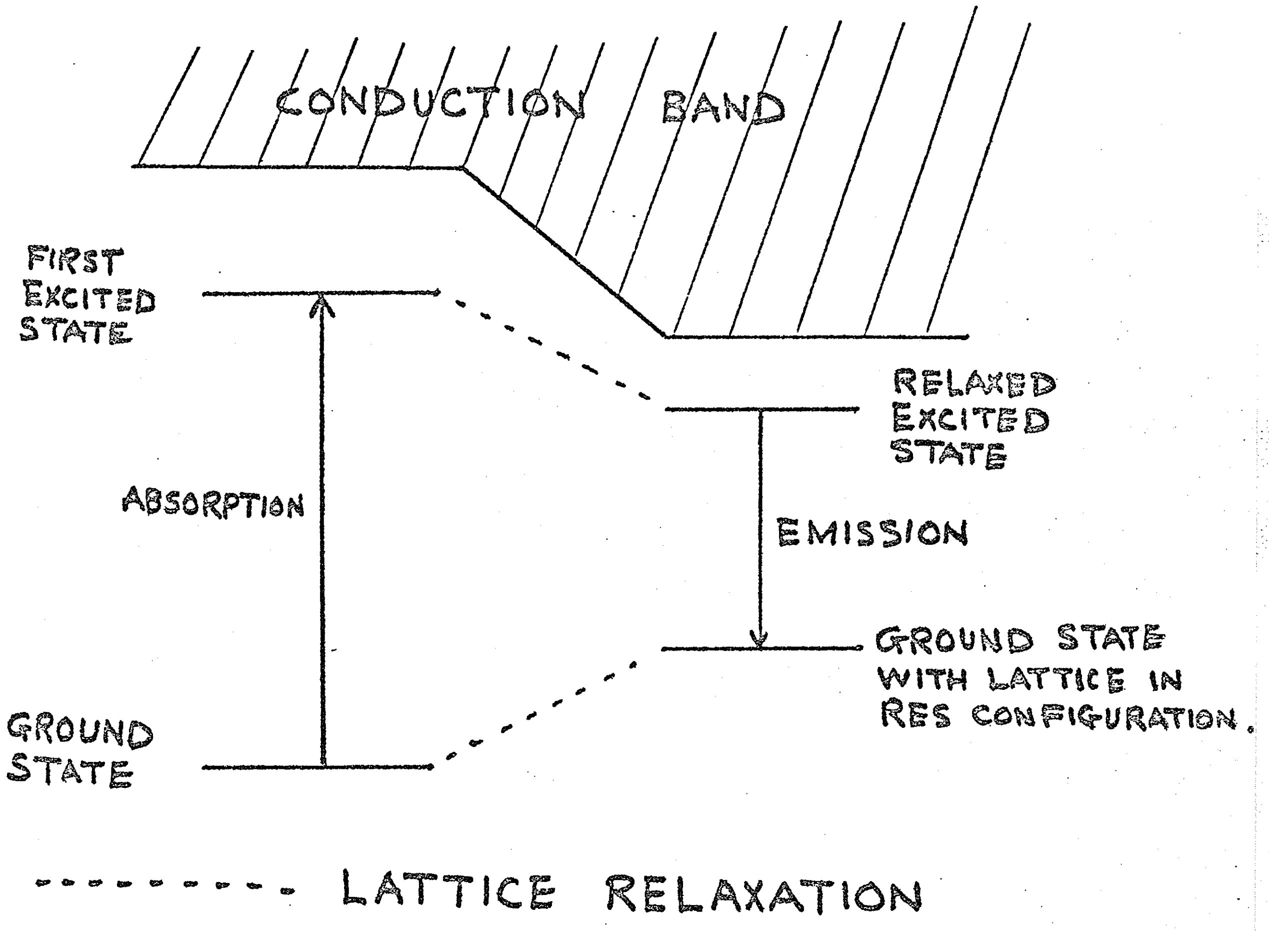
Fowler and Dexter(2) showed that the common Einstein's coefficients governing the various optical transition probabilities of the electrons in free atoms do not apply to excess electrons in a host lattice, such as F-centres. The qualitative picture is that the configuration of the host lattice is sensitive to the state of the excess electron. After optical excitation, the lattice around the defect will relax to a new configuration in such a way that the total energy of the system is a minimum. This is commonly known as the Relaxed Excited State (RES). Emission takes place between the RES and the ground state for which the lattice is in the same configuration as in the RES, in accordance with the Franck-Condon Principle. Finally, the electron goes back to the ground state through a radiationless transition. Thus, the emission energy is less than the absorption energy, giving rise to the Stöke's Shift. Both the energy level diagram and configuration co-ordinate diagrams are shown schematically in fig.1.

1.2. The Optical Transitions and Reorientation Energies in F_A- Centres.

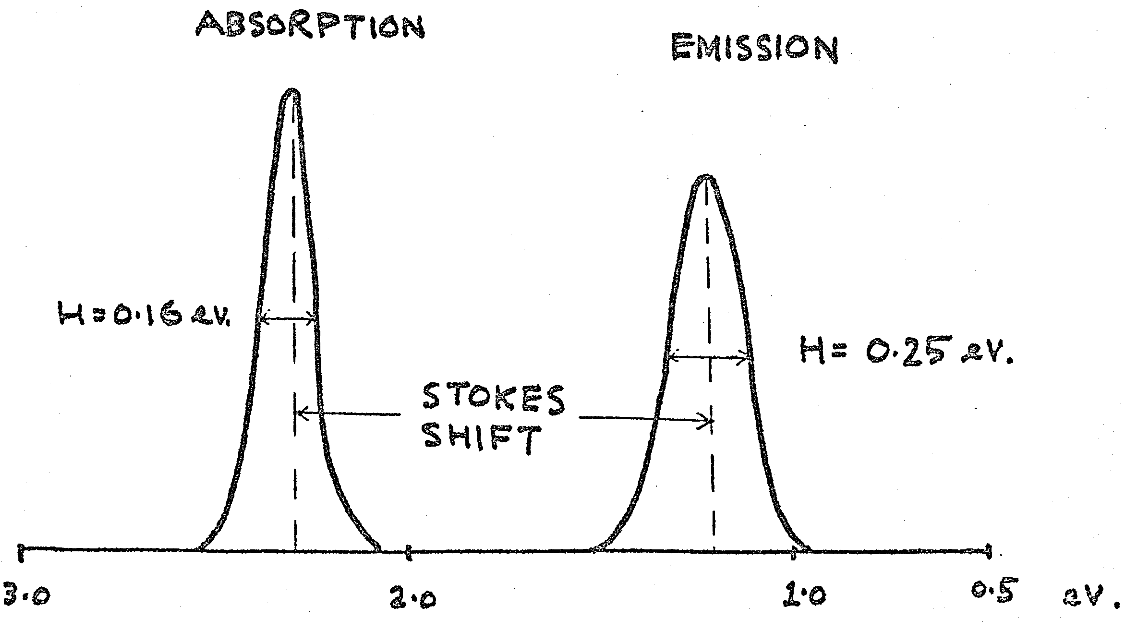
Because of the perfect cubic symmetry of the F-centre, the p-type excited state is triply degenerate,and according the the Jahn-Teller Theorem, this degeneracy is unstable to lattice distortion. One way of breaking the symmetry is to substitute one of the six nearest neighbour cations of the F-centre by a cation of another species. In alkali halides, if this substituted impurity is another alkali ion of smaller ionic size, then, the centre is called an F_A-centre. The model of this centre in KCl:Na (KCl doped with Na)

FIG. 1

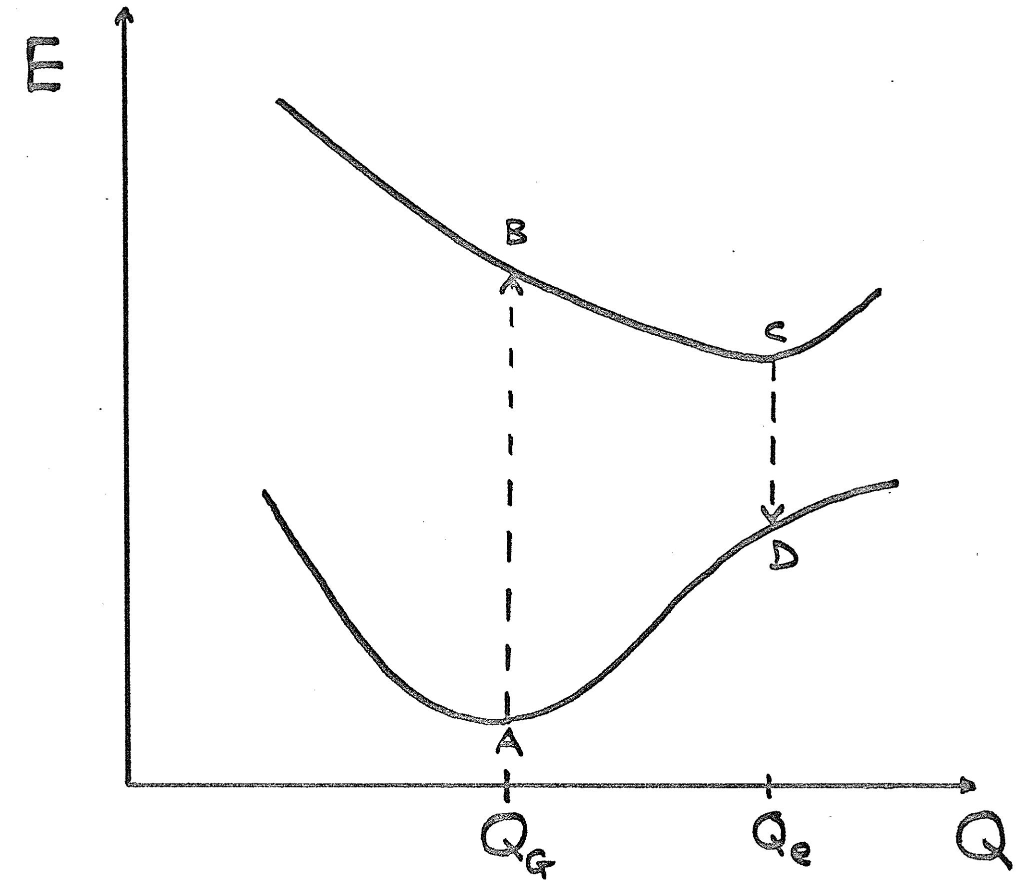
ENERGY LEVEL DIAGRAM OF OPTICAL PROCESS IN F-CENTRE



OPTICAL SPECTRUM OF F-CENTRE IN KCl



CONFIGURATION CO-ORDINATE DIAGRAM OF F_A-CENTRE



E : TOTAL ENERGY OF SYSTEM

AB : ABSORPTION

CD : EMISSION

Q_G, Q_E : CONFIGURATION CO-ORDINATES AT WHICH ABSORPTION AND EMISSION TAKE PLACE.

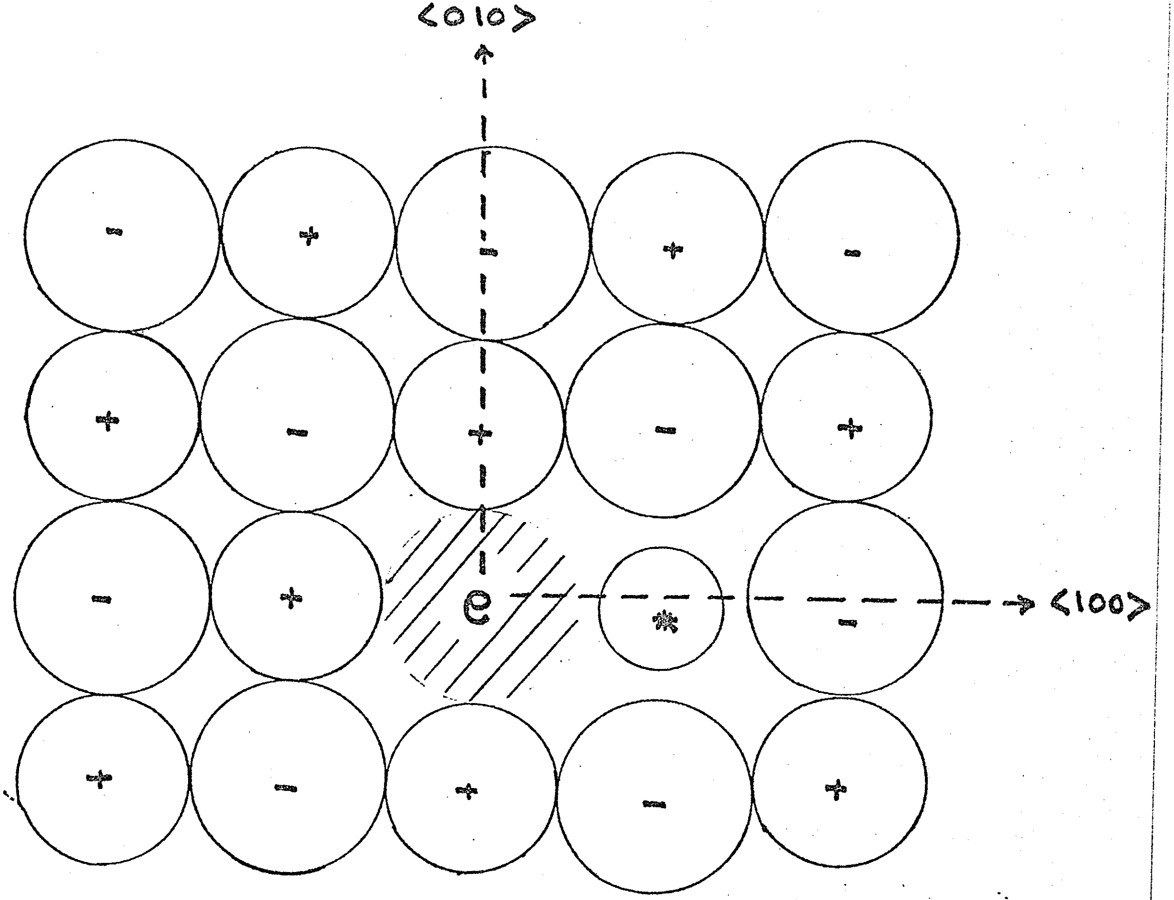
is shown in fig. 2. A thorough review on the physics of F_A-centres is given in ref. 3.

The presence of the impurity ion perturbs the F-centre in the (100) direction and as a consequence, the excited state is split into two. One is non-degenerate (100) oriented and the other is doubly degenerate, oriented perpendicular to (100). The absorption peak is thus dichroic, with the component parallel to the (100) perturbation called the F_{A1} band, and the other called the F_{A2} band. However, the emission peak remains a single one, showing that there is no splitting of energy levels in the RES. The absorption spectrum and energy level diagrams of the F_A centres are shown in fig. 3.

The size of the splitting in KCl:Na was treated quantitatively by Kojima, Nishimaki and Kojima(4), who wrote the wavefunction of the excess electron as a Linear Combination of Atomic Orbitals (L.C.A.O.) localized on the six nearest cations, assuming each orbital to be a mixture of s and p-type in the ratio of 3:1. After making certain approximations on the sizes of various matrix elements of the expectation values of their model Hamaltonian, they found that the perturbation due to the substituted impurity caused the ground state energy level to drop by a small amount. The splitting of the excited state is 0.25 ev., which agrees very well with the experimental result of 0.22 ev.

All the F_A- centres that have been investigated experimentally can be classified into two distinct catagories according to their emission properties which, from now on, will be referred to as type I F_A-centre (F_A(I)) and type II F_A-centre (F_A(II)).

FIG. 2. F_A-CENTRE IN ALKALI HALIDE



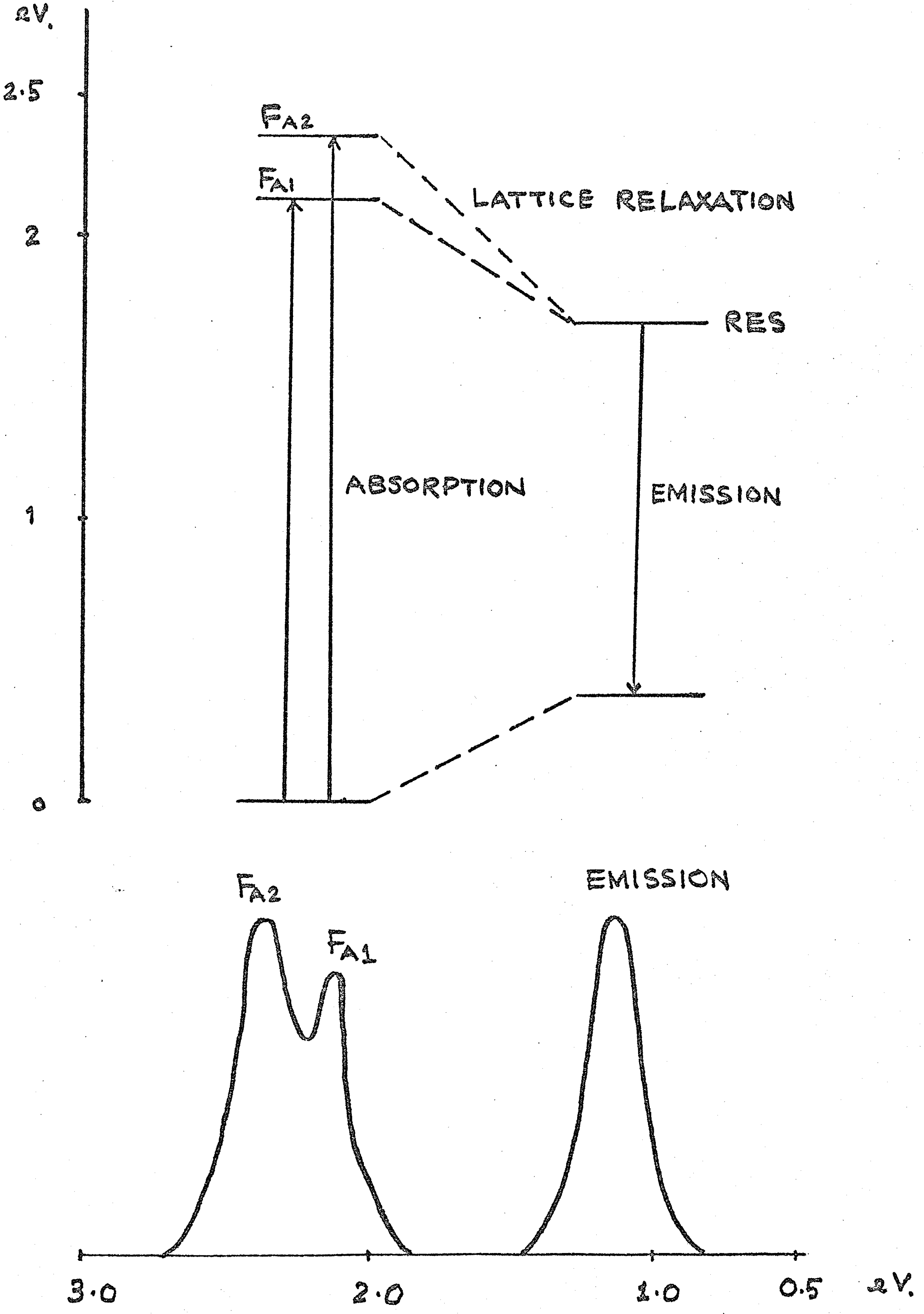
+ : ALKALI ION

– : HALOGEN ION

* : SUBSTITUTIONAL ALKALI ION WITH SMALLER IONIC RADIUS

e : EXCESS ELECTRON IN ANION VACANCY

FIG. 3 ENERGY LEVEL DIAGRAM AND OPTICAL SPECTRUM OF $F_A(I)$ CENTRE KCl:Na



1.2.1. Type I F_A-Centres

Up to now, there are seven experimentally known F_A centres that have type I behaviour. They are KCl:Na(3), KBr:Li(3), KBr:Na(3), RbCl:Na(3), RbBr:Li(5), RbBr:K(3), RbI:Li(5). The emission characteristics of these centres are quite similar to those of ordinary F-centres and are summarized below.

(a) The single emission band has a half-width similar to that of the F-centre. In KCl:Na at low temperature, it is 0.27 ev. with energy peaked at 1.12 ev.(6) The half-width broadens with temperature and roughly obeys the equation:

$$\frac{H^2(T)}{H^2(0)} = \coth\left(\frac{h\nu_e}{2kT}\right) \qquad (1.1)$$

where $H(T)$ = half-width at temperature T

k =Boltzmann Constant

ν_e = effective coupling frequency

The effective frequency ν_e here is to represent the overall coupling between the excess electron and all possible lattice vibration frequencies. In KCl:Na, it is found to be around 4.7×10^{12} sec^{-1}.

(b) The lifetime of the excited state of F-centre was first measured by Swank and Brown(7) who found that it is of the order of 10^{-6} sec. This is surprising on the basis that it is two orders of magnitude longer than that predicted by Mott and Gourney(8), whose theoretical argument gave the order of 10^{-8} sec. Spinolo and Brown(9) later made measurement on the lifetime of the RES of F_A-centres, and obtained somewhat smaller values than for the unperturbed F-centres. (E.g. the lifetime in KCl is found to be 0.58×10^{-6} sec. while that in KCl:Na is 0.53×10^{-6} sec.)

(c) Type I F_A-centres can be ionized at relatively high temperature or by applying an electric field. In both cases, electrons are excited into the conduction band and quantitative measurement of the conduction current elucidates the size of the energy gap between the RES and the conduction band, which is found to be around 0.1 ev.(11) The existence of such an electronic state just below the conduction band is also consistent with the presumed diffuse nature of the electronic wavefunction.

(d) The presence of the substituted cation adjacent to an F-centre reduces the O_h symmetry of the defect centre to C_{4v}. Thus, the F_A-centres are sensitive to directions in many respects. If the axis of the centre(i.e. the direction from the anion vacancy to the cation impurity) is (100), then, the centre is capable of reorientating itself into one of the four directions equivalent to (100), corresponding to the migration of one of the anions at (110), $(1\bar{1}0)$, (101) and $(10\bar{1})$ into the original vacancy. If the reorientation is to occur, the migrating anion must have sufficient energy to overcome the potential barrier on its path and thus the probability of reorientation is a function of temperature. This is found to be so for the F_A(I) centres and in fact at low temperature, we can write:

$$\eta_R = \eta_0 \exp.(-E_R/kT) \qquad (1.2)$$

where η_R = efficiency of reorientation
E_R = activation energy
η_0 = empirical constant of the order of 10^3

The reorientation process comes to saturation with $\eta_R \approx 2/3$ at high temperature and is frozen out at low temperature. Experimentally, it is observed that the activation energy E_R is much higher when the excess electron is in the ground state than when it is in the excited state. (1.25 ev. and 0.09 ev. respectively in KCl:Na)

1.2.2. Type II F_A-Centres

There are four F_A-centres that exhibit completely different emission properties from that described above. They are KCl:Li(3), RbCl:Li(5), KF:Li(12) and KF:Na(12). The peculiar behaviour of this group of centres was first observed by Spinolo and Brown(9) who were carrying out experiments to determine the lifetimes of the RES of KCl:Na, KBr:Na and KCl:Li, and reported the latter to be an 'interesting and anomalous case'. The details of the emission properties of F_A(II) centres are given in ref. 3 and are summarized below.

(a) Unlike F_A(I) centres, the F_A(II) centres show exceptionally large Stoke's Shifts and very narrow half-widths of their emission peaks (e.g. in KCl:Li, the half-width is 0.045 ev. and the energy peak is at 0.46 ev.).

(b) The lifetime of the RES of KCl:Li was measured by Gramm(13) to be 8×10^{-8} sec. This is about seven times shorter than that of an unperturbed F-centre in KCl. This is an unexpected result since the introduction of the Li ion lowered the emission energy from 1.24 ev. to 0.46 ev. and according to the relation :

$$A_{21} = \frac{1}{\tau} \propto \nu_{12}^{3}$$

where A_{21} = emission probability

τ = lifetime of the excited state from which emission takes place

ν_{12} = frequency of emitted energy

we should expect the lifetime of the RES in KCl:Li to be $(1.24/0.46)^3 \approx 20$ times longer than that in F-centre in KCl.

(c) Experiments performed by Link and Luty$^{(14)}$ have shown that F_A(II) centres cannot be ionised thermally or by applying electric field. This is an indication that the RES of type II centres are separated from the conduction band by a relatively large energy gap, a fact which is also consistent with the observation of large Stoke's Shift. Assuming

$$\eta_{ion} = \tau \nu \exp.(-\Delta E/kT) \qquad (1.3)$$

where η_{ion} = efficiency of ionization

τ = lifetime of RES

ν = effective coupling frequency

ΔE = energy gap between RES and conduction band

using measured values for τ and ν with the fact that η_{ion} is less than 1% at temperature 200°K, ΔE is found to be at least 0.27 ev., a value more than twice as large as it is in the F-or F_A(I)-centres.

(d) Reorientation of the centre's axis also occurs in type II centres after optical excitation. Whereas in type I centres, the reorientation efficiency depends on temperature due to the finite potential barrier, the reorientation efficiency of F_A(II) centres is completely independent of temperature, being 0.52± 15%

at all temperatures. Thus, after optical absorption, the anion has roughly a 50% probability of jumping into the vacancy where the F-centre originated.

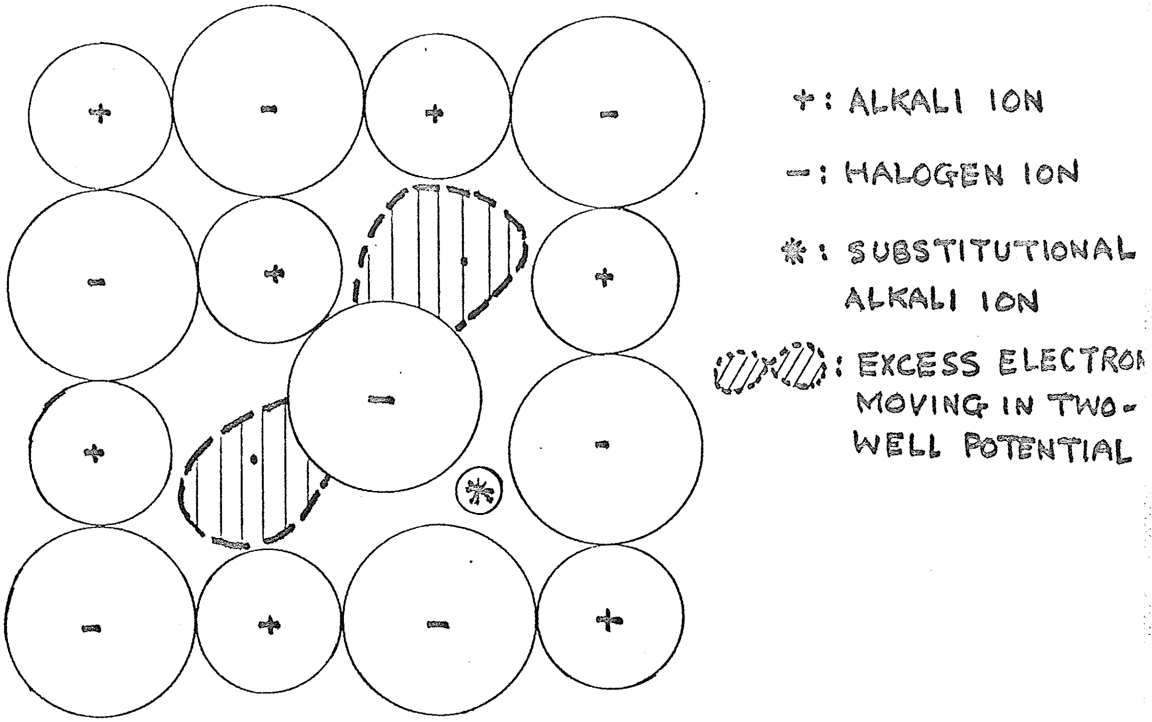
Since an activation energy of around 0.1 eV. is required for reorientation to occur in $F_A(I)$ centres, the process is frozen out at temperature below 100°K, whereas in $F_A(II)$ centres, the reorientation efficiency, being independent of temperature, still continues to be roughly 50%. Thus, measurement of the temperature dependence of the reorientation process forms an unambiguous experimental criterion in distinguishing $F_A(I)$ and $F_A(II)$ centres.

1.3. The Saddle Point Configuration (SPC) of F_A(II) Centres.

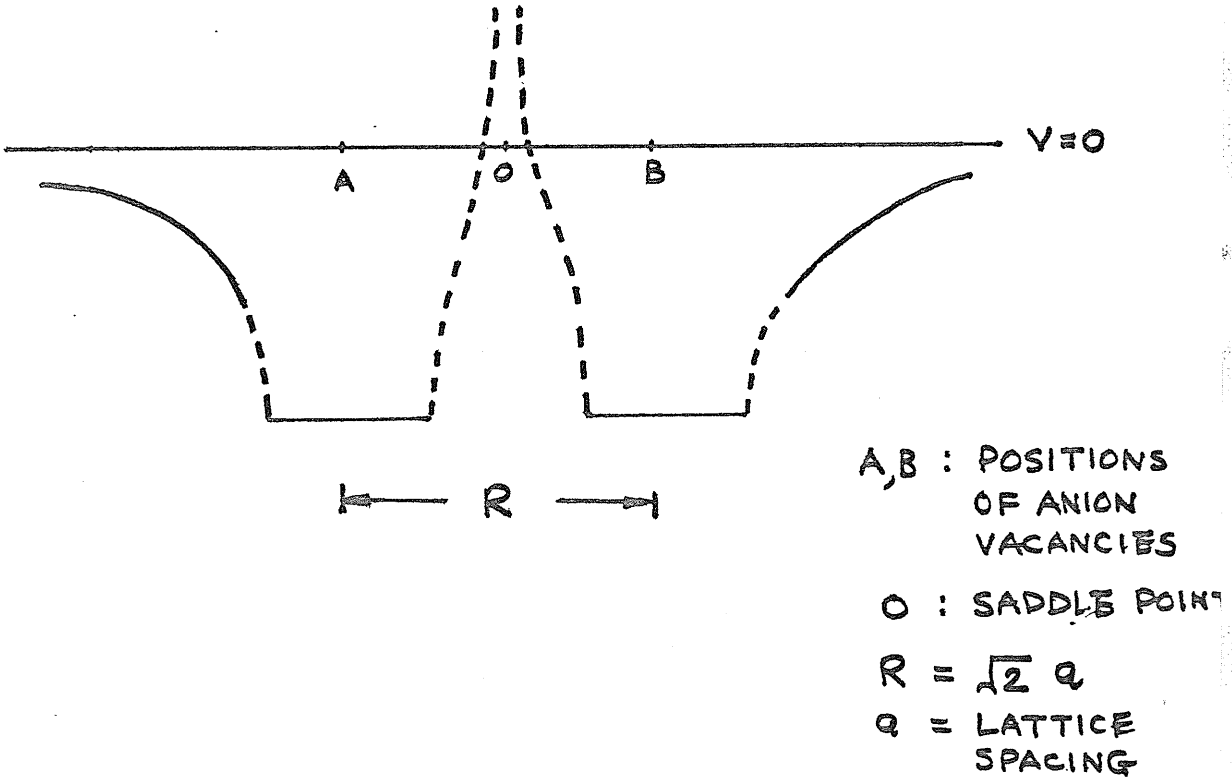
Following the discovery of the anomalous properties of KCl:Li, Lüty(3) proposed the Saddle Point Configuration (SPC) model to explain the anomality. The SPC is such that, in the lattice relaxation following optical absorption, one of the four (110) anions is drawn into the interstitial position $(\frac{1}{2},\frac{1}{2},0)$ so that the excess electron sees a two-well potential with a high barrier in the middle. (see fig. 4) The following mechanism for the stabilization of the SPC is proposed by Luty :

Normally, the SPC of the RES is not the minimum energy configuration due to the high repulsive potential betweem the Saddle Point (SP) ion and the various host ions, and actually, in the F_A(I) and F-centres, this is a maximum energy configuration, giving the height of the potential barrier in the reorientation process. Thus, in order to have reorientation to take place, the anion must have sufficient energy to overcome this barrier. However, as was pointed out by Guccione and Tosi(15), the mobility of the anion across the barrier is a sensitive function of the form of the repulsive potential used, and thus we expect the impurity cation in the F_A-centres to play a determining role in the formation of the SPC. In particular, since substitution of a small impurity will reduce the repulsive energy, the SPC should be more favoured in centres with small substitutional impurities (E.g. KCl:Li) than in those with larger ones (e.g. KCl:Na, KCl:Rb).

FIG. 4 THE SADDLE POINT CONFIGURATION OF F_A(II) CENTRE



THE TWO-WELL POTENTIAL WITH HIGH CENTRAL BARRIER AS SEEN BY THE EXCESS ELECTRON



Beside the energy economy amongst the ions, there is also the role of the excess electron. As was mentioned before, in the SPC, the excess electron sees essentially a two-well potential whereas in the Vacancy Configuration (VC), it sees a single potential well. Now, the simplest state for an electron moving in a single potential well are the 2p and 1s type of wavefunction, while in a two-well potential, they are approximated by antisymmetric and symmetric combination of 1s orbitals centred on the wells. However, in the alkali halide lattice, the two-well potential provides a stronger binding for an electron in the antisymmetric L.C.A.O. state than does the single well potential for a 2p electron. Thus, if the former is lower lying in energy, relaxation from the single well potential and 2p electronic state into the two-well potential SPC will result in the lowering of the energy of the system. Therefore, whether the SPC will be stabilized depends on the two competing energy considerations— the positive repulsive energy amongst the ions and the negative contribution due to the lower lying electronic state. In the type I F_A-centres, the repulsive part still dominates, and the VC results. However, the potential barrier is lowered to a large extent because of the cancellation of the two energies, and the reorientation energy becomes very small (0.09 ev. in KCl:Na). In the type II F_A-centres, the smaller size of the substitutional cation impurity reduces the repulsive part of the energy balance considerably and the overall result is that the SPC is fovoured energetically.

The above explanation due to Lüty is qualitative. Ong and Vail (OV)(21) have carried out a full scale calculation on the various contributions to the overall energetics in the VC and SPC. They used a point-ion model with ion-size correction due to Bartram, Stoneham and Gash(29), and lattice relaxation up to the fourth nearest neighbours are treated self-consistently with the excess electron wavefunction. What they found is different from the picture described by Luty, in that the electronic potential energy in the SPC is higher than that in the VC, but the contribution due to the ions in the lattice is more in favour of the SPC than the VC. The latter, however, cannot counterbalance the former and what actually stabilizes the SPC is the electronic kinetic energy which is lower in the SPC than in the VC.

The physical intrepretation that can come with the result of this calculation is that, although a two-well potential provides a tight binding for an antisymmetric L.C.A.O. wavefunction, the depth of both wells is shallower than the single well in the VC, due to the presence of the SP ion. Thus, the electronic potential energy in the SPC is higher. As far as the lattice energy is concerned, if the various ions in the neighbourhood of the defect are allowed to relaxed self-consistently with the excess electron wavefunction, the SPC is actually a lower energy configuration relative to the VC. On the other hand, the kinetic energy of the excess electron in the SPC is considerably lower than that in the VC due to its more diffused wavefunction. This, together with the lower lattice energy, counterbalances the high electronic potential energy and stabilizes the SPC in KCl:Li.

Thus, we see that the arguments of Lüty and OV for the stabilization of the SPC are based on different mechanisms. We cannot claim with certainty which one has a more reliable insight, since the former's reasoning is strictly intuitive, while the latter's calculations are based on a specific model. But, Lüty's reasoning is seen to fail in the context of OV's model.

Quantitatively, Lüty(3) has introduced the concept of 'misfit parameter' to explain the occurrence of F_A(II) centres. The misfit parameter is a function of the host lattice spacing and ionic radii. This will be described in section 5.1.

Because electric dipole transition requires the initial and final electronic states to be of opposite parity, and the Franck-Condon Principle requires that the same lattice configuration occurs before and after the transition, we should expect the final electronic state of the SPC emission to be a symmetric combination of orbitals centred on the two wells. Now, a two-well potential can only bind a wavefunction made up of symmetric combination of orbitals rather loosely, and a single well potential provides a relatively deeper binding for a 1s wavefunction, therefore, the saddle-point ground state becomes unstable and eventually relaxes to the VC ground state.

As indicated above, emission in F_A(II) centres is between antisymmetric and symmetric two-lobed wavefunction in the SPC, because these two states overlapped with each other more strongly than the 1s and 2p states. The higher transition probability and shorter lifetime than for the type I centres can readily be understood since :

$$A_{km} = \frac{1}{\tau_{km}} \propto \int \psi_k \vec{r} \psi_m d^3\vec{r}$$

where A_{km} = transition probability

τ_{km} = lifetime of state from which transition takes place

$\psi_{k,m}$ = initial and final electronic wavefunction

The SP ion retreats back to one of the two vacancy sites to restore the ordinary vacancy configuration, and the one to which it will go is essentially random. Thus, we should expect the reorientation efficiency to be exactly 50% and that it should be completely temperature independent. This is in agreement with experiments.

1.4. Application to Infra-Red Laser.

The optical processes of F-centres in alkali halides form a four-level system which is appropriate for laser action, but the broadness of their emission bands (typically of the order of 0.2 ev.) have prevented them from being of any practical value. The type II F_A-centres, because of the very narrow half-width and short lifetime, however, is a promising laser medium. Laser action in KCl:Li was first reported by Fritz and Menke(16), who observed laser emission at 2.7μ ($\approx$0.46 ev.) after pumping a crystal containing 10^{16} F_A-centres per c.c. with intensive flashes of 20-50 joules of 10 - 20 μ sec. duration. Following Fritz and Menke, Mollenauer and Olson(17) were recently successful in building a continous wave laser, operating on the same principle, and tunable over the range of 2.6-2.8μm. Their crystal contains 1-2 x 10^{17} F_A-centres per c.c. at 77°K, for an output of 5mW at 2.7μm. A 300 mW pumping input is required, the threshold for the laser action being 50 mW.

Lasers in the infrared and near infrared region can have a variety of practical advantages, especially in the field of molecular spectroscopy. The F_A(II) centres, beside providing the appropriate emission, can be obtained relatively inexpensively and thus lasers based on such a medium can be manufactured economically. One disadvantage is that the operating temperature has to be rather low (77°K). Although Mollenauer and Olson also reported that the same laser can be made to operate up to a temperature of 200°K, the threshold pumping power had to be tripled and the actual pumping power is considerably higher than that at low temperature. The major difficulty that prevents high temperature operation is that thermal agitation causes leakage through the conduction band and thus depopulate the RES to a point where population inversion cannot be maintained. In view of this, therefore, it is of both theoretical and practical interest to investigate the following questions :

(a) Of all the known F_A(II) centres, which one has the largest energy gap between the RES and conduction band? That is, which one is most stable thermally to enable operation with relatively low power and high temperature?

(b) Are there excited states between the first RES and the conduction band?

(c) Beside the four F_A-centres which are known to have type II behaviours, are there other undiscovered ones which have the same emission characteristics ?

(d) What are the emission energies of these undiscovered type II centres ?

To answer the first question we need to know the position of the conduction band relative to the RES of the excess electron. No experimental work had been done so far to give a conclusive answer. Furthermore, although, for the unperturbed F-centres, sufficient evidence has been gathered to indicate the existence of higher excited states beyond the first one, similar to those of the hydrogen atom, no serious effort had been directed on the same line for the F_A(II) centres. These topics by themselves deserve thorough investigation and we make no attempt to tackle them in the present project. We are here concerned with the last two questions, for which we try to simulate the emission process by a molecular model immersed in a dielectric medium and the SPC emission energies are calculated, without regard to whether the SPC is actually stabilized energetically.

With the four alkali cations (Li, Na, K, Rb) and four halogen anions (F, Cl, Br, I) we can construct 48 different crystals from the different combinations of the various host cations and anions and impurity cations. Discounting the 24 in which the impurity cation is larger than the host cations, we are left with 24 F_A-centres, of which most will likely have type I behaviours, and some have type II. In principle, the SP emission energies of all these 24 crystals can be calculated in the framework of our model, but those for which the SP is not stabilized would not be of immediate interest. In the course of our work, however, we shall see that we are led into a fairly tempting criterion to identify undiscovered F_A(II) centres, and their emission energies will be worked out.

A complete list of F_A-centres that have type II emission characteristics and their emission energies is of practical interest in the development of infrared lasers, as this can extend the range through which the laser can be tuned by selecting the appropriate medium. The following calculations are an attempt to tackle this problem.

CHAPTER 2

THE MOLECULAR MODEL FOR THE EMISSION PROCESS OF F_A(II) CENTRES.

2.1. F_A(II) Centre As a Hypothetical Molecule Immersed In a Dielectric Medium.

The optical absorption of F_2^+ centres, which consist of an electron trapped in a (110) anion vacancy pair, was first treated by Herman, Wallis and Wallis(18) theoretically as a H_2^+ ion immersed in a dielectric continuum. The H_2^+ ion is made up of an electron moving in the field of two positive charged nuclei separated at an equilibrium distance. Thus, each anion vacancy is simulated as a positive point charge and the lattice as a dielectric medium characterized by the optical frequency dielectric constant of the crystal. The calculation was greatly simplified because the various energy levels of the H_2^+ ion for a large range of internuclear separation was already well tabulated by Bates, Ledsham and Stewart(19). The calculated emission energy,absorption coefficient and oscillator strength in KCl based on this model are in very good agreement with experiments.

Following the success of the above authors, Aegerter and Lüty(20), while still using the same model, improved the calculation by allowing an effective dielectric constant in the place of the high frequency dielectric constant of the crystal, and an effective two-well separation in the place of simply the nearest neighbour distance between two anions used by the earlier authors. Further, by assuming the effective dielectric constant and the effective two-well separation to be related to the two unmodified crystal parameters by constants which are independent of the host lattice, they were able to obtain transition energies in close agreement with experimental results for the six crystals that had been investigated then, and predicted those that had not.

The RES of F_A(II) centres differ from the F_2^+ centres in that there is the SP anion situated in between the (110) anion vacancy pair. In view of the success of the calculations on the F_2^+ centres, it is suggested in ref. 12 to apply similar treatment to the F_A(II) emission process using a molecular model consisting of an electron moving in the field of two positive charges and a negative one situated midway along the line joining them. For reasons to be clarified in the next section, the charge of the negative ion in the middle is necessarily different from unity.

Neglecting ion-ion interaction, we can calculate the energy levels of the electron moving in the potential of these three ions as a function of the interionic separation. Then, we make appropriate modification to incorporate the effect of the dielectric medium into which the molecule is supposed to be immersed.

2.2. Effective Charge Z Of The Saddle Point Anion.

So far in the discussion on the RES of type II F_A-centres, we have neglected the relaxation of the lattice around the SP ion. The presence of of the SP ion and the vacancy pair would cause the ions in the immediate environment to shift from their perfect lattice equilibrium positions. Because of the presence of the impurity cation, the ionic displacements will not be symmetrical about the (110) axis, and consequently the SP ion itself is also displaced.

A rigorous treatment of the lattice relaxation would involve a self-consistent energy minimization between the set of ionic displacements and the excess electron wavefunction. This has been done, for the cases of of KCl:Li and KCl:Na, by Ong and Vail(21). Such sophistication, however, is not required in our context. Referring to fig. 5, the above authors had shown that it is energetically favourable for the various ions to remain in the y-z plane. For the three ions that we are considering, the displacements along the z-axis are taken to be zero. We will generalize this conclusion to all F_A-centres for the purpose of our calculation.

The displacement of SP ion along the y-direction means that the molecule we are interested in is not a linear one but the central anion is off-centred by an amount d_1 to be determined. Calculating the electronic energy levels of such a bent molecule would involve a lot of tedious integrals which are difficult to evaluate. Thus, we choose an alternative approach by asserting that our model molecule is still linear but now the central anion will be carrying an effective charge of -Ze. The value of Z is determined in such a way that the potential seen at the vacancy site due to the three displaced ions would be the same as that due to the undisplaced ions but with the central anion carrying a charge of -Ze. It is easy to derive the equation connecting Z and the set of displacements, with the various symbols as shown in fig. 5. The potential at the vacancy site due to the three undisplaced ions is given by :

$$V(Z) = \frac{|e|}{a}\left(2 - \sqrt{2}\,Z\right) \qquad (2.1)$$

where a = lattice parameter

e = electronic charge

The potential due to the displaced ions are given by :

$$V(d_1, d_2, d_3) = \frac{e}{a}\left\{ -\left(\frac{1}{2} + \frac{d_1^2}{a^2}\right)^{-1/2} + \left(1 - \frac{\sqrt{2}\,d_2}{a} + \frac{d_2^2}{a^2}\right)^{-1/2} + \left(1 + \frac{\sqrt{2}\,d_3}{a} + \frac{d_3^2}{a^2}\right)^{-1/2} \right\}$$

FIG. 5a. THE PERFECT KCl LATTICE

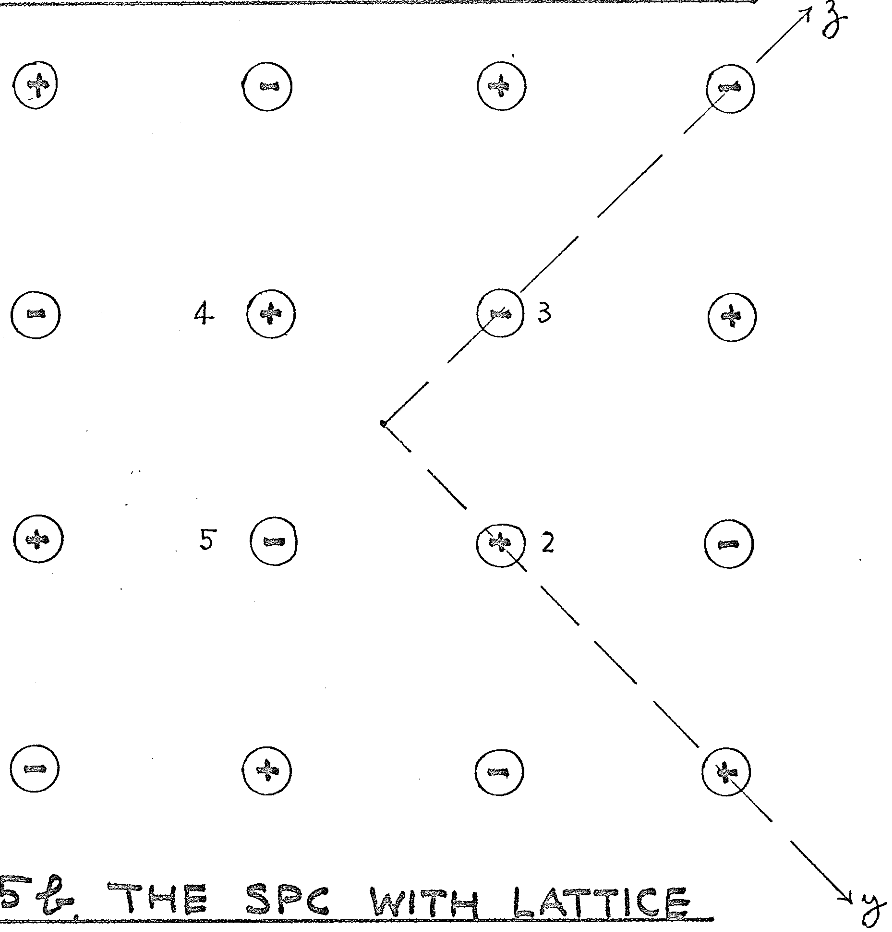
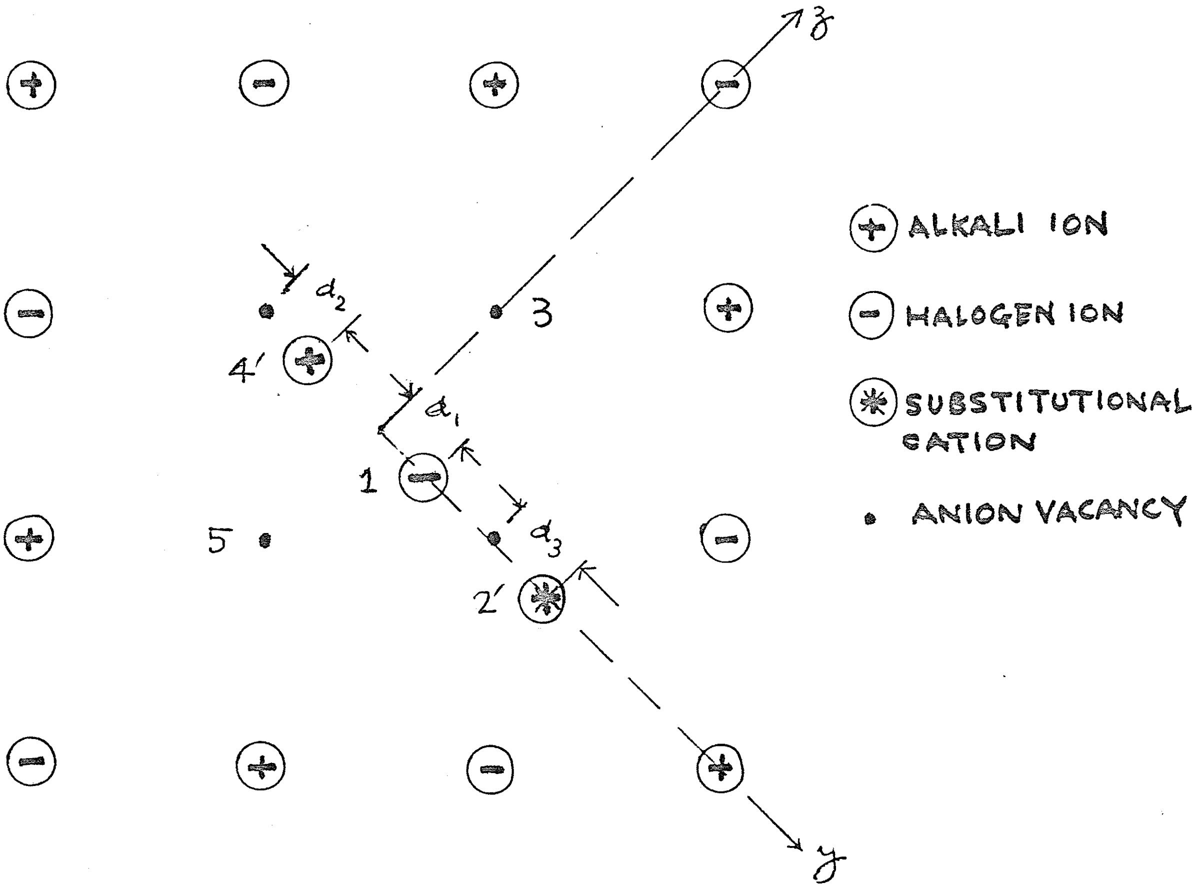


FIG. 5b. THE SPC WITH LATTICE RELAXATION IN $F_A(II)$ CENTRE



Writing d_1, d_2, d_3 in units of lattice parameters,

we obtain :

$$V(d_1, d_2, d_3) = \frac{\sqrt{2}\,e}{a}\left\{ -(1+2d_1^2)^{-1/2} + (2-2\sqrt{2}\,d_2+2d_2^2)^{-1/2} + (2+2\sqrt{2}\,d_3+2d_3^2)^{-1/2} \right\} \qquad (2.2)$$

$$= \frac{\sqrt{2}\,e}{a}\left(-D_1 + D_2 + D_3 \right)$$

where $D_1 = (1+2d_1^2)^{-\frac{1}{2}}$

$D_2 = \left[d_2^2 + (\sqrt{2}-d_2)^2 \right]^{-\frac{1}{2}}$

$D_3 = \left[d_3^2 + (\sqrt{2}+d_3)^2 \right]^{-\frac{1}{2}}$

and the d's are in units of lattice parameter.

For $V(Z) = V(d_1, d_2, d_3)$, we get :

$$(2-\sqrt{2}Z) = \sqrt{2}\,(-D_1 + D_2 + D_3)$$

$$Z = \sqrt{2} + D_1 - D_2 - D_3 \qquad (2.3)$$

We are going to evaluate the d's for the various crystals and dopings in Chapter 5. Then we will make use of equation (2.3) to calculate the effective charge of the SP ion.

2.3 An empirical scheme for estimating the emission energies of all potential type II F_A-centres from the molecular model

The Schrodinger equation for our molecule in space can be written as :

$$\nabla^2\Psi + \left(\frac{2}{r_a} + \frac{2}{r_b} - \frac{2Z}{r}\right)\Psi + E'(R,Z)\Psi = 0 \qquad (2.4)$$

where Ψ = electronic wavefunction

r_a, r_b, r = distance of electron from the two positive ions at sites A and B and the central anion respectively.(see fig. 6)

R = separation between the two positive ions.

E' (R,Z) = free space electronic energy as a function of R and Z.

All lengths in equation (2.4) are measured in units of Bohr radii a_0 and energy measured in Rydbergs.

$$1\ a_0 = \hbar^2/me^2 = 0.529\ \text{A} \qquad (2.5)$$

$$1\ \text{Rydberg} = e^2/2a_0 = 13.605\ \text{ev.}$$

and $\hbar$ is the Planck's constant divided by 2π and m and e are the electronic mass and charge respectively.

If the same molecule is immersed into a dielectric medium characterized by dielectric constant k_o, the corresponding Schrodinger equation will take the form :

$$\nabla^2\Psi + \frac{2}{k_o}\left(\frac{1}{r_a} + \frac{1}{r_b} - \frac{Z}{r}\right)\Psi + E(r_{ab}, k_o, Z)\Psi = 0 \qquad (2.6)$$

where r_{ab} = effective separation between the positive charges inside the dielectric medium.

$E(r_{ab}, k_o, Z)$ = electronic energy inside dielectric medium.

It is shown in Appendix 3 that equations (2.4) and (2.6) become equivalent if we make the following scalings:

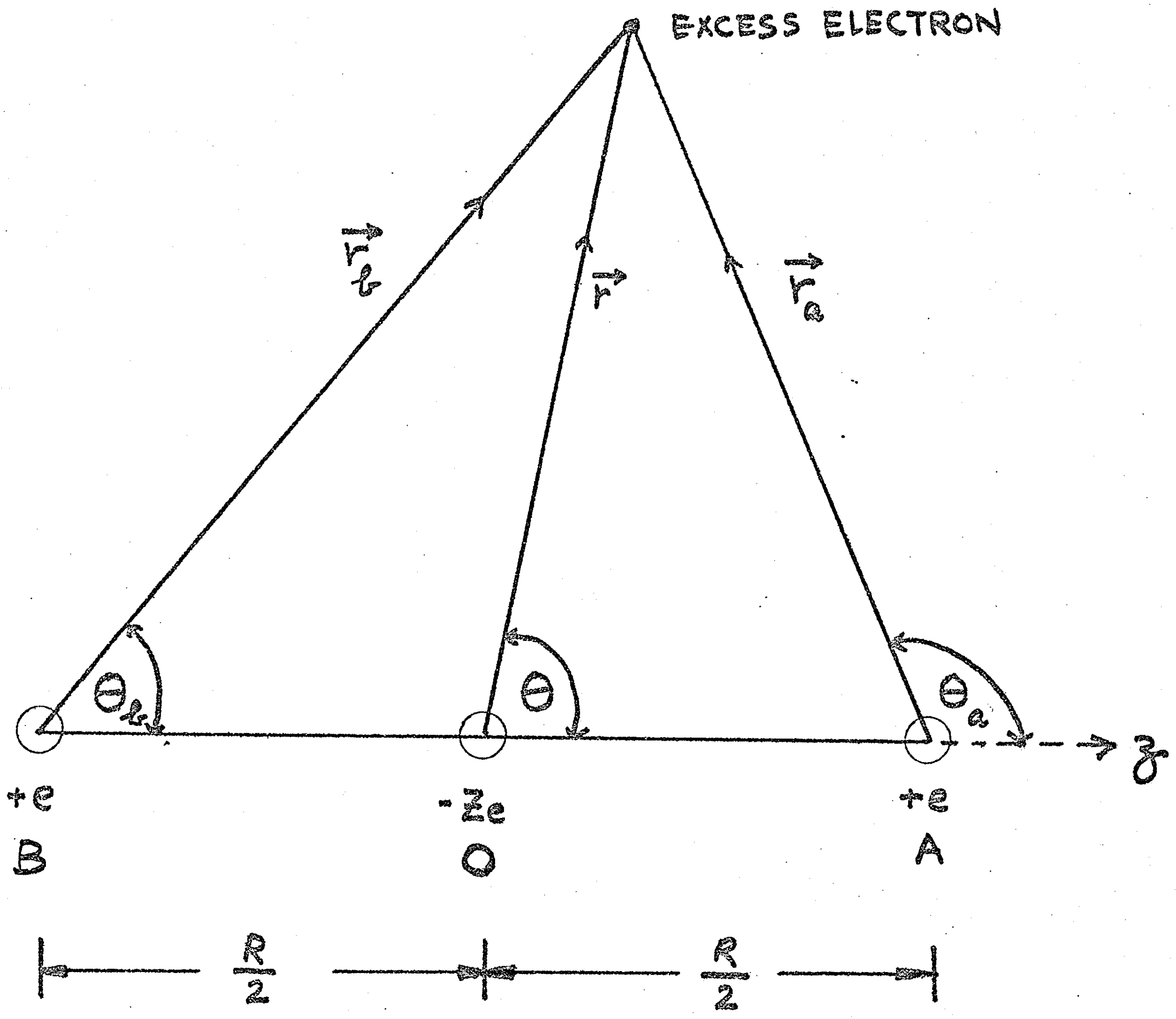
$$r_{ab} = k_o R \qquad (2.7)$$

$$E(r_{ab}, k_o, Z) = k_o^{-2} E'(R,Z)$$

With equation (2.7) allowing us to convert the energy and separation freely from free space to dielectric medium, the following approach was suggested by Vail, by analogy with the approach of Aegerter and Lüty(20) for the F_2^+ centre.

Assuming for the moment that the energy curves of the ground and first excited states of our hypothetical molecule in free space (E' vs. R) are mapped out, choose a F_A(II) centre whose emission energy E is known experimently, fit the quantity k_o^2E (which is equal to E'(R) from equation (2.7)) into the energy curves to determine R. Then, $r_{ab} = k_oR$ determines

FIG. 6 THE HYPOTHETICAL MOLECULE FOR F_A(II) CENTRE



an effective two-well separation of the centre in the lattice. By letting

$$r_{ab} = c\sqrt{2}\ a \qquad (2.8)$$

we determines a constant c which relates the effective two-well separation and the actual separation between the vacancy pair in the defect centre.

The value of c is characteristic of the particular centre concerned and thus can be thought of as a function of Z :

$$c = f\ (Z) \qquad (2.9)$$

So far, there are four type II centres whose emission energies are known. These give four pairs of (c,Z) values from which the form of f in equation (2.9) can hopefully be deduced empirically. This will be discussed again in Chapter 7. We will proceed here as if c is a known function of Z.

For a new crystal with new parameters $\tilde{a}$, $\tilde{Z}$, $\tilde{k}_o$, $\tilde{c}$, we first determine $\tilde{c}$ by equation (2.9) and then its effective two-well separation $\tilde{r}_{ab}$ by equation (2.8). $\tilde{r}_{ab}/\tilde{k}_o$ then determimes $\tilde{R}$ and from the energy curves we can read out $\tilde{E}'(\tilde{R},\tilde{Z})$. According to equation (2.7), dividing $\tilde{E}'$ by $\tilde{k}_o^{\,2}$ gives $\tilde{E}(\tilde{r}_{ab},\tilde{k}_o)$, the emission energy of the F_A(II) centre in the new crystal.

The above theory has the disadvantage that it contains no criterion to judge whether SPC in a given F_A-centre is stabilized — it simply calculates the emission energies of all F_A-centres as if they are all type II. Thus, a supplementary criterion to give a guideline as to which F_A-centres are likely to be type II would be desirable. We shall see later that this can actually be accomplished by examining the values of Z.

CHAPTER 3

GROUND AND FIRST EXCITED STATES ENERGIES OF THE HYPOTHETICAL MOLECULE — ANALALYTICAL RESULTS.

3.1. The Variational method.

We rewrite equation (2.4) for the Hamaltonian of our molecule, with the meaning of the various symbols as shown in fig. 6.

$$\nabla^2\Psi + \left(\frac{-2}{r_a} + \frac{-2}{r_b} + \frac{2Z}{r}\right)\Psi = E\Psi$$

$$\begin{aligned} \vec{r}_a &= \vec{r} + R\hat{k}/2 \\ \vec{r}_b &= \vec{r} - R\hat{k}/2 \\ r_a^{\,2} &= r^2 + R^2/4 + rR\cos\theta \\ r_b^{\,2} &= r^2 + R^2/4 - rR\cos\theta \end{aligned} \qquad (3.1)$$

and θ is the polar angle measured from the z-axis.

To solve equation (3.1) formally for the eigenvector Ψ and eigenvalue E would be a formidable task. We therefore take the variational approach. A concise review of the variational method can be found in ref. 23.

To solve the expectation value of a certain Hamaltonian $\mathcal{H}$ by the variational method, we essentially start by making an intelligent guess on the form of the wavefunction Ψ and make it to be function of some variational parameters $(\alpha_1 \ldots\ldots\ldots \alpha_n)$. Then we calculate the quantity :

$$E(\alpha_1 \ldots \alpha_n) = \frac{\langle \Psi(\alpha_1 \ldots \alpha_n) | \mathcal{H} | \Psi(\alpha_1 \ldots \alpha_n) \rangle}{\langle \Psi(\alpha_1 \ldots \alpha_n) | \Psi(\alpha_1 \ldots \alpha_n) \rangle} \qquad (3.2)$$

and we minimize this quantity w.r.t. the whole set of variational parameters. This is equivalent to solving the set of simultaneous equations:

$$\frac{\partial E(\alpha_1 \ldots\ldots \alpha_n)}{\partial \alpha_j} = 0$$

$j = 1,2,\ldots\ldots\ldots,n$

On substituting the values of the α's back to equation (3.2), we get the optimized value for the energy E.

The reliability of the calculated result depends critically on the form of the trial wavefunction (twf) that we choose to start with. The exact eigenvalue to the original Hamaltonian can be reproduced if the twf corresponds exactly to the true eigenvector. Deviation of the twf from the correct one causes the calculated energy to take a higher value.

3.2. The Trial Wavefunction

In treating a one-electron molecular problem, the L.C.A.O. form of twf is usually adopted and has proved to be satisfactory in many cases. It is especially suitable for problems when the overlap of the electronic wavefunction between neighbouring centres is small. Slater(22) has calculated the ground state energy of the H_2^+ ion using twf of L.C.A.O. of two 1s hydrogenic orbitals centred on each positive charge. (The H_2^+ ion consists of an electron moving in the field of two positive charges.) The results he obtained agreed very well with the exact calculations by Bates et al(19). In view of the similarity between the H_2^+ problem and the present one, it seemed reasonable for us to write down the ground and first excited states twf in the same way:

$$\begin{aligned} \psi_g &= \frac{1}{\sqrt{N_g}}\left(e^{-\alpha r_a} + e^{-\alpha r_b}\right) \\ \psi_u &= \frac{1}{\sqrt{N_u}}\left(e^{-\alpha r_a} - e^{-\alpha r_b}\right) \end{aligned} \qquad (3.3)$$

where $\Psi_{g,u}$ = ground and first excited states twf

$N_{g,u}$ = normalization constants

α = variational parameters

However, closer examination revealed that equation (3.3) which is L.C.A.O. of two Slater orbitals could be unsatisfactory in two respects :

(a) For the even parity ground state, we would expect the amplitude of wavefunction at the vacinity of the anion to be very small since Coulomb interaction between the electron and the anion is repulsive. The only way Ψ_g of equation (3.3) can accomplish this is to have very localized orbitals centred on the two positive ionic sites. The requirement of localization may place unnecessary constraint to the energetics of the system, since localization is usually accompanied with increase in kinetic energy.

(b) As the separation between the ions approach zero, we would expect our molecule to become a hydrogen atom if Z = 1. Thus, it is reasonable to require that Ψ_g and Ψ_u should go to the 1s and 2p hydrogenic orbitals in this limit. In equation (3.3), Ψ_g does go over to the 1s orbital as R goes to zero, but it is obvious that Ψ_u would not become the 2p state.

To overcome these objections we introduce a third orbital to our twf, centred on the anion in both the ground and excited states :

$$\Psi_g = \frac{1}{\sqrt{N_g}}\left(e^{-\alpha r_a} + e^{-\alpha r_b} + C_g e^{-\alpha r}\right) \qquad (3.4)$$

$$\Psi_u = \frac{1}{\sqrt{N_u}}\left(e^{-\alpha r_a} - e^{-\alpha r_b} + C_u r\cos\theta\, e^{-\alpha r}\right)$$

and C are variational parameters.

The presence of the third orbital $C_g e^{-\alpha r}$ in Ψ_g is to help reduce the wavefunction amplitude around the anion. The value of C_g would have to turn out to be negative. The term $C_u r\cos\theta e^{-\alpha r}$ in Ψ_u is the 2p hydrogen orbital weighted by the factor C_u. Its presence assures the correct behaviour of the twf in the limit of small ionic separation.

It is not absolutely correct to assume all the three orbitals to have the same localization (i.e. same value of α). The localization of the central orbital is actually different from the other two. We have made such approximation in order to reduce the complexity of the computation.

3.3. Analytical Results.

The ground and excited state energies, E_g and E_u respectively, are the expectation values of the Hamaltonian $\mathcal{H}$ given in equation (3.1) with wavefunctions given in equation (3.4). Thus,

$$E_g(\alpha, R, C_g, Z) = \frac{\langle \Psi_g | \mathcal{H} | \Psi_g \rangle}{\langle \Psi_g | \Psi_g \rangle}$$

$$E_u(\alpha, R, C_u, Z) = \frac{\langle \Psi_u | \mathcal{H} | \Psi_u \rangle}{\langle \Psi_u | \Psi_u \rangle}$$

The calculations leading to the final results of E_g and E_u involve very messy algebra, and in the course of which, many two- and three- centre integrals are come across. Most of the two-centre integrals can be evaluated in closed form in either spherical or spheroidal co-ordinates. The three-centre integrals, however, cannot be obtained in closed form and have to be solved numerically.

We merely present the final analytic form of E_g and E_u here:

$$
\begin{aligned}
E_g(\alpha, R, C_g, Z) = \frac{1}{N_g} \Bigg\{ & \frac{2\pi}{\alpha}\Big[1 + e^{-\alpha R}\left(1 + \alpha R - \frac{\alpha^2 R^2}{3}\right) \\
& + 2C_g e^{-\alpha R/2}\left(1 + \frac{\alpha R}{2} - \frac{\alpha^2 R^2}{12}\right) + \frac{C_g^2}{2}\Big] \\
& - \frac{4\pi}{\alpha^2}\Big[1 + \frac{1}{\alpha R} - e^{-2\alpha R}\left(1 + \frac{1}{\alpha R}\right) + 2e^{-\alpha R}(1 + \alpha R)\Big] \\
& - \frac{8\pi C_g}{\alpha^2}(1 - Z)e^{-\alpha R/2}\left(1 + \frac{\alpha R}{2}\right) \\
& - 8C_g I_1(\alpha, R) + 4Z I_5(\alpha, R) \\
& + \frac{8\pi}{\alpha^3 R}(Z - C_g^2)\Big[1 - e^{-\alpha R}\left(1 + \frac{\alpha R}{2}\right)\Big] \\
& + \frac{2\pi C_g^2 Z}{\alpha^2} \Bigg\} \qquad (3.5)
\end{aligned}
$$

AND

$$
\begin{aligned}
N_g = \frac{2\pi}{\alpha^3}\Bigg\{ & 1 + e^{-\alpha R}\left(1 + \alpha R + \frac{\alpha^2 R^2}{3}\right) \\
& + 2C_g e^{-\alpha R/2}\left(1 + \frac{\alpha R}{2} + \frac{\alpha^2 R^2}{12}\right) \\
& + \frac{C_g^2}{2} \Bigg\} \qquad (3.6)
\end{aligned}
$$

$$
\begin{aligned}
E_\mu(\alpha, R, C_\mu, Z) = \frac{1}{N_\mu}\Big\{ & \frac{2\pi}{\alpha}\Big[1 - e^{-\alpha R}\Big(1 + \alpha R - \frac{\alpha^2 R^2}{3}\Big)\Big] \\
& - 4C_\mu(\alpha + 2Z + 2)\, I_3(\alpha, R) \\
& + \frac{\pi C_\mu R}{\alpha} e^{-\alpha R/2}\Big(1 + \frac{\alpha R}{2} - \frac{\alpha^2 R^2}{12}\Big) + \frac{\pi C_\mu^2}{\alpha^3} \\
& - \frac{4\pi}{\alpha^2}\Big[1 + \frac{1}{\alpha R} - e^{-2\alpha R}\Big(1 + \frac{1}{\alpha R}\Big) - 2e^{-\alpha R}(1 + \alpha R)\Big] \\
& + 4C_\mu R\, I_1(\alpha, R) - \frac{4\pi C_\mu R}{\alpha^2} e^{-\alpha R/2}\Big(1 + \frac{\alpha R}{2}\Big) \\
& + 8C_\mu I_4(\alpha, R) - 4C_\mu^2\, \xi(\alpha, R) \\
& + \frac{8\pi Z}{\alpha^3 R}\Big[1 - e^{-\alpha R}\Big(1 + \frac{\alpha R}{2}\Big)\Big] \\
& - 4Z\, I_5(\alpha, R) + \frac{\pi Z C_\mu^2}{\alpha^4}\Big\}
\end{aligned}
\qquad (3.7)
$$

$$
\begin{aligned}
N_\mu = & \frac{2\pi}{\alpha^3}\Big[1 - e^{-\alpha R}\Big(1 + \alpha R + \frac{\alpha^2 R^2}{3}\Big)\Big] \\
& - 4C_\mu I_2(\alpha, R) + \frac{\pi C_\mu^2}{\alpha^5}
\end{aligned}
\qquad (3.8)
$$

$$I_1(\alpha, R) = \int d^3\vec{r}\, \frac{e^{-\alpha r_a}\, e^{-\alpha r}}{r_b}$$

$$I_2(\alpha, R) = \int d^3\vec{r}\; r\cos\theta\; e^{-\alpha r}\, e^{-\alpha r_b}$$

$$I_3(\alpha, R) = \int d^3\vec{r}\; \cos\theta\; e^{-\alpha r}\, e^{-\alpha r_b}$$

$$I_4(\alpha, R) = \int d^3\vec{r}_a\; \cos\theta_a\; e^{-\alpha r}\, e^{-\alpha r_b}$$

$$I_5(\alpha, R) = \int d^3\vec{r}\, \frac{e^{-\alpha r_a}\, e^{-\alpha r_b}}{r}$$

$$\xi(\alpha, R) = -2\pi e^{-\alpha R}\left\{\frac{R^2}{8\alpha^2} + \frac{3R}{4\alpha^3} + \frac{11}{4\alpha^4} + \frac{7}{\alpha^5 R} + \frac{12}{\alpha^6 R^2} + \frac{12}{\alpha^7 R^3} - \frac{e^{\alpha R}}{\alpha^5 R} - \frac{12\, e^{\alpha R}}{\alpha^7 R^3}\right\}$$

$$|\vec{r}_a| = \left(r^2 + \frac{R^2}{4} - rR\cos\theta\right)^{1/2}$$

$$|\vec{r}_b| = \left(r^2 + \frac{R^2}{4} + rR\cos\theta\right)^{1/2}$$

3.4. The limits as interionic separation R goes to zero and infinity.

3.4.1. $R \rightarrow 0$

As our hypothetical molecule consists of an electron moving in the field of two cation and one anion, we would expect that as the interionic separation goes to zero, the molecule will be reduced to a hydrogen atom if $Z = 1$. In this section, we want to derive the energies of the ground and first excited state in the limit of $R \rightarrow 0$, and show that by putting $Z = 1$, the energy expressions (3.5) and (3.7) will give the appropriate energies of hydrogen atom. This will serve the purpose of checking the correctness of the energy equations, which is desirable since the derivation leading to the latter involved complicated algebra from which analytical errors are likely to arise.

(a) Ground state

We want ot look at:

$$\lim_{R \to 0} E_g(\alpha, R, C_g, Z) = \lim_{R \to 0} \left[E_g''(\alpha, R, C_g, Z)/N_g \right]$$

where $E_g''(\alpha, R, C_g, Z)$ is identical with equation (3.5) apart from the normalization factor N_g.

It is easy to see from equation (3.6) that :

$$\lim_{R \to 0} N_g = (\pi/\alpha^3)(4 + 4C + C^2) \qquad (3.9)$$

To evaluate E_g'' in the limit of R goes to zero, we first note that:

$$\begin{aligned} \lim_{R \to 0} I_1(\alpha, R) &= \pi/\alpha^2 \\ \lim_{R \to 0} I_2(\alpha, R) &= 0 \\ \lim_{R \to 0} I_3(\alpha, R) &= 0 \\ \lim_{R \to 0} I_4(\alpha, R) &= 0 \\ \lim_{R \to 0} I_5(\alpha, R) &= \pi/\alpha^2 \end{aligned} \qquad (3.10)$$

The various indeterminate terms arising from equation (3.5) in this limit can be worked out easily by l'Hopital's Rule. The results are as follows:

$$\lim_{R\to 0}\left(\frac{4\pi e^{-2\alpha R}}{\alpha^3 R} - \frac{4\pi}{\alpha^3 R}\right) = -\frac{8\pi}{\alpha^2}$$

$$\lim_{R\to 0}\left(\frac{8\pi C_g^2 e^{-\alpha R}}{\alpha^3 R} - \frac{8\pi C_g^2}{\alpha^3 R}\right) = -\frac{8\pi C_g^2}{\alpha^2}$$

With these, we can write down the value of E_g'' in this limit:

$$\lim_{R\to 0} E_g''(\alpha, R, C_g, Z) = \frac{\pi}{\alpha}(4 + 4C_g + C_g^2) + \frac{2\pi}{\alpha^2}(Z - 2)(C_g^2 + 4C_g + 4)$$

Then,

$$\lim_{R\to 0} E_g(\alpha, R, C_g, Z) = \lim_{R\to 0}(E_g''/N_g) = \alpha^2 + 2\alpha(Z - 2) \qquad (3.11)$$

Equation (3.11) gives the ground state energy at R = 0 as a function of α and Z. For a given value of Z, the stable configuration is of minimum energy, which we obtain by minimizing (3.11) w.r.t. α :

$$\lim_{R\to 0}\frac{\partial E_g}{\partial \alpha} = 0 = \alpha_0 + Z - 2$$

$$\alpha_0(Z) = 2 - Z \qquad (3.12)$$

Substituting this into equation (3.11), we have

$$\lim_{R\to 0} E_g(Z) = -Z^2 + 4Z - 4 \qquad (3.13)$$

We see from equation (3.13) that if Z = 1, $E_g = -1$ Rydberg and $\alpha_0 = 1$. This corresponds to a free hydrogen atom, as it should be. If Z = 2, $\alpha_0 = 0$ and $E_g = 0$ which corresponds to a completely dislocalized electron seeing no potential. This is again consistent with the physical structure of the model.

<u>(b) First excited state.</u>

Inspecting equation (3.8) and using equation (3.10), we get

$$\lim N_u = \pi C_u^2/\alpha^5 \qquad (3.14)$$

The value of ξ in the limit of $R \to 0$ can be found by using l'Hopital's rule after expanding the exponents in power series. This has worked out to be:

$$\lim_{R\to 0} \xi = \frac{\pi}{2\alpha^4}$$

Again, writing $E_u = E_u''/N_u$ where E_u'' is the same as E_u apart from the Normalization factor N_u, we can show that :

$$\lim_{R\to 0} E_u''(\alpha, R, C_u, Z) = \frac{\pi c^2}{\alpha^3} + \frac{\pi c^2 (Z-2)}{\alpha^4}$$

$$\lim_{R\to 0} E_u(\alpha, R, C_u, Z) = \lim_{R\to 0}\left(\frac{E_u''}{N_u}\right)$$

$$= \alpha^2 - (Z-2)\alpha \qquad (3.15)$$

C_u disappears from the final expression and the energy in this limit is only a function of α for a given value of Z. Minimizing the energy expression w.r.t. α , we have :

$$\lim_{R\to 0} \frac{\partial E_u(\alpha, R, C_u, Z)}{\partial \alpha} = 0 = 2\alpha - Z + 2$$

$$\alpha_0(Z) = -1 + Z/2 \qquad (3.16)$$

$$\lim_{R\to 0} E_u(Z) = -(-2 + Z)^2/4 \qquad (3.17)$$

For Z = 1, equation (3.16) gives $\alpha_0 = \frac{1}{2}$, and (3.17) gives $E_u = -\frac{1}{4}$ Rydberg. These are exactly the localization and energy respectively of the 2p state of the hydrogen atom.

3.4.2. $R \to \infty$

We now investigate the convergence of the energy equations at the other extreme, i.e., when the interionic separation becomes infinite. Intuitively, we would expect the electron to localize on either one of the positive ions at $\pm\infty$ with equal probability, the central anion should have no effect on the energy of the system at all in this limit. Thus, we should find $C_{g,u} \to 0$ as $R \to \infty$, and that our energy equations (3.5) and (3.7) should both give -1 Rydberg which is the ground state hydrogen atom energy. Further, both α and $E_{g,u}$ should not be a function of Z in this limit.

(a) Ground state.

We first note that

$$\lim_{R\to\infty} N_g = \frac{\pi}{\alpha^3}(2 + C^2)$$

$$\lim_{R\to\infty} E_g'' = \frac{\pi}{\alpha^3}\left[2\alpha(ZC_g^2 - 2) + \alpha^2(C_g^2 + 2)\right]$$

$$\lim_{R\to\infty} E_g = \frac{2\alpha(ZC_g^2 - 2) + \alpha^2(C_g^2 + 2)}{C_g^2 + 2} \qquad (3.18)$$

Equation (3.18) is a function of C_g, α, Z. We first minimize the energy w.r.t. the variables α and C_g, assuming Z to be a fixed constant.

$$\frac{\partial E_g}{\partial \alpha} = (\alpha + Z)C_g^2 + 2\alpha - 2 = 0 \qquad (3.19)$$

$$\frac{\partial E_g}{\partial C_g} = 8\alpha C_g(Z + 1) = 0 \qquad (3.20)$$

The values of α and C_g that solve (3.19) and (3.20) simultaneously are:

(i) $\alpha = 1$; $C_g = 0$

(ii) $\alpha = 0$; $C_g = \sqrt{2}$

The first solution indicates binding of the electron to either of the positive ions at ±∞ and there is no wave amplitude at the origin. Substituting $\alpha = 1$ and $C_g = 0$ into (3.18) yields an energy of -1 Rydberg, as expected.

The second solution is one of a free electron indicating a state in which there is no binding at all. Substituting $\alpha = 0$ and $C_g = \sqrt{2}$ into (3.18) yields zero energy. This solution, arising inevitably through the quadratic form of the equations , is not inconsistent with the physics of our model, for the ions now are infinitely apart and the Coulomb energy between two charged particles of infinite separation is zero. It therefore becomes possible for the electron to see the ions situated at infinity and therefore feel no effect of them. However, solution (i) gives a lower energy and should be taken to represent the physical situation.

The final energy does not depend on Z, as long as Z remain intrinsically positive. The situation changes, however, when $Z \leq -1$ ($Z = -1$ corresponds to replacing the central anion with a cation, the three ionic centres then becoming equivalent). At $Z = -1$, equation (3.18) becomes independent of C_g and the minimized energy is again -1 Rydberg. Physically, this corresponds to the situation when the electron is equally likely to localize on one of the three ionic centres.

It can also be shown that at $Z = -2$(doubly positively charged central ion), the electron would localize on the central ion with $\alpha = 2$, $E_g = -4$ Rydberg and $C_g = \infty$. The system becomes a He^+ ion.

(b) First excited state

Similarly, we can show that

$$\lim_{R\to\infty} E_u(\alpha, R, C_u, Z) = \frac{2\alpha^4 - 4\alpha^3 + C_u^2\alpha^2 + C_u^2\alpha Z}{2\alpha^2 + C_u^2} \qquad (3.21)$$

Minimizing w.r.t. α and C_u

$$\frac{\partial E_u}{\partial \alpha} = 8\alpha^5 - 8\alpha^4 + 8C_u^2\alpha^3 - 2C_u^2\alpha^2(Z+6) + 2C_u^4\alpha + C_u^4 Z = 0 \qquad (3.22)$$

$$\frac{\partial E_u}{\partial C_u} = 4 C_u \alpha^3 (Z + 2) = 0 \qquad (3.23)$$

Solving for α and C_u simultaneously, we get two solutions, one of which corresponds to the hydrogen atom ground state and the other a free electron.

(i) $\alpha = 1$; $C_u = 0$; $E_u = -1$ Rydberg

(ii) $\alpha = 0$; $C_u = 0$; $E_u = 0$

These can also be intrepreted by the reasoning given in the previous section. We again assert that the first solution, being lower in energy and corresponding to a bound state, is the physical one.

We also note that, in this case, changing the sign of the charge of the central ion does not alter the energy nor the localization of the electron, since by nature of the type of wavefunction, the amplitude at the origin has to vanish.

CHAPTER 4

EVALUATION OF THE EFFECTIVE CHARGE Z

4.1. The magnitude of Z in terms of the displacements of the saddle-point anion, and impruity and host cations.

In the last chapter, we have considered Z, the effective charge of the SP ion, as a given constant, characteristic of the individual crystal and substitutional impurity. We have said in Section 2.2. that the concept of introducing Z is to simulate lattice relaxation around the excess electron of the defect centre. We have also indicated that previous calculation by OV$^{(21)}$ has shown that the ions that are significantly displaced are the SP ion itself and its nearest neighbour impurity and host cations, and that they are assumed to be displaced only along the y-axis (fig.5). An equation was derived in section 2.2. relating the effective charge Z and the set of displacements, which, for convenience, we are going to rewrite

$$Z = \sqrt{2} + D_1 - D_2 - D_3$$

where

$$D_1 = (1 + 2d_1^2)^{-\frac{1}{2}}$$
$$D_2 = \left[d_2^2 + (\sqrt{2} - d_2)^2\right]^{-\frac{1}{2}} \qquad (4\cdot1)$$
$$D_3 = \left[d_3^2 + (\sqrt{2} + d_3)^2\right]^{-\frac{1}{2}}$$

and d_1, d_2 and d_3 are displacements of the SP anion, host and impurity cations respectively in units of host lattice spacing.

To make use of the energy equations derived in the last Chapter, we require the value of Z which in turn requires the values of the d's.

4.2. Determination of the ionic displacements.

Each ion in the point-ion lattice will be treated to interact with the rest of the ions through Coulombic force and with its nearest neighbours through Born-Mayer repulsion. The Coulomb energy inside the unit cell of a perfect f.c.c. lattice had been calculated and tabulated by Slater(24) and the result can be adapted for our purpose. We will also use the Born-Mayer repulsive parameters calculated by Fumi and Tosi(25). With this, the displacements of the three ions are uniquely determined by minimizing the defect energy w.r.t. the set of displacement co-ordinates.

In order to avoid the complication of self-consistency between the excess electron wavefunction and lattice relaxation, we are going to make one further assumption—— that the effect of the presence of the excess electron is to contribute a charge of $-\frac{1}{2}e$ to each of the two anion vacancies. Physically, this refers to a situation where the excess electron is localized completely in the anion vacancies with equal probability, and the assumption would be valid if the wavefunction of the excess electron is distributed symmetrically about the vacancies.

Starting with a perfect lattice, the energy of which we labelled zero, we are going to calculate the defect energy by establishing the SPC systematically. Referring to fig. 5 for the meanings of the various symbols, we proceed as follows:

(a) Removing anion at site (2) from the perfect lattice, the work required is

$$V_2 = \frac{\alpha_M e^2}{a} - 6 B e^{-a/\rho}$$

where α_M = Madelung's Constant

a = lattice spacing of the host lattice

B, ρ = Born-Mayer Repulsive parameters of host lattice

The factor of 6 in the second term in the above equation refers to the number of nearest neighbours adjacent to the ion being removed.

(b) Removing ion at site (3)

$$V_3 = \left(\frac{\alpha_M e^2}{a} - \frac{e^2}{a}\right) - 5Be^{-a/\rho}$$

(c) Removing ion at site (4)

$$V_4 = \left(\frac{\alpha_M e^2}{a} - \frac{e^2}{a} + \frac{e^2}{\sqrt{2}\,a}\right) - 5Be^{-a/\rho}$$

(d) Removing ion at site (5)

$$V_5 = \left(\frac{\alpha_M e^2}{a} - \frac{2e^2}{a} + \frac{e^2}{\sqrt{2}\,a}\right) - 4Be^{-a/\rho}$$

We then insert the various ions back to the appropriate positions:

(e) Putting the SP anion at site (1)

$$V_1 = \sum_{lk}{}''' \frac{-q_{lk}\, e^2}{|\vec{R}_{lk} - d_1 \hat{j}|}$$

where $\vec{R}_{lk}$ = lattice vector to the k-th ion in the l-th unit cell.

q_{lk} = charge of the k-th ion in the l-th unit cell.

d_1 = displacement of the SP ion from the SP position.

$\sum'''$ = summation over all ions in the lattice <u>EXCEPT</u> the ones at sites (2), (3), (4) and (5)

(f) Putting a charge of $-\frac{1}{2}e$ into site (3)

$$V_3' = \frac{e^2}{2a}\left\{-\alpha_M + 2 - \frac{1}{\sqrt{2}} + \frac{1}{\left[\frac{1}{2} + \left(\frac{d_1}{a}\right)^2\right]^{1/2}}\right\}$$

(g) Putting a charge of $-\frac{1}{2}e$ into site (5)

$$V_5' = \frac{e^2}{2a}\left\{-\alpha_M + 2 - \frac{1}{\sqrt{2}} + \frac{1}{\left[\frac{1}{2} + \left(\frac{d_1}{a}\right)^2\right]^{1/2}}\right\}$$

(h) Inserting the impurity ion at site (2')

$$V_2' = \sum_{\ell k}'' \frac{q_{\ell k}\, e^2}{|\vec{R}_{\ell k} - d_3 \hat{j}|} - \frac{e^2}{\frac{a}{\sqrt{2}} + d_3 - d_1}$$

$$+ B^* \left\{ e^{-(\frac{a}{\sqrt{2}} + d_3 - d_1)/\rho^*} + 2 e^{-(a^2 + d_3^2 - \sqrt{2}\, a d_3)^{1/2}/\rho^*} + 2 e^{-(a^2 + d_3^2)^{1/2}/\rho^*} \right\}$$

where $\sum''$ = summation over all ions in the lattice except the ones at sites (2) and (4). The various vectors under this summation are designated to have site(2) as origin.

d_3 = displacement of the impurity ion.

B^*, ρ^* = Born-Mayer parameters between impurity cation and host halogen ion.

(i) Inserting host cation at site (4)

$$V_4' = \sum_{\ell k}' \frac{q_{\ell k}\, e^2}{|\vec{R}_{\ell k} - d_2 \hat{j}|} - \frac{e^2}{\frac{a}{\sqrt{2}} + d_1 - d_2}$$

$$+ B \left\{ e^{-(\frac{a}{\sqrt{2}} + d_1 - d_2)/\rho} + 2 e^{-(a^2 + d_2^2 + \sqrt{2}\, a d_2)^{1/2}/\rho} + 2 e^{-(a^2 + d_2^2)^{1/2}/\rho} \right\}$$

where $\sum'$ = summation over all lattice sites except (4), the various vectors have origin at site (4).

d_2 = displacement of host cation.

The energy of formation of the defect centre in the SPC will be given by the sum of the terms from (a) to (i). It is given as a function of the Born-Mayer parameters and the set of ionic displacements. We collect all the energy terms and after simplification, we can write :

$$
\begin{aligned}
E_f(B, \rho, B^*, \rho^*, d_1, d_2, d_3) \\
= \frac{e^2}{2a} \Bigg\{ & 6\alpha_M + \frac{5\sqrt{2}-8}{2} + \frac{2}{\left[\frac{1}{2} + \left(\frac{d_1}{a}\right)^2\right]^{1/2}} \\
& - \frac{2}{\frac{1}{\sqrt{2}} + \left(\frac{d_3}{a}\right) - \left(\frac{d_1}{a}\right)} - \frac{2}{\frac{1}{\sqrt{2}} + \left(\frac{d_1}{a}\right) - \left(\frac{d_2}{a}\right)} \Bigg\} \\
& + \sum_{lk}{}''' \frac{-q_{lk}\, e^2}{|\vec{R}_{lk} - d_1 \hat{j}|} + \sum_{lk}{}'' \frac{q_{lk}\, e^2}{|\vec{R}_{lk} - d_3 \hat{j}|} \\
& + \sum_{lk}{}' \frac{q_{lk}\, e^2}{|\vec{R}_{lk} - d_2 \hat{j}|} + 20\, B\, e^{-a/\rho} \\
& + B \Big\{ e^{-\left(\frac{a}{\sqrt{2}} + d_1 - d_2\right)/\rho} + 2\, e^{-(a^2 + d_2^2 + \sqrt{2}\, a\, d_2)^{1/2}/\rho} \\
& \qquad + 2\, e^{-(a^2 + d_2^2)^{1/2}/\rho} \Big\} \\
& + B^* \Big\{ e^{-\left(\frac{a}{\sqrt{2}} + d_3 - d_1\right)/\rho^*} + 2\, e^{-(a^2 + d_3^2 - \sqrt{2}\, a\, d_3)^{1/2}/\rho^*} \\
& \qquad + 2\, e^{-(a^2 + d_3^2)^{1/2}/\rho^*} \Big\} \qquad (4.2)
\end{aligned}
$$

We now have to evaluate the three lattice sums in the above equation. Both the Evjen and Ewald's method are not applicable in our case because we have an imperfect lattice with no symmetry.

Slater in ref. 24 had calculated the potential at a thousand points inside the unit cell of a f.c.c. lattice made up of positive charges. In Appendix 1, we show how we can adapt this information to give an empirical equation for the potential along the (110) direction in the vicinity of a cation vacancy in a NaCl-type lattice. It is given as :

$$V_c\left(\frac{r}{2a}\right) = -\alpha_M + C_4\left(\frac{r}{2a}\right)^4 + C_6\left(\frac{r}{2a}\right)^6 \qquad (4.3)$$

where r = displacement along (110) direction from a cation vacancy. C_4 and C_6 are empirical constants determined by least square fit into Slater's data, and are found to be 35.03887 and 62.65809 respectively. We can make use of equation (4.3) to evaluate the lattice sums, taking care to add or subtract extra terms corresponking to the missing or extra ions in our lattice. Thus, for example, in calculating $\sum'''$, we note that the SP anion would feel the potential due to an otherwise perfect lattice with a cation vacancy at site (2) and missing ions at sites (3), (4) and (5). Therefore :

$$\sum_{\ell k}''' \frac{-q_{\ell k}\, e^2}{|\vec{R}_{\ell k} - d_1 \hat{j}|} = -\left\{ V_c\left(\frac{d_1'}{2a}\right) + \frac{1}{\left(\frac{a^2}{2} + d_1^2\right)^{1/2}} - \frac{1}{\frac{a}{\sqrt{2}} + d_1} + \frac{1}{\left(\frac{a^2}{2} + d_1^2\right)^{1/2}} \right\} \qquad (4.4)$$

where $d_1' = a/\sqrt{2} - d_1$

and V_c is as given in equation (4.3)

$\sum''$ and $\sum'$ can be written down in similarly manner :

$$\sum_{lk}'' \frac{q_{lk}\, e^2}{|\vec{R}_{lk} - d_3 \hat{j}|} = V_c\left(\frac{d_3}{2a}\right) + \frac{1}{\left[1 + \frac{d_3}{a} + \left(\frac{d_3}{a}\right)^2\right]^{1/2}} - \frac{1}{\sqrt{2} + \left(\frac{d_3}{a}\right)} \qquad (4{\cdot}5)$$

$$\sum_{lk}' \frac{q_{lk}\, e^2}{|\vec{R}_{lk} - d_2 \hat{j}|} = V_c\left(\frac{d_2}{2a}\right) + \frac{2}{\left[1 - \frac{d_2}{a} + \left(\frac{d_2}{a}\right)^2\right]^{1/2}} - \frac{1}{\sqrt{2} - \left(\frac{d_2}{a}\right)} \qquad (4{\cdot}6)$$

The R.H.S. of equations (4.4), (4.5) and (4.6) are energy terms in Hartree units (1 Hartree unit = 2 Rydbergs)

Equations (4.4), (4.5) and (4.6) are now substituted into (4.2) to obtain the overall defect energy in terms of the set of d's. In doing so, the unit of lengths are expressed in host lattice spacings and energy in Rydberg.

$$
\begin{aligned}
E_f(d_1, d_2, d_3) = 2 \Big\{ & 3\,\alpha_M + \frac{5\sqrt{2} - 8}{4} - \left(\tfrac{1}{2} + d_1^2\right)^{-1/2} \\
& + \left(\tfrac{1}{2} + d_1\right)^{-1} - \left(\tfrac{1}{\sqrt{2}} + d_1 - d_2\right)^{-1} \\
& - \left(\tfrac{1}{\sqrt{2}} + d_3 - d_1\right)^{-1} + \left(1 - d_2 + d_2^2\right)^{-1/2} \\
& - \left(\sqrt{2} - d_2\right)^{-1} + \left(\sqrt{2} - d_2 + d_3\right)^{-1} \\
& + \left(1 + d_3 + d_3^2\right)^{-1/2} - \left(\sqrt{2} + d_3\right)^{-1} \\
& - V_c\left(\frac{1}{2\sqrt{2}} - \frac{d_1}{2}\right) + V_c\left(\frac{d_2}{2}\right) + V_c\left(\frac{d_3}{2}\right) \Big\} \\
& - 20\,B\,e^{-1/\rho} + B \Big\{ e^{-\left(\frac{1}{\sqrt{2}} + d_1 - d_2\right)/\rho} \\
& + 2\,e^{-\left(1 + d_2^2 + \sqrt{2}\,d_2\right)^{1/2}/\rho} + 2\,e^{-\left(1 + d_2^2\right)^{1/2}/\rho} \Big\} \\
& + B^* \Big\{ e^{-\left(\frac{1}{\sqrt{2}} + d_3 - d_1\right)/\rho^*} \\
& + 2\,e^{-\left(1 + d_3 - \sqrt{2}\,d_3\right)^{1/2}/\rho^*} + 2\,e^{-\left(1 + d_3^2\right)^{1/2}/\rho^*} \Big\}
\end{aligned}
\tag{4.7}
$$

E_f is then minimized w.r.t. the set of d's for given pairs of Born-Mayer parameters (B, ρ) and (B^*, ρ^*). Harwell Subroutine VA13AD(26) is used for the minimization. The results returned by the Computer are listed in the next section. The values of the three partial derivatives w.r.t. the d's at the completion of the search are all of the order of 10^{-5} or less, so, there should be no doubt about the validity of the returned results.

4.3. Results

We tabulate in Table I the ionic displacements (d_1, d_2, d_3) in the 48 possible crystals formed by the combinations of (Li, Na, K, Rb) and (F, Cl, Br, I). A lot of these are superfluous since F_A-centres are not generally thought to form in crystals with doping cation larger in ionic radius than the host cation (There are 24 belonging to this catagory). For the rest, some are known to be type I in which the SPC will not form a stable state. Nevertheless, we are tabulating them all for the sake of completness. Alongside with each crystal, the effective charge Z is also calculated by equation (4.1) based on the values of (d_1, d_2, d_3). The column of Misfit Parameter $(D/d\_)$ will be explained in the next Chapter.

Lattice relaxation in the cases of KCl:Li and KCl:Na had also been computed by OV(21). Their results are given in Table II along with ours for comparison.

There is a qualitative difference in the direction of the displacement of the host cation in KCl:Li, the present calculation indicates that the host cation would move towards the Saddle-Point whereas the calculation of OV indicates that it would move away from it. Besides, the displacements obtained presently are generally larger in comparison.

TABLE I

Displacement of the SP ion (d_1), nearest host cation (d_2) and impurity cation (d_3) along the y-direction (fig. 5) in the SPC of F_A(II) centres in alkali halides in units of host lattice spacing. Z and (D/d_-) are effective charge and misfit parameter calculated from equations (4.1) and (5.1) respectively in text.

crystals	d_1	d_2	d_3	Z	(D/d_-)
RbF:Li	0.393	0.219	0.237	0.8654	1.203
RbF:Na	0.257	0.095	0.190	0.9791	0.772
RbF:K	0.075	−0.054	0.134	1.0836	0.431
RbCl:Li	0.287	0.097	0.220	0.9769	1.027
RbCl:Na	0.910	0.015	0.204	1.0519	0.749
RbCl:K	0.067	−0.081	0.153	1.1067	0.509
RbBr:Li	0.267	0.079	0.223	0.9963	0.996
RbBr:Na	0.180	0.006	0.199	1.0572	0.745
RbBr:K	0.057	−0.089	0.154	1.1116	0.525
RbI:Li	0.254	0.058	0.202	1.0040	0.959
RbI:Na	0.171	−0.009	0.194	1.0656	0.740
RbI:K	0.056	−0.096	0.158	1.1171	0.544
KF:Li	0.355	0.208	0.229	0.8876	1.023
KF:Na	0.203	0.071	0.169	1.0034	0.644
KF:Rb	−0.240	−0.278	−0.063	1.0381	0.174
KCl:Li	0.247	0.081	0.208	0.9976	0.918
KCl:Na	0.133	−0.013	0.176	1.0715	0.660
KCl:Rb	−0.125	−0.210	0.050	1.1054	0.326
KBr:Li	0.222	0.051	0.206	1.0224	0.898
KBr:Na	0.127	−0.027	0.174	1.0754	0.663
KBr:Rb	−0.096	−0.195	0.071	1.1155	0.356
KI:Li	0.220	0.043	0.191	1.0210	0.875
KI:Na	0.124	−0.033	0.171	1.0809	0.667
KI:Rb	−0.093	−0.196	0.079	1.1120	0.393

Crystals	d_1	d_2	d_3	Z	(D/d_-)
NaF:Li	0.203	0.110	0.164	0.9805	0.772
NaF:K	−0.348	−0.334	−0.148	0.9648	0.091
NaF:Rb	−0.369	−0.350	−0.130	0.9694	−0.046
NaCl:Li	0.128	−0.013	0.160	1.0634	0.715
NaCl:K	−0.231	−0.287	−0.030	1.0621	0.265
NaCl:Rb	−0.305	−0.345	−0.061	1.0359	0.166
NaBr:Li	0.108	−0.027	0.153	1.0736	0.714
NaBr:K	−0.237	−0.290	−0.029	1.0617	0.300
NaBr:Rb	−0.299	−0.339	−0.059	1.0373	0.209
NaI:Li	0.115	−0.017	0.142	1.0620	0.713
NaI:K	−0.248	−0.295	−0.037	1.0548	0.343
NaI:Rb	−0.305	−0.340	−0.059	1.0353	0.262
LiF:Na	−0.348	−0.327	−0.192	0.9382	0.168
LiF:K	−0.388	−0.358	−0.158	0.9476	−0.121
LiF:Rb	−0.413	−0.377	−0.153	0.9444	−0.253
LiCl:Na	−0.294	−0.317	−0.093	1.0140	0.320
LiCl:K	−0.355	−0.366	−0.111	0.9927	0.111
LiCl:Rb	−0.390	−0.394	−0.115	0.9826	0.016
LiBr:Na	−0.251	−0.292	−0.063	1.0392	0.350
LiBr:K	−0.340	−0.363	−0.093	1.0085	0.158
LiBr:Rb	−0.372	−0.389	−0.104	0.9957	0.070
LiI:Na	−0.304	−0.316	−0.115	0.9973	0.388
LiI:K	−0.355	−0.356	−0.104	0.9933	0.216
LiI:Rb	−0.382	−0.379	−0.106	0.9860	0.137

TABLE II

Displacements of SP ion, host cation and impurity cation (d_1, d_2, d_3) in the SPC of KCl:Na and KCl:Li, the displacements are along the y-direction (fig. 5) and are expressed in units of host lattice spacing.

	KCl:Na			KCl:Li		
	d_1	d_2	d_3	d_1	d_2	d_3
Ong and Vail(21)	0.076	−0.094	0.160	0.134	−0.068	0.142
Present	0.133	−0.013	0.176	0.247	0.081	0.208

CHAPTER 5

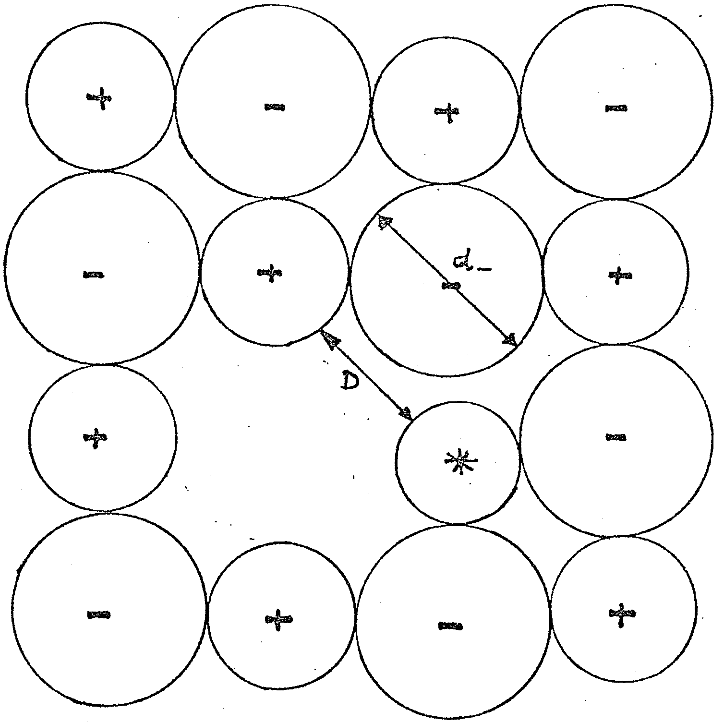
THE INTREPRETATION AND DISCUSSION OF EFFECTIVE CHARGE NUMBER Z.

5.1. The Misfit Parameters.

We recall that type I or type II behaviours of F_A-centres is a consequence of the detailed energy balance between the lattice configuration and electronic states, in which the size of the substitutional cation plays a crucial role. In order to avoid the complexity of a self-consistent calculation, Lüty in ref. 3 has suggested a much simplified idea based on ionic sizes to determine F_A-centre RES configurations. The criterion is that, if there is sufficient space within the interstitial for the SP ion to squeeze in, type II behaviour will result. This can be measured quantitatively by the ratio (D/d_-) which he called Misfit Parameter, where d_- is the diameter of the SP anion and D is the maximum space available to the SP anion when the host and impurity ions are pushed to touch their respective nearest neighbours. These quantities are shown in fig. 7.

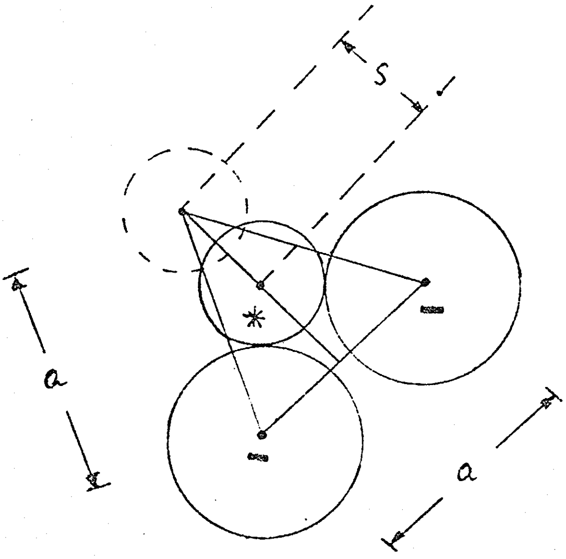
We can derive an equation relating the misfit parameter to the various radii based on this geometric picture. Referring to fig. 7 for the meanings of the various symbols, it can be seen that, <u>if</u> the substitutional impurity remains at the perfect lattice site, the quantity D would be given by $\sqrt{2}\,a - r_+ - r_+^*$ where r_+ and r_+^* are the radii of the host and substitutional cations respectively. Now, if the substitutional cation does retreat until it touches its nearest neighbour tangentially, the extra space that is made available is given by the quantity s labelled in the figure, and

FIG. 7. THE MISFIT PARAMETER (D/d_-)



d_- : DIAMETER OF ANION

D : MAXIMUM INTERSTITIAL SPACING



a : LATTICE SPACING

S : DISPLACEMENT OF SUBSTITUTIONAL CATION FROM THE PERFECT LATTICE POINT.

$$S = \frac{a}{\sqrt{2}} - \left[(r_{+}^{*} + r_{-})^{2} - \frac{a^{2}}{2} \right]^{1/2}$$

where r_- = radius of host anion

$$D = \sqrt{2}\, a - r_{+}^{*} - r_{+} + S$$

noting that $r_+ + r_- = a$, we can write :

$$\left(\frac{D}{d_-}\right) = \frac{1}{2} \left\{ \frac{3}{\sqrt{2}}(1+R) - (R+R^{*}) - \left[(1+R^{*})^{2} - \frac{1}{2}(1+R)^{2} \right]^{1/2} \right\} \qquad (5.1)$$

where $R = r_+/r_-$

$R^{*} = r_+^{*}/r_-$

All lengths in (5.1) are expressed in units of lattice spacing. Using the ionic radii calculated by Fumi and Tosi$^{(25)}$, the Misfit Parameters for all the 48 crystals are tabulated in Table I in the last Chapter.

Based on this geometrical picture, one would expect that F_A(II) centres are likely to be those with $D \gtrsim d_-$, or $(D/d_-) \gtrsim 1$. Lüty plotted the reorientation energy (which measures the relative easiness of formation of the SPC) as a function of the Misfits (D/d_-) in the various F_A-centres RES, and actually found that for $(D/d_-) \gtrsim 0.9$, the reoientation energy is extrapolated to the negative region, meaning that the SPC is automatically stabilized. This had led Lüty into proposing the Misfit Parameter as a criterion to determine the emission behaviour of F_A-centres, namely, that those with (D/d_-) greater than 0.9 are type II, while those with Misfits less than 0.9 are type I. Inspecting the Table in the last Chapter show that there are six crystals that have Misfits greater than 0.9, they are KF:Li, KCl:Li, RbF:Li, RbCl:Li, RbBr:Li and RbI:Li, all of them being lithium-doped large host cation crystals.

Lüty's criterion has not proved to be totally successful. Experimently, it was found that KF:Li(12), KCl:Li(5), RbCl:Li(5) are type II, but RbBr:Li and RbI:Li were shown to be type I(5). Moreover, KF:Na was found to be type II recently(12), while under the Misfit Parameter criteria, it belongs to type I.

Thus, we are led to believe that the Misfit is not a valid criterion, nor a particularly good guideline.

5.2. Z as a new criterion for the type II behaviour of F_A-centres.

We have derived the effective charge Z of the SP anion based on the ionic displacements at the vicinity of the Saddle-Point. In effect, while the concept of Misfit Parameter dwells on the actual geometrical space that is available to the SP anion, the effective charge approximately measures the size of the potential barrier that is between the two-wells. The size of the barrier determines the relative easiness with which the excess electron can localize in the two-well potential.

Therefore, we can look into the magnitudes of Z of the crystals and hope to discover a new criterion, which is less contradictory with experimental evidence.

We pick out crystals that are of potential interest from Table I and plot the values of their Misfits (D/d_-) against the corresponding values of effective charge Z. This is shown in fig. 8. We also take it that F_A-centres will not form in crystals in which the substitutional cation is larger than the host cation and therefore have omitted them from the following discussion.

The horizontal line in fig. 8 is drawn at $(D/d_-) = 0.9$ which is Lüty's dividing line for the type I and type II centre. We see that RbBr:Li and RbI:Li are lying above the line and KF:Na is lying below, in constrast to experiments. However, in glancing at the distribution of the points in the (D/d_-) vs. Z plot, we discover that if a vertical line is drawn at $Z = 1.0035$, all the known F_A(II) and F_A(I) centres are resolved to the left and right of the line respectively except RbBr:Li ($Z = 0.9963$), which is a type I centre but falls into the type II region according to this classification. There are three other crystals, beside the four experimentally known ones, that lie in this small Z (type II) region. They are RbF:Li, RbF:Na and NaF:Li. All the other known type I centres lie to the right of the vertical line with the addition of KI:Li, on which no experimental work has been done.

5.3. The predicted new type II centres.

We cannot claim here that our criterion is a very conclusive one, since, beside RbBr:Li that overlaps the type II region, there are many others in the lithium series tht have small Z values but which we had disregarded because of their large substitutional cations. The fact that all the experimentally known type II centres have $Z < 1.0035$ is encouraging, the case of RbBr:Li is peculiar as it is predicted to be type II both by Lüty's and the present scheme.

Anyway, the three crystals RbF:Li, RbF:Na and NaF:Li that fall into the type II region deserve particular attention. Physically, they all have the characteristics of type II centres, namely, large host cation, small host anion and small impurity cation. Further, the discovery that KF:Li and KF:Na are type II makes RbF:Li and RbF:Na likely to be type II as well. The case of NaF:Li is quite unique since it is the only member with Na as host cation. Of the three above, only RbF:Li is type II according to Luty's classification, both RbF:Na and NaF:Li have Misfits smaller than 0.9.

With the above consideration, we can think of RbF:Li, RbF:Na and NaF:Li as the favourite candidates for F_A(II)-centres. We will proceed to treat these as the new type II centres, and we are going to apply our molecular model to estimate their emission energies.

CAPTIONS OF FIG. 8

THE MISFIT PARAMETERS VS. EFFECTIVE CHARGES OF F_A-CENTRES

⊙ EXPERIMENTALLY KNOWN TYPE II CENTRE

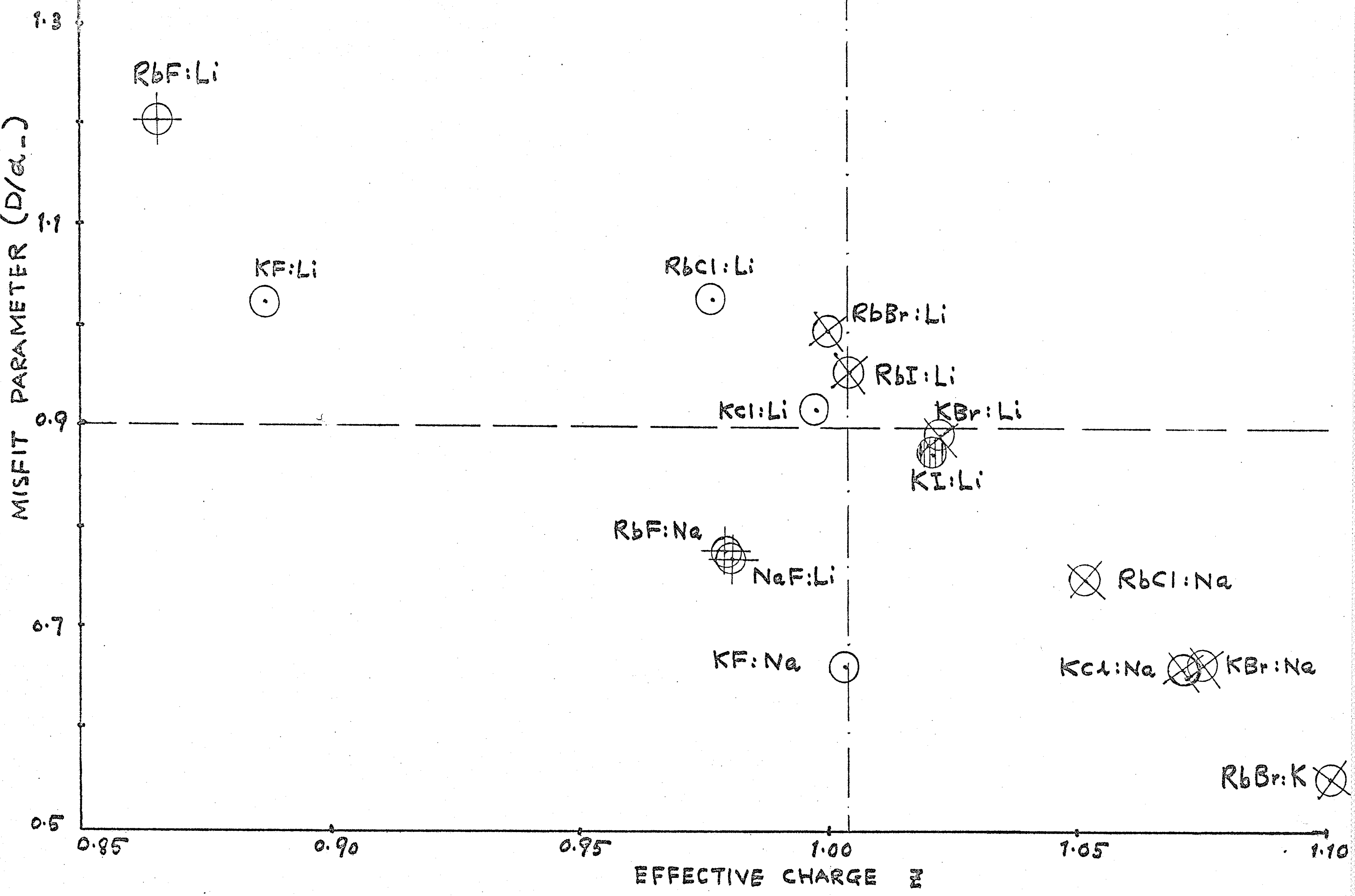
⊕ POSSIBLE NEW TYPE II CENTRE

⊗ EXPERIMENTALLY KNOWN TYPE I CENTRE

⦶ POSSIBLE NEW TYPE I CENTRE

– – – – – – – – LÜTY'S CRITERION FOR F_A(II) CENTRES.
TYPE II CENTRES ARE TO LIE ABOVE
THE LINE ($\frac{D}{d_-} = 0.90$)

—·—·—·—·— EFFECTIVE CHARGE AS A CRITERION
FOR F_A(II) CENTRES.
TYPE II CENTRES ARE TO LIE TO
THE LEFT OF THE LINE. ($Z = 1.0035$)


MISFIT PARAMETER (D/α₋)
1·3
1·1
0·9
0·7
0·5
0·85
0·90
0·95
1·00
1·05
1·10
EFFECTIVE CHARGE z
RbF:Li
KF:Li
RbCl:Li
RbBr:Li
RbI:Li
Kcl:Li
KBr:Li
KI:Li
RbF:Na
NaF:Li
RbCl:Na
KF:Na
Kcl:Na
KBr:Na
RbBr:K

CHAPTER 6

GROUND AND FIRST EXCITED STATE ENERGIES OF THE HYPOTHETICAL MOLECULE——NUMERICAL RESULTS.

6.1. The numerical procedure.

With the list of values of Z available, we are now ready to pick up equations (3.5) and (3.7) for optimization w.r.t. the variational parameters. We first remark on the numerical procedure.

The five multicentre integrals listed on P.34, except $I_5(\alpha, R)$, cannot be solved in closed form, and are evaluated numerically. They all have azimuthal symmetry and therefore, are reduced to two dimensional ones. Integral I_5 was evaluated analytically by Vail; we only give the result here :

$$I_5(\alpha, R) = \int d^3\vec{r}\, \frac{e^{-\alpha r_a}\, e^{-\alpha r_b}}{r}$$

$$= \frac{\pi}{4\alpha^2}\left\{w^2 \phi(w) - 2e^{-w}(1+w)\right\}$$

where $w = \alpha R$

$$\phi(w) = \left[-\frac{d^2}{dw^2} + 1\right]\left\{\frac{1}{w}\left[e^{w} S(w) + 2\ln(2w)\sinh w\right]\right\}$$

$$S(w) = \sum_{n=1}^{\infty} \frac{(-2w)^n}{n!\,n}$$

This analytical form, however, is not used during the final calculation because for $w > 3$, the convergence of the series $S(w)$ becomes slow, and this caused a computational problem when the many-digit number $n!$ for $n \geq 20$ is being stored.

The integrals are evaluated by Harwell Subroutines QA04AD and QA05AD(26) in succession. Both subroutines are written to perform one-dimensional integration.

We then want to minimize equations (3.5) and (3.7) w.r.t. α and C simultaneously. Again because of the complexities of the equations, the minimization has to be done numeracally. In principle, a multidimensional minimization subroutine could be used and a straight forward programme could be written to compute the set of integrals as well as carrying out the minimization at the same time. However, the fact that these integrals are functions of α, which is also the minimization variable, would render it necessary to compute the whole set of integrals once per iteration during the minimization process. This would bring the computing time required beyond justification for the present work.

We then take an alternative approach. To the energy equations, we supply a series of values of α, and for each value of α, we minimize the equations w.r.t. $C_{g,u}$. Then we spot the minimum energy through the range of α, which is then taken as the required result. Harwell Subroutine VD02AD(26) is used for the minimization w.r.t. the single variable $C_{g,u}$, α is accurate to two places after decimal.

6.2. Comparison between results by using twf of L.C.A.O. of two orbitals and three orbitals.

We are going to present the results after the minimization. First, we would like to examine the validity of the statements that we made earlier in Section 3.2., whether the inclusion of the third central orbital to the twf would give any substantial improvement to the energy. We give in Table III the ground state energies as a function of R for twf of L.C.A.O. of three orbitals and the corresponding energies with $C_g = 0$ (two orbitals). Z is set to equal to one in both cases for clarity. Table IV give the same for the first excited state. Both data are plotted in fig. 9.

We first note from the data that they have the correct asymtoptic limits as described in section 3.4. For the ground state energy curve, inclusion of the third orbital does improve the energy quite substantially between R = 2 and R = 6, which is the range of interionic distance we are interested in. There is no such clearcut improvement to the energy curves in the excited state, where the energy of the three orbital twf is a few tenths of an ev. lower in the region of interest and it converges faster to the $R = \infty$ limit. Also, the former starts at the correct energy at R = 0, (-3.401 ev.) whereas the latter starts at a somewhat higher value.

Thus, as a whole, the three orbital twf gives a more realistic result.

6.3. Results.

The energy curves of the ground and first excited state as a function of R are plotted in fig. 10 to fig.16 for seven different values of Z, corresponding to the seven established and predicted F_A(II) centres. Tables of calculated numbers are given in Appendix 2.

We note that variation in Z shifts the curves up or down by a non-negligible amount but the general shape of the curves are preserved, and that the gap between the curves, which gives the emission energy, is less affected since the curves are shifted up or down by roughly the same amount. As expected, curves with smaller Z tend to lie lower than those of larger Z

TABLE III AND IV

Ground and first excited state energies of model molecule calculated from twf of L.C.A.O. of two and three orbitals as functions of R. Distances are measured in units of Bohr radius a_o and energy in units of electron volt. R is the interionic separation of the molecule, $C_{g,u}$ is the weight attached to the central orbital, α is the localization parameter and $E_{g,u}$ are the ground and first excited state energy respectively.

TABLE III

GROUND STATE

R	C_g	α_g	E_g
0	0	1.00	-13.605
0	Arbitrary	1.00	-13.605
1	0	0.89	-10.900
1	-0.764	0.86	-11.140
2	0	0.77	-8.890
2	-0.642	0.79	-9.447
3	0	0.75	-7.898
3	-0.509	0.79	-8.774
4	0	0.93	-7.964
4	-0.365	0.83	-8.706
5	0	0.99	-8.542
5	-0.235	0.89	-8.989
6	0	1.00	-9.190
6	-0.144	0.94	-9.419
7	0	1.00	-9.756
7	-0.087	0.98	-9.890
20	0	1.00	-12.245
20	0	1.00	-12.245

TABLE IV

EXCITED STATE

R	C_u	α_u	E_u
0	0	0.50	-2.988
	Arbitrary	0.50	-3.401
1	0	0.30	-3.430
	1.616	0.53	-3.653
2	0	0.45	-4.78
	0.005	0.45	-4.78
3	0	0.63	-6.12
	-0.136	0.53	-6.138
4	0	0.83	-7.43
	-0.257	0.67	-7.601
5	0	0.90	-8.36
	-0.228	0.79	-8.606
6	0	0.95	-9.15
	-0.160	0.88	-9.314
20	0	1.00	-12.238
	0	1.00	-12.238

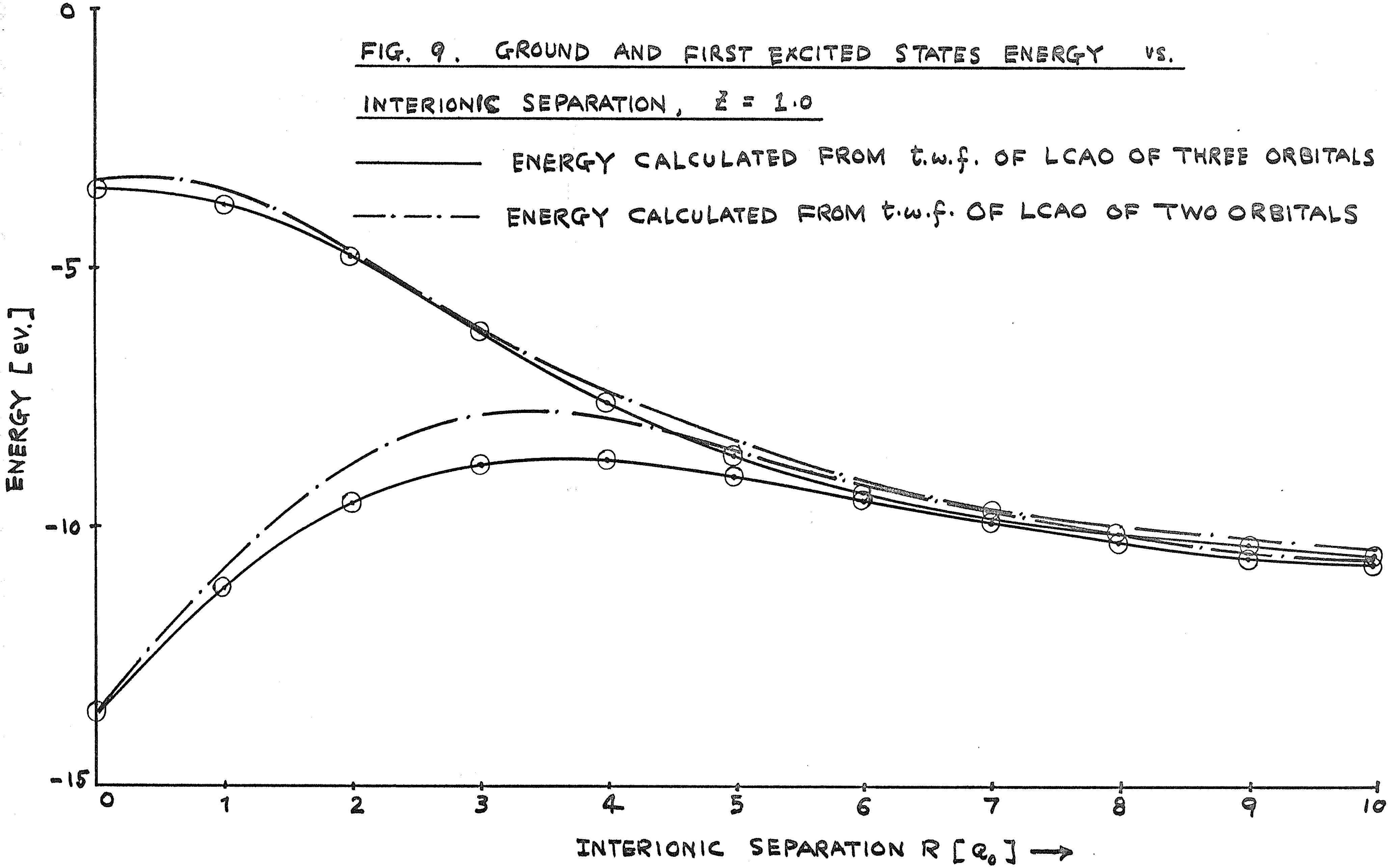


FIG. 9. GROUND AND FIRST EXCITED STATES ENERGY VS. INTERIONIC SEPARATION, $Z = 1.0$

Fig. 10 —— Fig. 16

Ground state (lower) and first excited state (upper) energy plotted vs. interionic separation R for seven values of effective Z corresponding to seven F_A(II) centres. R_o is the interionic separation that will give an emission energy k_o^2E where k_o is the high frequency dielectric constant and E is the experimental emission energy.

FIG. 10

KCl : Li , Z = 0.9976

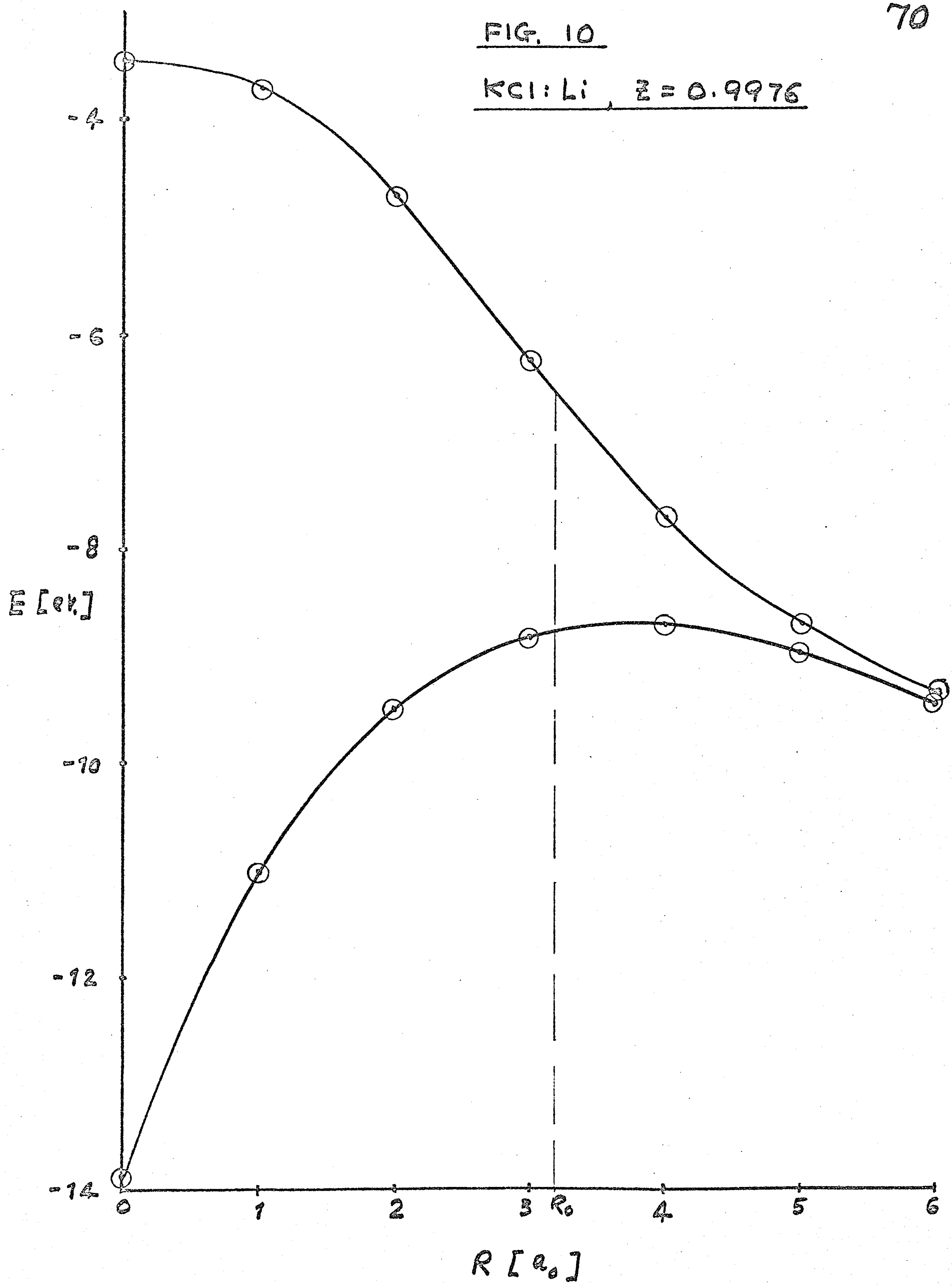
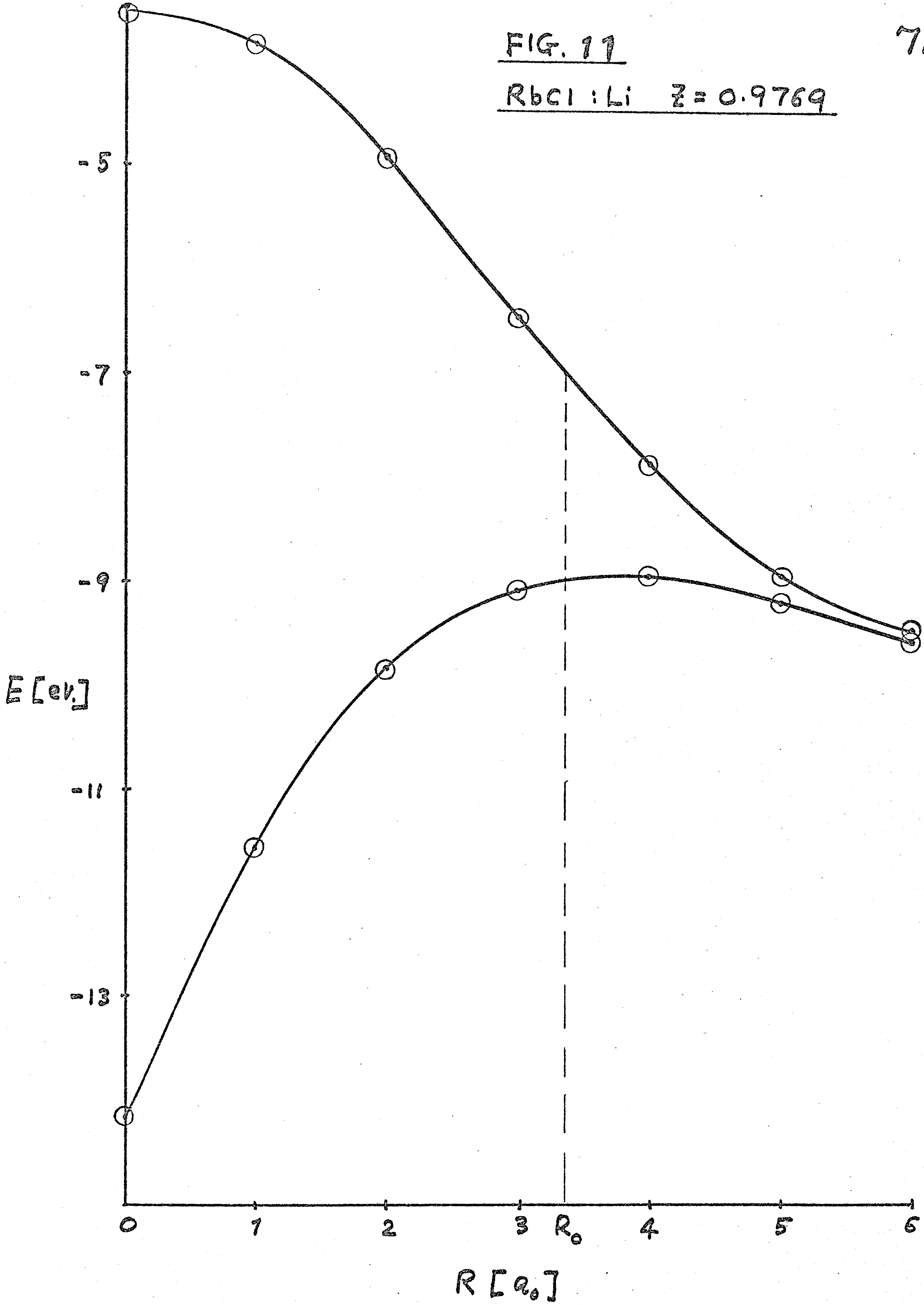


FIG. 11

RbCl : Li Z = 0.9769



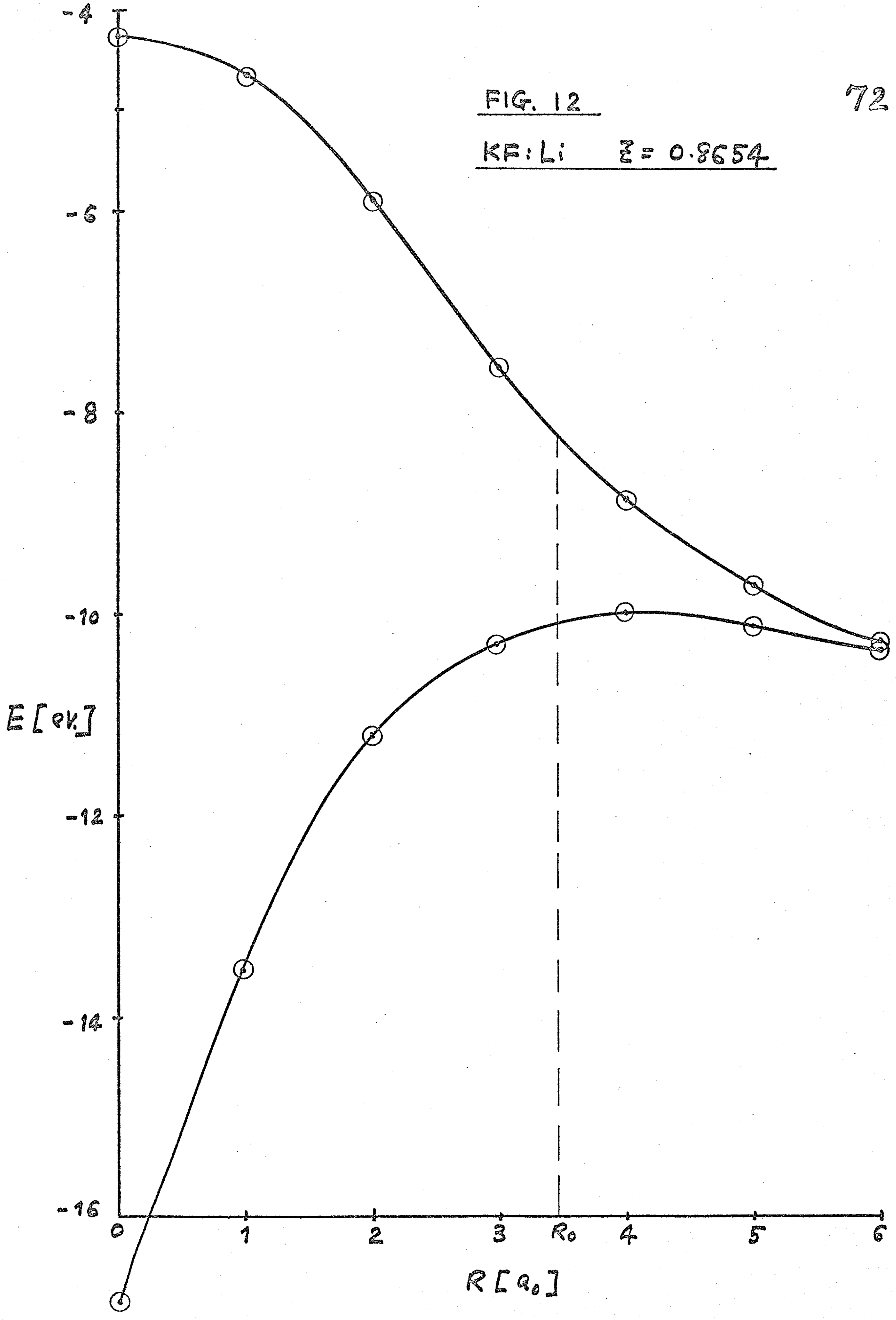


FIG. 12

KF:Li $Z = 0.8654$

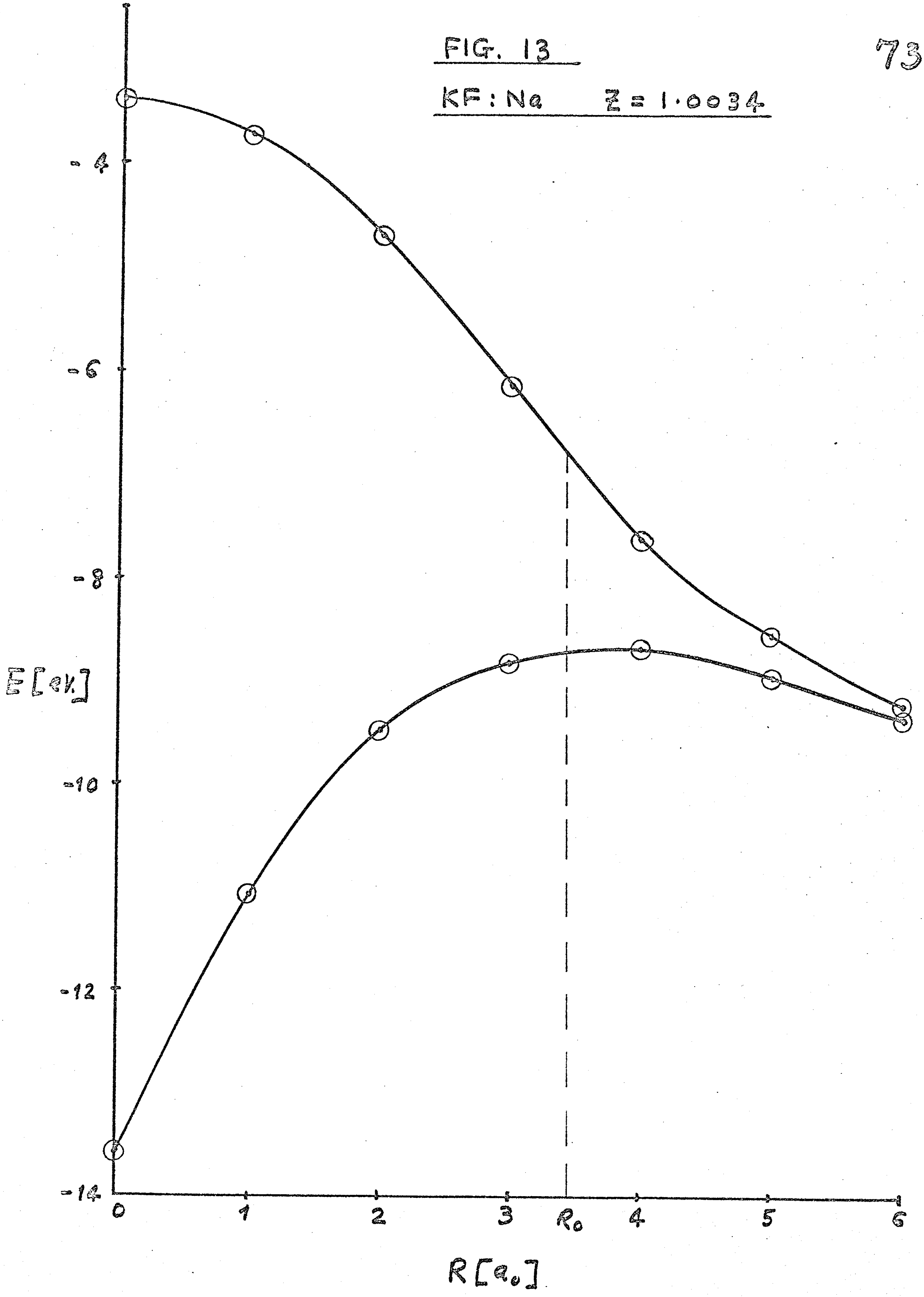


FIG. 13

KF : Na   Z = 1·0034

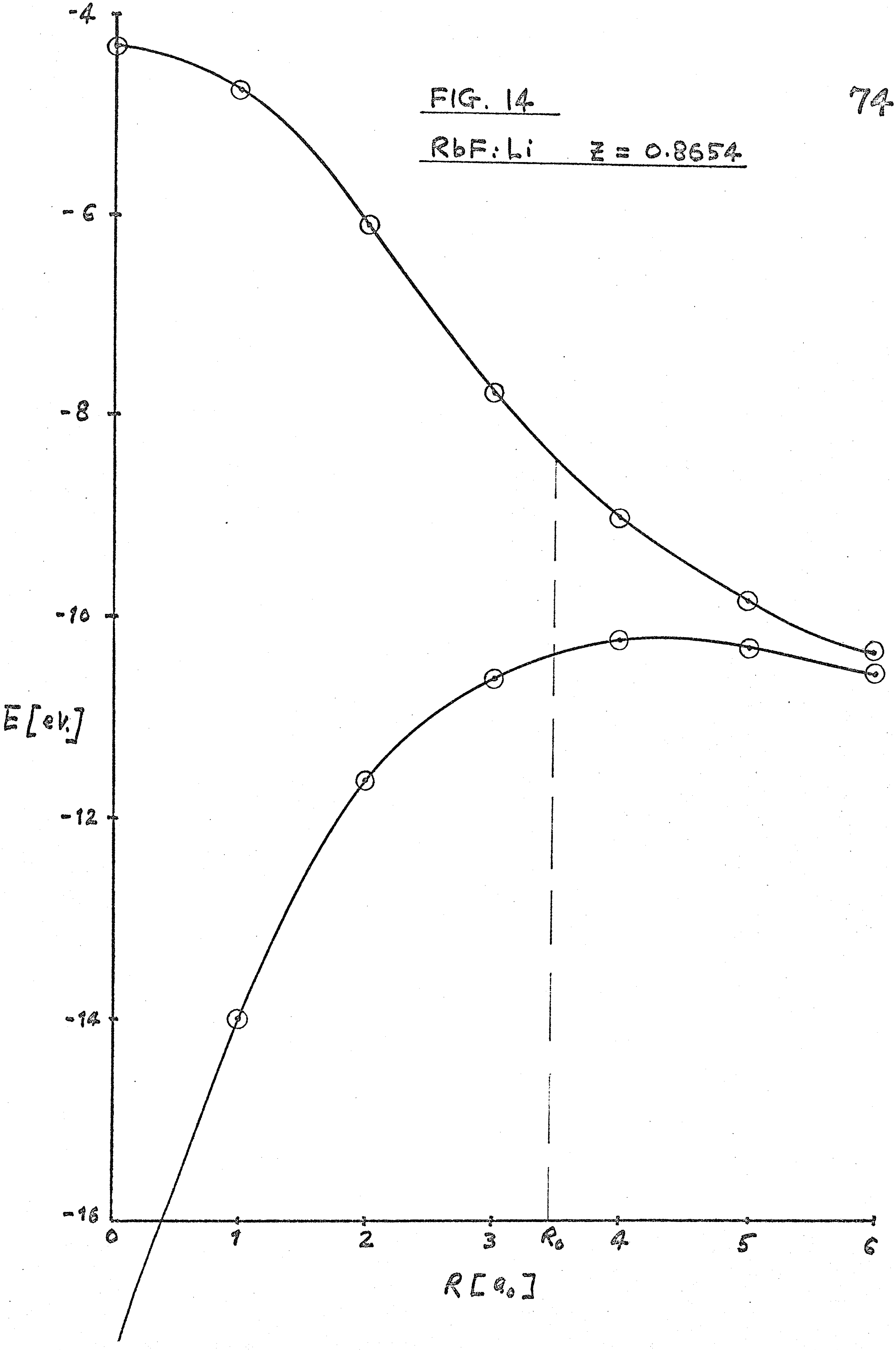


FIG. 14

RbF:Li   Z = 0.8654

FIG. 15

RbF:Na Z = 0.9791

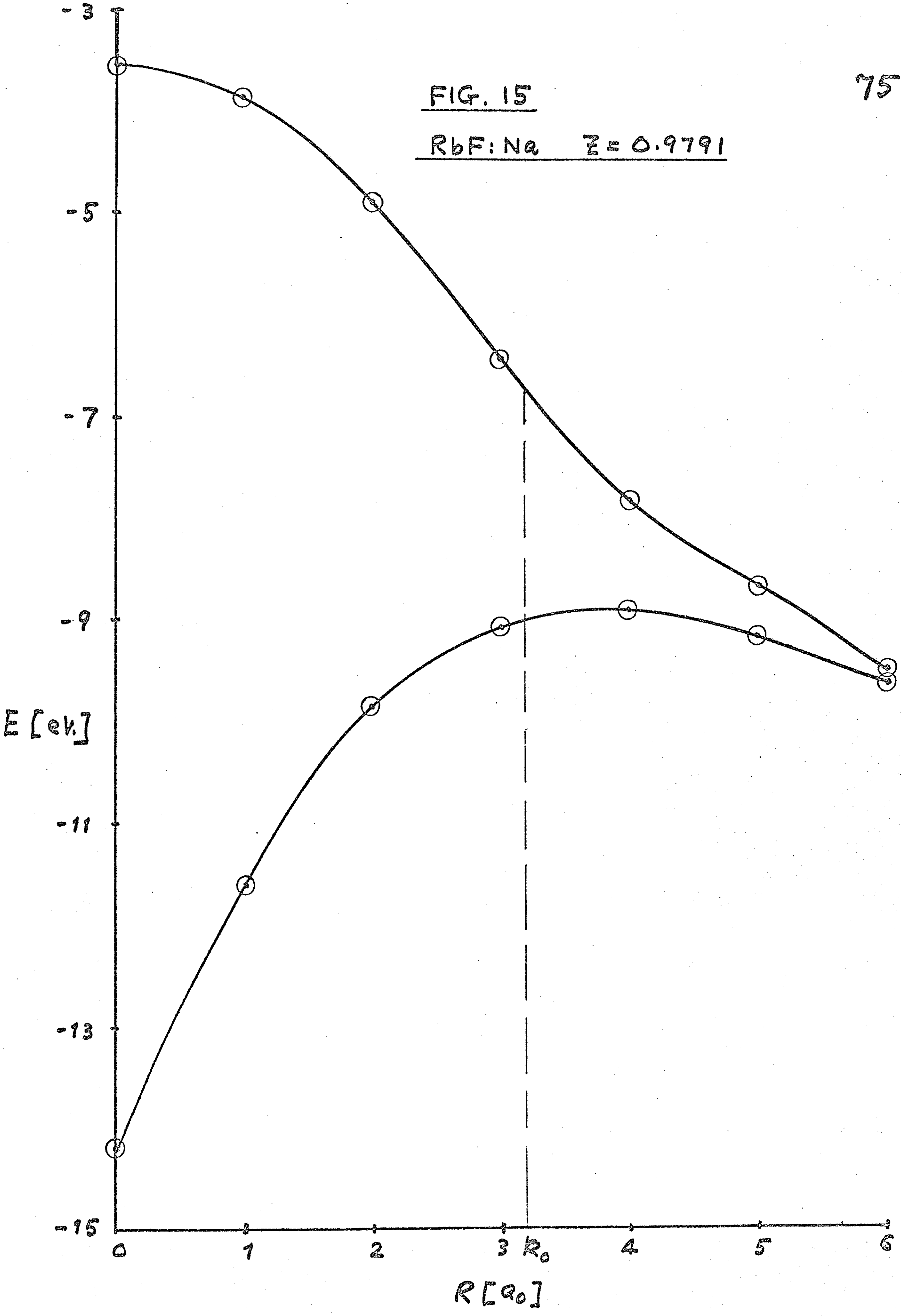
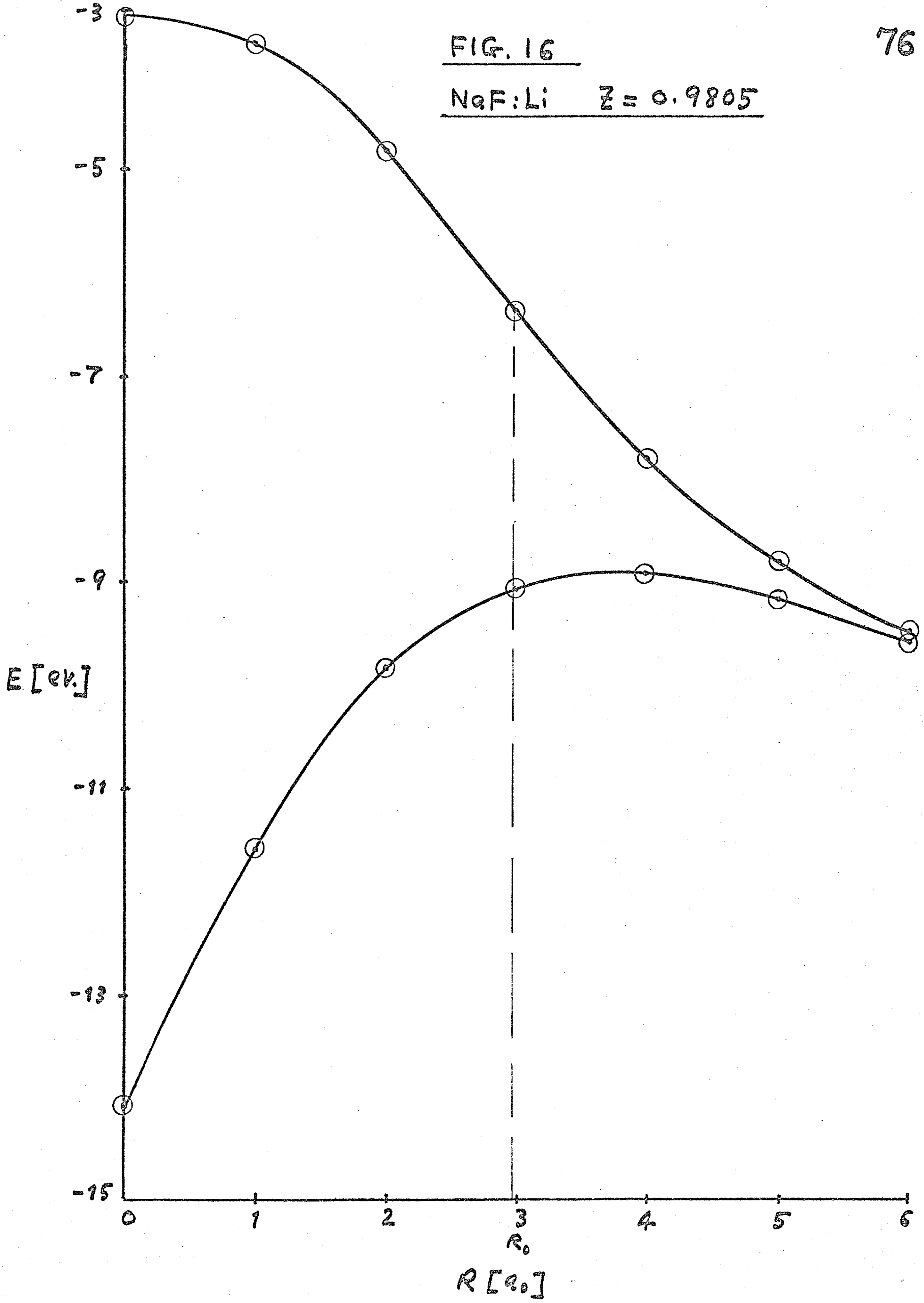


FIG. 16

NaF:Li Z = 0.9805



CHAPTER 7

ESTIMATED EMISSION ENERGIES OF THE NEW TYPE II CENTRES.

7.1. Information available from the existing experimental data.

The emission energies of RbF:Li, RbF:Na and NaF:Li are now calculated according to the scheme outlined in Section 2.3. We pick $F_A(II)$ centres whose emission energies, E , are known experimentally and fit the quantity $k_o{}^2E$ (k_o is the high frequency dielectric constant of the crystal) into the energy curves to determine R, the molecular size, then, a constant c is determined through the the relation $c = (k_oR/\sqrt{2}\ a)$ which relates R to the lattice defect.

There are four $F_A(II)$ centres whose emission energies are known at the time when this work is performed. Thus, we can carry through the priscription for each of these . The results are listed in Table V. The quantity R which is the interionic separation of the model molecule in free space that will give the molecule an emission energy $k_o{}^2E$, is marked in figure 10 to figure 13.

7.2. Variation of the effective two-well separation as a function of effective charge Z.

The dimensionless constant c in Table V, given by

$$c = r_{ab}/(\sqrt{2}\ a) \qquad (7.1)$$

where r_{ab} = effective two-well separation in crystal

a = host lattice spacing

essentially measures the relative separation of the potential wells amongst the crystals, and is characteristic of the particular host and doping. We have seen that Z is derived from the ionic displacements, which are in turn

TABLE V

Effective two-well separation r_{ab} in the SPC of the four known $F_A(II)$ centres. a is the host lattice spacing, k_o is the high frequency dielectric constant, Z is the effective charge, E is the experimental emission energy, R is the interionic separation of the model molecule in free space and c is calculated from equation (7.1). Lengths are in units of lattice spacing and energy in units of ev.

	KF:Li	KF:Na	KCl:Li	RbCl:Li
a	5.055	5.055	5.949	6.221
k_o	1.85	1.85	2.19	2.19
Z	0.8876	1.0034	0.9976	0.9769
E	0.553	0.578	0.46	0.43
$k_o{}^2E$	1.893	1.978	2.206	2.062
R	3.49	3.44	3.22	3.35
r_{ab}	6.4565	6.3640	7.0518	7.3365
c	0.9033	0.8903	0.8383	0.8340

determined by Born-Mayer parameters characteristic of the crystal species, also characterizes the particulars of each centre. Thus, we can think of c as a function of Z. The values of c for the four known type II centres are plotted vs. Z in fig. 17.

Because of the limited amount of experimental data, it is difficult to guess from fig. 17 the functional form between c and Z. A simple and possible form would be :

$$c(Z) = C_1 - C_2 Z + C_3/(Z - Z_o)$$

where $Z_o = 1.0035$ is the value of Z that divides the type I and type II F_A-centres, and C_1, C_2 and C_3 are to be determined by least square fit method. The fitting, however, is not very good due to the rapid divergence of c as Z approaches Z_o.

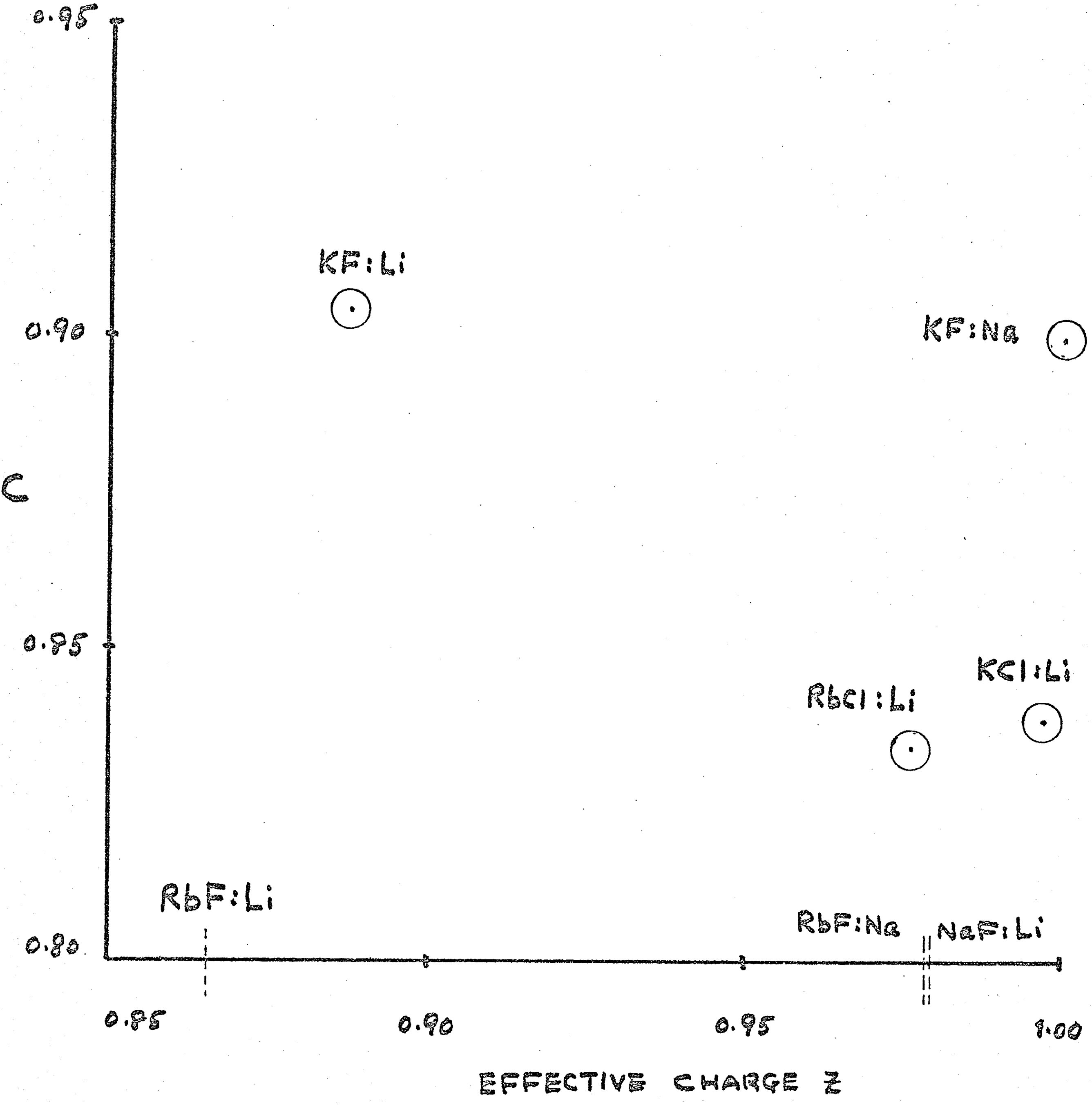
On the other hand, since Z roughly parametrizes the various centres, we would expect that centres having similar values of Z have similar characteristics. In calculating the emission energies of the new type II centres, therefore, we can, as an alternative, use the value of c of the experimentally known centre that has the closest value of Z. Thus, we use the value of c of RbCl:Li (c = 0.8340) for RbF:Na and NaF:Li and that of KF:Li (0.9030) for RbF:Li. In fig. 17, we also show the Z values of RbF:Li, RbF:Na and NaF:Li. This approximation should be a reasonable one if the variation between c and Z is smooth, for then the values of c of RbF:Na and NaF:Li cannot differ significantly from that of RbCl:Li.

7.3. The emission energies of RbF:Li, RbF:Na and NaF:Li

The SPC emission energies of the three predicted $F_A(II)$ centres are now calculated in the context of our model. The procedures were described in Section 2.3. and will be sketched here again for convenience.

The effective two-well separation of an individual crystal is

FIG. 17 EFFECTIVE TWO-WELL SEPARATION C VS. EFFECTIVE CHARGE Z



first determined by $r_{ab} = c\sqrt{2}\,a$ which then fix the interionic separation of the model molecule in free space through $r_{ab} = k_o R$. From the appropriate energy curves we determine the emission energy of the molecule in free space, E' and E'/k_o^2 gives the corresponding emission energy of the lattice defect. We tabulate the calculation systematically in Table VI.

According the present calculation, NaF:Li is found to have the highest emission energy 0.915 ev., followed by RbF:Na,0.591 ev., and RbF:Li, 0.513 ev.

TABLE VI

Emission energy E of NaF:Li, RbF:Li and RbF:Na in the SPC. E' is the emission energy of the model molecule at interionic separation R. The meanings of the other symbols are the same as those in Table V. Lengths are in units of Bohr radius and energy in units of ev.

	NaF:Li	RbF:Li	RbF:Na
a	4.380	5.321	5.321
k_o	1.74	1.96	1.96
c	0.8340	0.9033	0.8340
Z	0.9805	0.8654	0.9791
r_{ab}	5.165	6.794	6.275
R	2.97	3.47	3.20
E'	2.77	1.97	2.27
E	0.915	0.513	0.591

CHAPTER 8

DISCUSSION AND CONCLUSION

The above consideration has led us into postulating that NaF:Li, RbF:Li and RbF:Na are F_A(II) centres and we have worked out their respective emission energies. We point out some factors pertaining to the validity of the calculation.

(a) The crystal lattice.

We have used an very simple model. The continuum model is inherently an oversimplification of a crystal lattice, and is most applicable in cases where the electron is not highly localized. A more rigorous treatment would be to describe the ions at and near the Saddle-Point in the context of the Shell Model, which allows for the polarizability of the ion's outer electrons.

(b) The form of the trial wavefunction.

The twf that we used may not have sufficient flexibility. The major deficiency is that we have required the central orbital to have the same localization as the other two. Self-consistent treatment between the electronic wavefunction and lattice relaxation in the energy minimization is not included.

We could have avoided a lot of technical difficulties if we had used twf of L.C.A.O. of Gaussian orbitals, $\exp(-\alpha^2 r^2)$, since integrals involving Gaussian orbitals can usually be evaluated analytically in closed form. Alternatively, we can reduce the problem to one of single-variable minimization by writing the twf as :

$$\Psi = \phi_a + \phi_b + \phi_c \qquad (8.1)$$

$$\phi_{a,b,c} = \sum_i C_i \, e^{-\alpha_i r_{a,b,c}}$$

ϕ_a, ϕ_b and ϕ_c are orbitals centred on the ion sites, α_i is a set of supplied values and C_i are the variational set. Since we can have a good intuition of the localization of each orbital, three or four terms (with three or four corresponding guesses on the α_i's) in the summation series in (8.1) for each orbital are usually sufficient in bringing the result very close to the two-parameter minimization (α and C). By doing this, we can avoid the tedious procedures of optimizing the exponentials, and at the same time, allows the centre orbital to have different localization from the other two.

(c) The dielectric constant describing the continuum crystal.

The success of Aegerter and Lüty in applying a similar treatment to the F_2^+ problem is partly due to the availability of previous data on the energy levels of H_2^+ ion, and the simplicity of not having an associated impurity. This enables them to derive an effective dielectric constant different from the usual high frequency one. We do not have sufficient information here to do the same.

(d) Effective charge Z.

The idea of assigning an effective charge Z to the SP ion to simulate its displacement is but an approximation. A more realistic approach would be taking the displacement into account explicitly by using a bent molecular model in which the central anion is shifted from the origin perpendicular to the line joining the two positive ions.

The model of a bent molecule is actually what we took when we started the calculation but was gradually yielded to the effective charge approach due to the great complexity involved. There are far more difficult three-centre integrals to be evaluated, and there is also the problem of introducing the orbital centred on the displaced anion because L.C.A.O.

centred on these ions would not produce twf of definite even and odd parities and the orthogonality condition of the ground and first excited state wavefunction would not be satisfied.

(e) Ion-size effect.

Our criterion based on the magnitude of Z to differentiate between type I and II F_A-centres is violated by numerous crystals with dopings larger than host cations, all of which we had disregarded in Section 5.2 on the basis that F_A-centres will not formed with such combinations. It may be worthwhile here to re-examine the justification.

In deriving the magnitude of Z, we have not taken any ion-size effect into account, we have simply treated each ion as a point charge and completely neglected the presence of the outer electrons. In crystals with large substitutional cation and/or large host anion, this can play an important role in increasing the effective height of the potential barrier in the electronic potential through Pauli's repulsion, and therefore increases the magnitude of Z. It may be that by including proper treatment of the ion-size effect, the values of Z of those crystals with large substitutional cation, and also RbBr:Li will be shifted to the type I region. The ion-size correction of Bartram, Stoneham and Gash(29) might provide a convenient starting point to introduce this effect into the present problem.

There is no serious theoretical justification for the way we assigned the values of c to RbF:Li, RbF:Na and NaF:Li. Therefore, the calculated emission energies will be somewhat uncertain. This is inevitable, however, in the framework of our model and approach.

A reliable theoretical method to determine whether a given F_A-centre is type I or II is by no means easily attainable. Even the detail consideration on the energetics of the defect system in ref. 21 have not been completely successful due to the very delicate self-consistent balances of the various contributions to the total energy. Thus, our criterion based on the effective charge Z must not be taken very seriously. Nevertheless, the results obtained in the present work have definitely rendered NaF:Li, RbF:Li and RbF:Na outstanding for future investigation into new F_A(II) centres. If small emission energy is taken as a criterion for stability relative to the vacancy configuration and also relative to the conduction band, then, RbF:Li would be the most stable of our proposed new F_A(II) centres.

We believe that Mollenauer's(12) original suggestion was reasonable, but feel that the approach cannot yield reliable results without further refinement.

REFERENCES

(1) Seitz, F., Rev. Mod. Phy. 18, 384, (1946).
Rev. Mod. Phy. 26, 7, (1954).

(2) Fowler, W.B. and Dexter, D.L., Phy. Rev. 128, 2157, (1962).

(3) Lüty, F., Physics of Colour Centres, edited by Fowler, Chapter 3.

(4) Kojima, K., Nishimaki, N. and Kojima, T., J. Phy. Soc. Japan, 16, 2033, (1961).

(5) Ohkura, H. Supp. of Prog. Theor. Phy. 46, 11, (1970).

(6) Fritz, B., Lüty, F. and Rausch, G. Phy. Stat. Sol. 11, 635, (1965).

(7) Swank, R.K. and Brown, F.C., Phy. Rev. 130, 34, (1963).

(8) Mott, N.F. and Gourney, R.W., Electronic Process in Ionic Crystals, Oxford Press, (1940).

(9) Spinolo, G. and Brown, F.C., Phy. Rev. 135, A450, (1964).

(10) Fowler, W.B., Phy. Rev. 135, A1725, (1964).

(11) Spinolo G., Phy. Rev. 137, A1495, (1965).

(12) Mollenauer, L.F., Hatch, B.A., Olson, D.H. and Guggenheim, H.J., Phy. Rev. 12, B731, (1975).

(13) Gramm, G., Physics Letter 8, 157, (1964).

(14) Link, E. and Lüty, F., Inter. Symp. Colour Centres Alkali Halides, Illinois. Unpublished. Reported in ref.3.

(15) Guccione, R. and Tosi, M.P., J. Phy. Chem. Sol. 10, 162, (1959).

(16) Fritz, B. and Menke, E., Solid State Comm. 3, 61, (1965).

(17) Mollenauer, L.F. and Olson, D.H., App. Phy. Letters, 24, 386, (1974).

(18) Herman, R., Wallis, M.C. and Wallis, R.F., Phy. Rev. 103, 87, (1956).

(19) Bates, D.R., Ledsham, K. and Stewart, A.L., Tran. Roy. Soc.(London), A246, 215, (1953).

(20) Aegerter, M.A. and Lüty, F., Phy. Stat. Sol.(b) 43, 245, (1971).

(21) Ong, C.K. and Vail, J.M., Phy. Rev. 8, 1636, (1973).

(22) Slater, J.C., Quantum Theory of Molecules and Solids, Vol. 1, McGraw Hill, (1963).

(23) Moiseitsch, B.L., Quantum Theory, I-elements., edited by Bates, Academic Press, (1961).

(24) Slater, J.C., Quantum Theory of Molecules and Solids, Vol. 3, McGraw Hill, (1967).

(25) Fumi, F.G. and Tosi, M.P., J. Phy. Chem. Sol., 25, 31, (1964).

(26) Harwell Subroutine Library, A.E.R.E., Harwell, Oxon., England.

(27) Tosi, M.P., Solid State Physics, edited by Seitz and Turnbull, 16, 48, (1964).

(28) C.R.C. Handbook of Chemistry and Physics,

(29) Bartram, R.H., Stoneham, A.M. and Gash, P., Phy. Rev. 176, 1014, (1968).

APPENDIX 1

DETERMINATION OF THE POTENTIAL ALONG THE (110) DIRECTION FROM A CATION VACANCY IN A NaCl-TYPE LATTICE.

In this Section, we wish to show how equation (4.3) in Chapter 4 was obtained, based on the result published by Slater(24).

In ref. 24, the potential at a thousand points inside the unit cell of a f.c.c. lattice of positive charges plus a uniformly distributed negative charge sufficient to neutralize the positive point charges are calculated by Ewald's Method. We extract from it the potential at some points of such a lattice in Table VII.

To get the potential of a NaCl-lattice, we superpose to our positive lattice an identical negative lattice (made up of f.c.c. array of point negative charges plus uniformly distributed positive charges), with each lattice point displaced from the former one by an amount (a/2) where a is the lattice spacing. The potential of the points of the superposed lattice are then given by the sum of the two. Thus, for example, in order to get the potential V_p at the point (.20,.20,0) of a NaCl-lattice, we add the potential at (.20,.20,0) to the negative of the potential at (.30,.20,0), both of these are read from Table VII.

We did this to five points in the (110) direction. These will be the potentials V_P for a perfect NaCl-lattice. To obtain the potential in the vicinity of a cation vacancy, we simply subtract from V_p the appropriate Coulomb energies $(r/2a)^{-1}$. These are tabulated in Table VIII as V_c.

V_c is plotted vs. (r/2a) in fig. 18. We want an explicit functional relationship between the two. At r = 0, it is obvious that the potential is just the Madulung's energy α_M. For $r > 0$, we can write V_c in terms of a power series in r,

TABLE VII

Potential of a f.c.c. lattice of positive charges plus an equal amount of uniformly distributed negative charges. (x/2a, y/2a, z/2a) are the Cartesian components of spatial points within the lattice, using orthogonal, non-primitive basis vector of length 2a. The last column is the potential expressed in dimensionless unit . The factor of 2 appears because of the different defination of 'a' used by Slater.

x/2a	y/2a	z/2a	$2a\Phi$
0.05	0.05	0	9.599
0.10	0.10	0	2.655
0.15	0.15	0	0.514
0.20	0.20	0	-0.343
0.25	0.25	0	-0.583
0.30	0.20	0	-0.639
0.35	0.15	0	-0.778
0.40	0.10	0	-0.934
0.45	0.05	0	-1.049

TABLE VIII

Potential V_c along (110) direction from a cation vacancy in a NaCl-type lattice. V_p is the potential due to a perfect lattice and $(r/2a)^{-1}$ is the missing Coulomb energy due to the missing cation. (x/2a, y/2a, z/2a) are the Cartesian Components of the spatial point, potential is in dimensionless unit $2a\phi$.

x/2a	y/2a	z/2a	V_p	$(r/2a)^{-1}$	$V_c = V_p - (r/2a)^{-1}$
0.05	0.05	0	10.684	14.142	-3.494
0.10	0.10	0	3.589	7.071	-3.488
0.15	0.15	0	1.292	4.714	-3.422
0.20	0.20	0	0.296	3.536	-3.240
0.25	0.25	0	0.0	2.828	-2.828

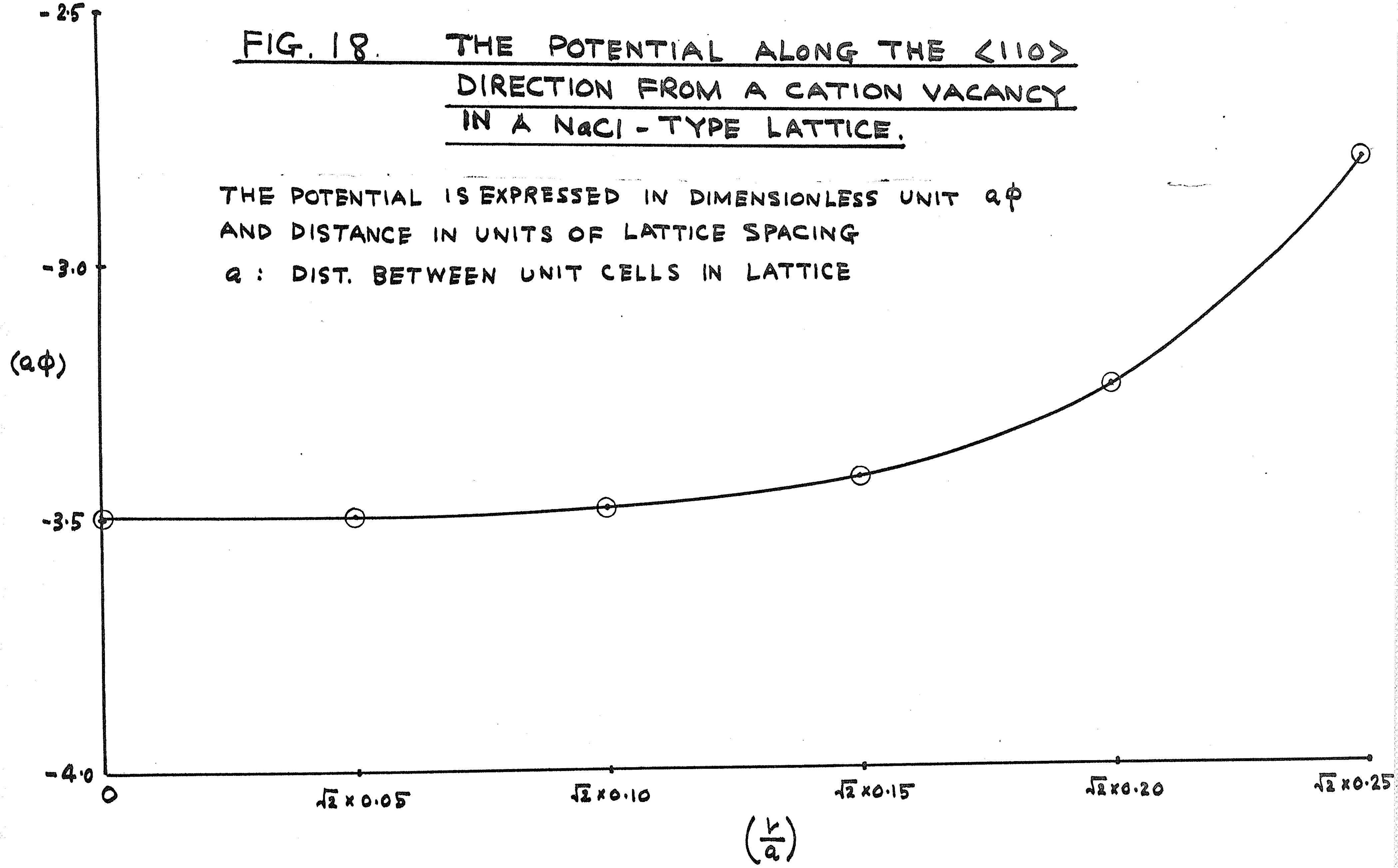


FIG. 18. THE POTENTIAL ALONG THE <110> DIRECTION FROM A CATION VACANCY IN A NaCl - TYPE LATTICE.

THE POTENTIAL IS EXPRESSED IN DIMENSIONLESS UNIT $a\phi$
AND DISTANCE IN UNITS OF LATTICE SPACING
a : DIST. BETWEEN UNIT CELLS IN LATTICE

$$V_c\left(\frac{r}{2a}\right) = -\alpha_M + \sum_{n=\text{even}} C_n\left(\frac{r}{2a}\right)^n \qquad \text{(A1.1)}$$

odd power terms in the above series cannot exist because of symmetry. It is also pointed out by Slater that r^2 terms also vanish when the two lattices of different signs are superposed. Thus, the loest order term is r^4. Taking two terms in the series should be sufficient for our purpose:

$$V_c\left(\frac{r}{2a}\right) = -\alpha_M + C_4\left(\frac{r}{2a}\right)^4 + C_6\left(\frac{r}{2a}\right)^6 \qquad \text{(A1.2)}$$

The constants C_4 and C_6 are then determined by least squares fit method with the data in Table 8. We can derive analytical expressions for them :

$$C_6 = \frac{\sum x_i^6 y_i + \alpha_M \sum x_i^6 - \sum x_i^{10}\left[\dfrac{\sum x_i^4 y_i + \alpha_M \sum x_i^4}{\sum x_i^8}\right]}{\sum x_i^{12} - \dfrac{\sum x_i^{10}\sum x_i^{10}}{\sum x_i^8}} \qquad \text{(A1.3)}$$

$$C_4 = \frac{\sum x_i^4 y_i + \alpha_M \sum x_i^4 - C_6 \sum x_i^{10}}{\sum x_i^8}$$

y_i and x_i in the last equation are the values of V_c and (r/2a) in Table VIII and the summation is from i = 1 to i = 5, corresponding to the five available data. The results are

$C_4 = 35.03887$

$C_6 = 62.65806$

substituting these values into equation (Al.2) reproduces equation (4.3) exactly.

APPENDIX 2

In this section, we tabulate the ground and first excited state energies as functions of molecular size R for the predicted and experimentally known $F_A(II)$ centres, as calculated from equations (3.5) and (3.7) with optimized values of α and C. They are given in Table IX to Table XV. R is in units of Bohr radius, energy in ev. The $F_A(II)$ centres are characterize according the their effective charges Z.

TABLE IX

KF:Li, $Z = 0.8876$

R	α_g	C_g	E_g	α_u	C_u	E_u
0			−16.834			−4.209
1	0.94	−0.640	−13.544	0.58	1.454	−4.552
2	0.84	−0.546	−11.291	0.39	−0.054	−5.788
3	0.83	−0.435	−10.296	0.57	−0.161	−7.439
4	0.86	−0.314	−10.001	0.69	−0.259	−8.796
5	0.91	−0.204	−10.117	0.83	−0.199	−9.659
6	0.95	−0.128	−10.399	0.90	−0.141	−10.249

TABLE X

KF:Na, $Z = 1.0035$

R	α_g	C_g	E_g	α_u	C_u	E_u
0			-13.511			-3.378
1	0.85	-0.770	-11.064	0.52	1.373	-3.627
2	0.78	-0.652	-9.392	0.34	-0.046	-4.648
3	0.79	-0.509	-8.806	0.53	-0.135	-6.099
4	0.83	-0.366	-8.667	0.66	-0.259	-7.565
5	0.88	-0.242	-8.953	0.79	-0.228	-8.575
6	0.94	-0.144	-0.389	0.88	-0.160	-9.285

TABLE XI

KCl:Li, $Z = 0.9976$

R	α_g	C_g	E_g	α_u	C_u	E_u
0			-13.670			-3.418
1	0.86	-0.762	-11.185	0.53	1.577	-3.418
2	0.79	-0.641	-9.485	0.34	-0.047	-4.648
3	0.79	-0.509	-8.806	0.53	-0.137	-6.165
4	0.83	-0.365	-8.733	0.67	-0.267	-7.627
5	0.89	-0.234	-9.012	0.80	-0.222	-8.629
6	0.94	-0.143	-9.440	0.88	-0.160	-9.333

TABLE XII

RbCl:Li, $Z = 0.9769$

R	α_g	C_g	E_g	α_u	C_u	E_u
0			-14.241			-3.560
1	0.87	-0.740	-11.614	0.54	1.566	-3.560
2	0.80	-0.623	-9.817	0.35	-0.049	-4.854
3	0.80	-0.492	-9.082	0.54	-0.141	-6.400
4	0.84	-0.351	-8.971	0.67	-0.259	-7.846
5	0.89	-0.231	-9.219	0.80	-0.222	-8.822
6	0.94	-0.142	-9.620	0.88	-0.158	-9.505

TABLE XIII

NaF:Li, Z = 0.9805

R	α_g	C_g	E_g	α_u	C_u	E_u
0			-14.141			-3.535
1	0.87	-0.743	-11.540	0.54	1.621	-3.802
2	0.80	-0.625	-9.759	0.35	-0.049	-4.818
3	0.80	-0.494	-9.034	0.54	-0.140	-6.360
4	0.84	-0.352	-8.930	0.67	-0.258	-7.808
5	0.89	-0.232	-9.184	0.80	-0.222	-8.789
6	0.94	-0.142	-9.589	0.88	-0.159	-9.477

TABLE XIV

RbF:Li, Z = 0.8654

R	α_g	C_g	E_g	α_u	C_u	E_u
0			-17.514			-4.379
1	0.95	-0.617	-14.045	0.58	1.224	-4.379
2	0.84	-0.534	-11.667	0.39	-0.063	-6.031
3	0.83	-0.428	-10.604	0.58	-0.165	-7.704
4	0.87	-0.301	-10.271	0.69	-0.260	-9.034
5	0.91	-0.200	-10.342	0.84	-0.192	-9.870
6	0.95	-0.125	-10.594	0.90	-0.139	-10.434

TABLE XV

RbF:Na, Z = 0.9791

R	α_g	C_g	E_g	α_u	C_u	E_u
0			-14.179			-3.545
1	0.87	-0.742	-11.568	0.54	1.600	-3.813
2	0.80	-0.624	-9.781	0.35	-0.049	-4.832
3	0.80	-0.493	-9.052	0.54	-0.140	-6.375
4	0.84	-0.352	-8.946	0.67	-0.258	-7.846
5	0.89	-0.231	-9.197	0.80	-0.222	-8.801
6	0.94	-0.142	-9.601	0.88	-0.159	-9.487

APPENDIX 3

The Schrodinger equation of the model molecule in free space and in a dielectric medium.

We want to demonstrate here that the Schrodinger equation of the model molecule in free space (equation 2.4) is equavalent to that in a dielectric medium (equation 2.6) if we make the transformation given in equation 2.7. First, we rewrite the free space equation (2.4):

$$\nabla^2\psi(\vec{r}) + 2\left(\frac{1}{r_a} + \frac{1}{r_b} - \frac{Z}{r}\right)\psi(\vec{r}) + E'(R,Z)\psi(\vec{r}) = 0$$

This will not change if we multiply the L.H.S. by k_o^{-2} where k_o is a constant later taken to be the dielectric constant of the medium:

$$\frac{1}{k_o^2}\nabla^2\psi(\vec{r}) + \frac{2}{k_o^2}\left(\frac{1}{r_a} + \frac{1}{r_b} - \frac{Z}{r}\right)\psi(\vec{r}) + \frac{E'(R,Z)}{k_o^2}\psi(\vec{r}) = 0$$

or $$\nabla'^2\psi(\vec{r}) + \frac{2}{k_o}\left(\frac{1}{r_a'} + \frac{1}{r_b'} - \frac{Z}{r'}\right)\psi(\vec{r}) + \frac{E'(R,Z)}{k_o^2}\psi(\vec{r}) = 0 \qquad \text{(A3.1)}$$

where $$\nabla'^2 = \frac{\partial^2}{\partial(k_o r)^2} + \frac{2}{k_o r}\frac{\partial}{\partial(k_o r)}$$

$r' = k_o r$

$r_{a,b}' = k_o r_{a,b}$

If all lengths in equation (A3.1) are now scaled by a factor of k_o:

$$\vec{r} \longrightarrow \vec{r}\,' = k_o\vec{r}$$

$$R \longrightarrow k_oR$$

we have:

$$\nabla'^2\psi(\vec{r}\,') + \frac{2}{k_o}\left(\frac{1}{r'_a} + \frac{1}{r'_b} - \frac{Z}{r'}\right)\psi(\vec{r}\,') + \frac{E'(k_oR,Z)}{k_o^2}\psi(\vec{r}\,') = 0$$

and this is exactly the Schrodinger equation of the molecule in a dielectric medium if we identify:

$$r_{ab} = k_oR$$

$$E = k_o^{-2}E'$$