

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

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submitted in partial fulfilment of
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Andrew Yum Sing Kung
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ANDREW YUM SING KUNG

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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_0 : 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_0 : 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.

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CHAPTER 1

F_A - CENTRES IN ALKALI HALIDES

1.1. Introduction

Colour Centres has been one of the major research 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.

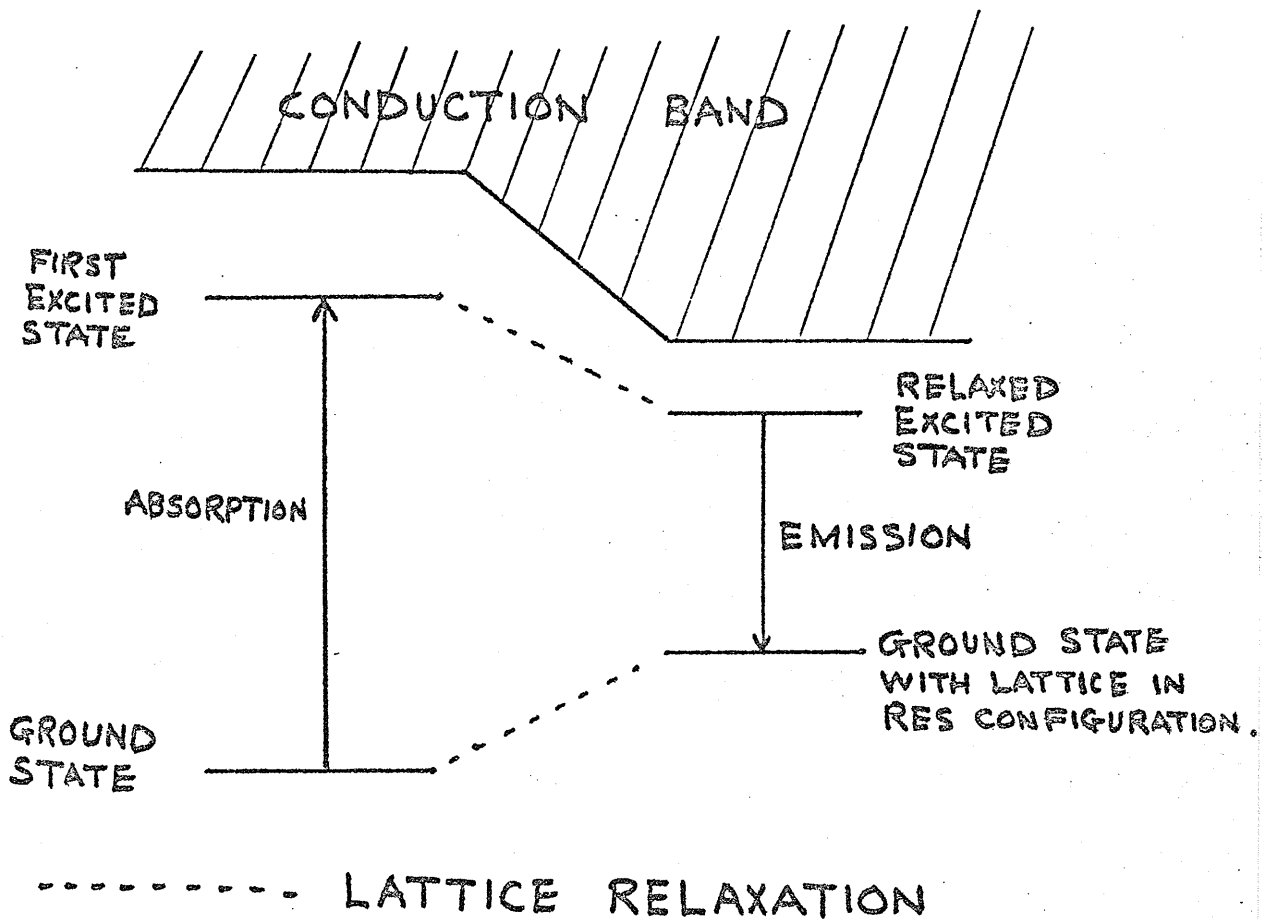
Fowler and Dexter⁽²⁾ showed that the common Einstein's coefficients governing the various optical transition probabilities of the electrons in free atoms do not apply to excess electrons in a host lattice, such as F-centres. The qualitative picture is that the configuration of the host lattice is sensitive 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 Stoke'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.

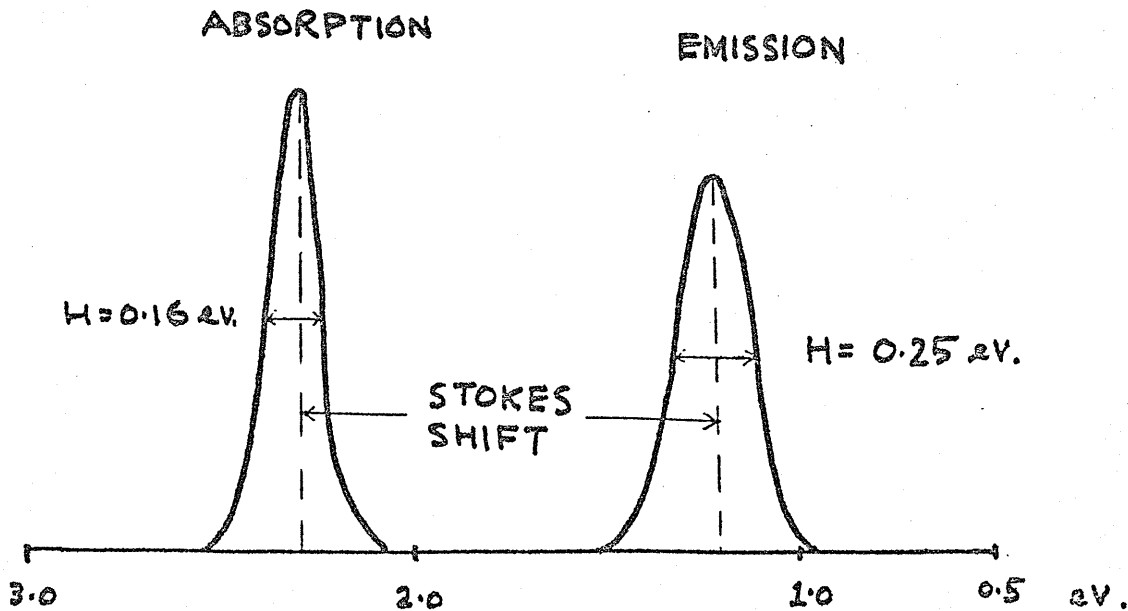
Because of the perfect cubic symmetry of the F-centre, the p-type excited state is triply degenerate, and according to the Jahn-Teller Theorem, this degeneracy is unstable to lattice distortion. One way of breaking the symmetry is to substitute one of the six nearest neighbour cations of the F-centre by ^acation 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

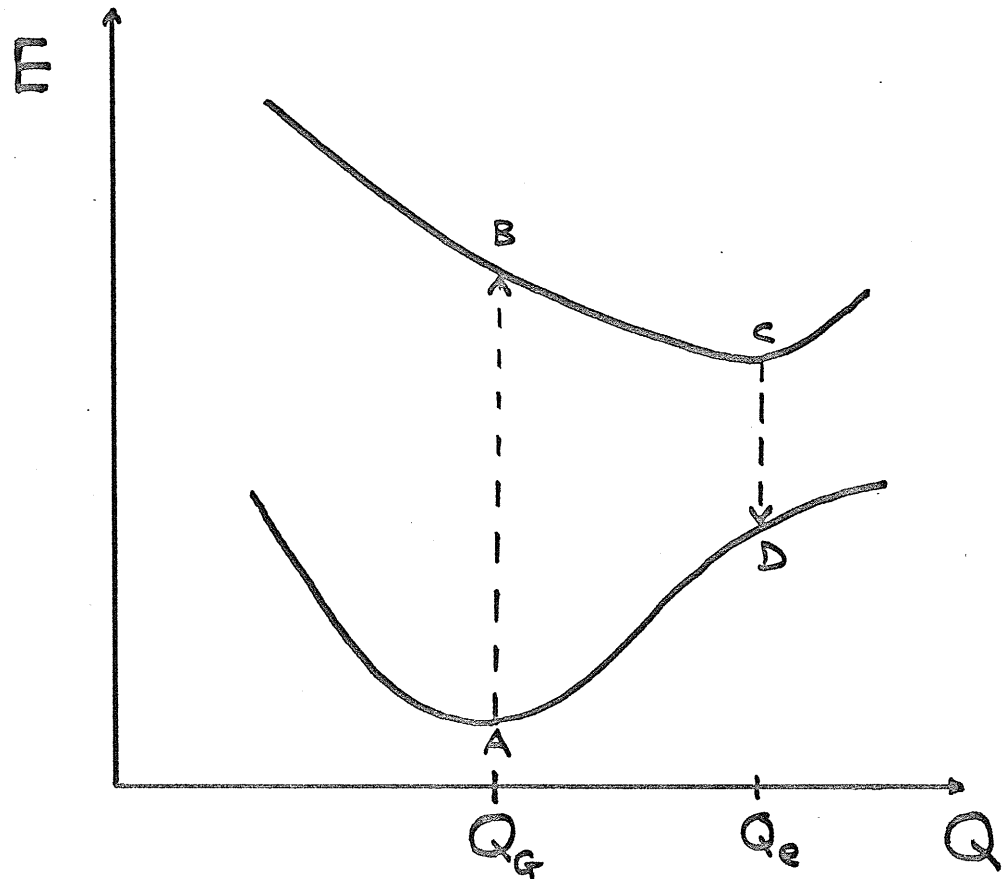
ENERGY LEVEL DIAGRAM OF OPTICAL PROCESS IN F-CENTRE



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.

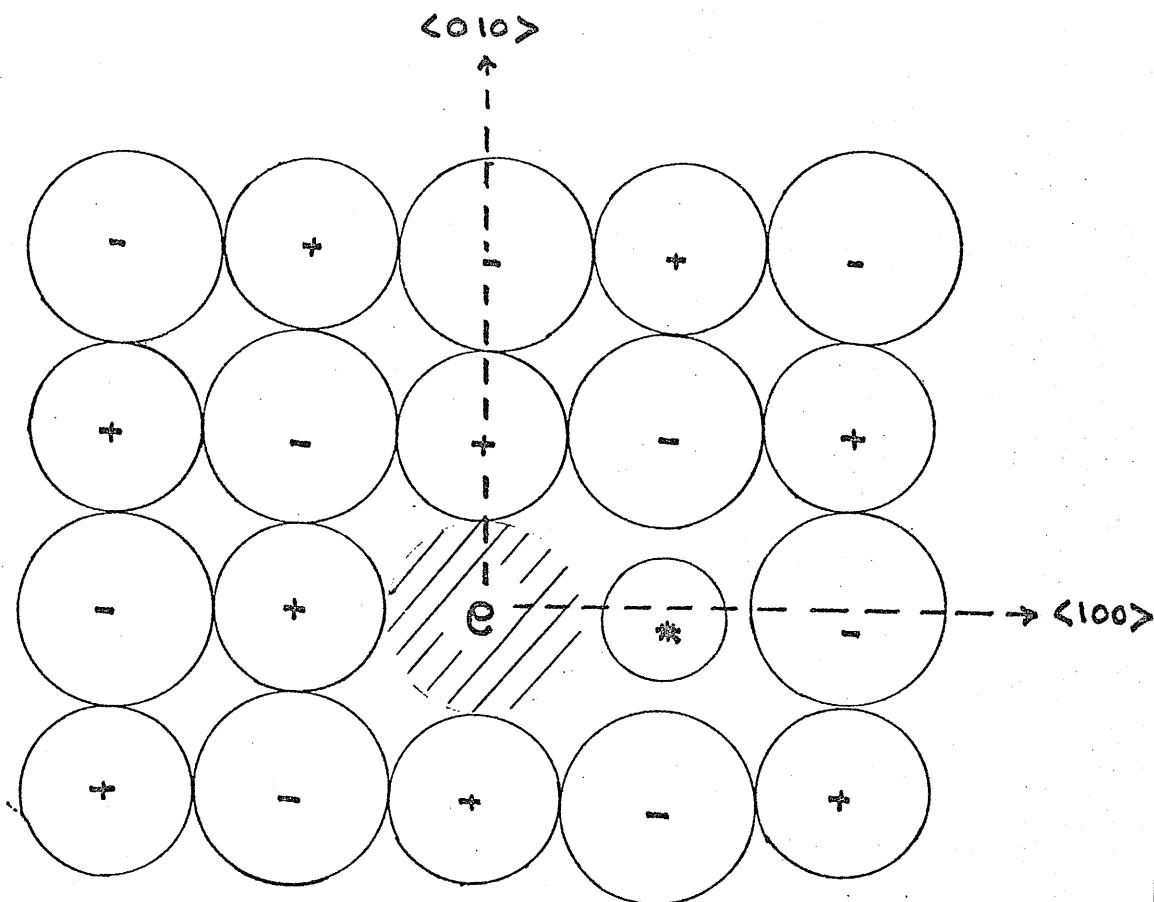
is shown in fig. 2. A thorough review on the physics of F_A -centres is given in ref. 3.

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 Hamiltonian, 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.

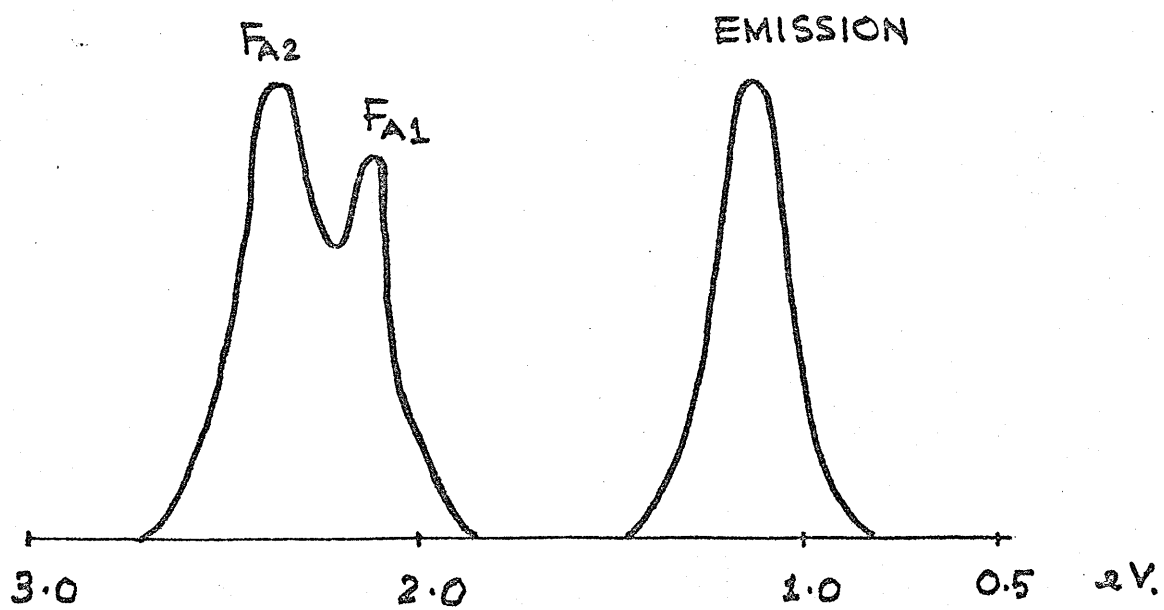
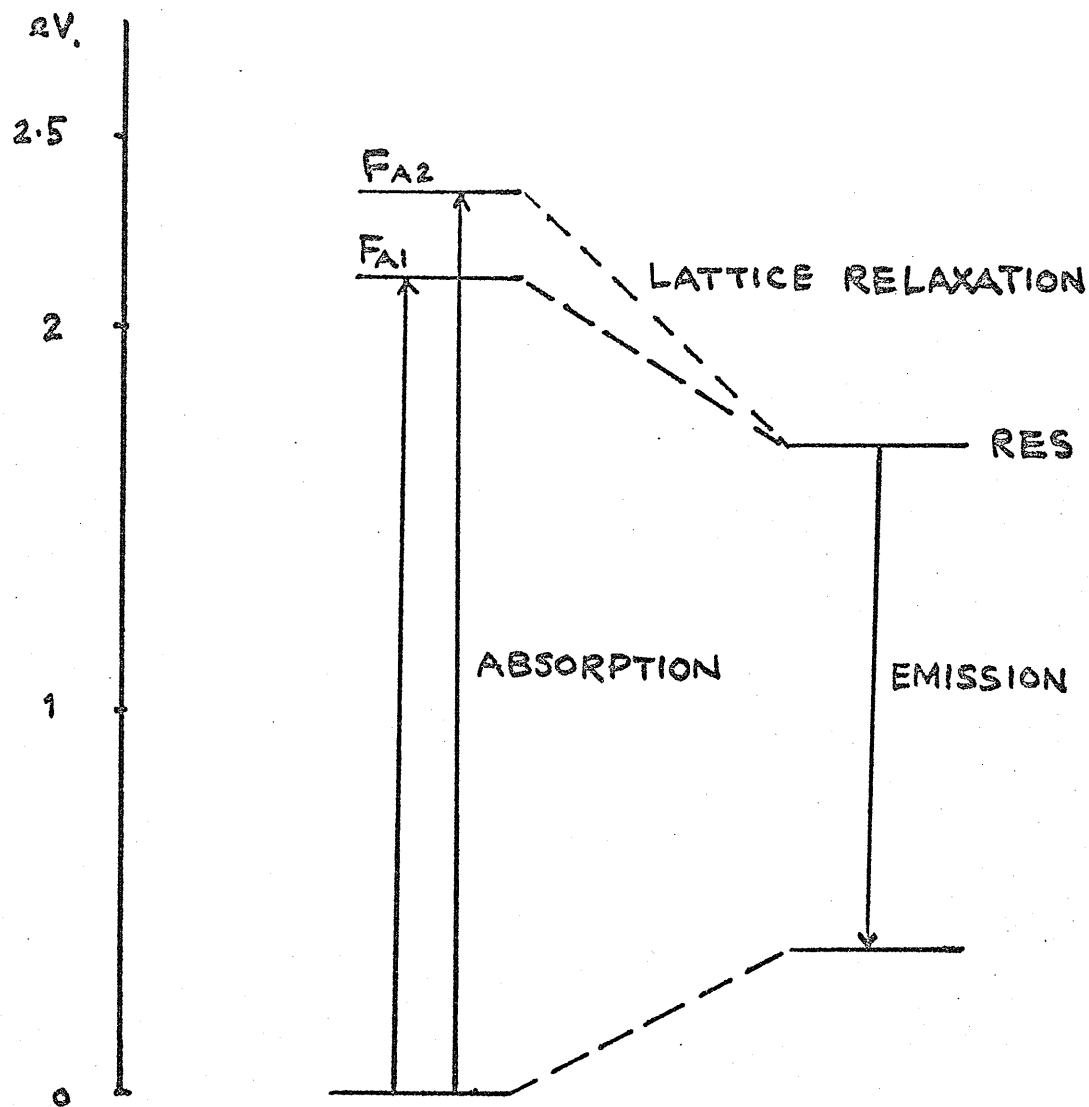
All the F_A -centres that have been investigated experimentally can be classified into two distinct categories according to their emission properties which, from now on, will be referred to as type I F_A -centre ($F_A(I)$) and type II F_A -centre ($F_A(II)$).

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:

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

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 $4.7 \times 10^{12} \text{ sec}^{-1}$.

- (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), ($\bar{1}\bar{1}0$), (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:

$$\eta_R = \eta_0 \exp.(-E_R / RT) \quad (1.2)$$

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