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## Effect of the Crystal Lattice on the Optical Absorption of the $V_K$ Center<sup>1)</sup>

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(25. I. 68)

*Summary.* The influence of the crystal lattice on the optical properties of the  $V_K$  center in alkali halides has been investigated. For this purpose a combined model of the lattice and the molecule-ion has been used which yields a theoretical value of 3.64 eV for the ultraviolet absorption energy of KCl (to be compared with the experimental value of 3.38 eV).

The ground state energy of the  $V_K$  center is not affected by the variation of the lattice parameters while the first excited state and consequently the absorption energy appreciably depend on it.

Estimation of the absorption energies for the various chlorides gives order of magnitude agreement with the experiment (mean deviation 12%), but with the opposite variation from LiCl to RbCl.

### 1. Introduction

The  $V_K$  center<sup>3)</sup> has been found in alkali halide crystals with sodium chloride structure by KAENZIG (1955; CASTNER and KAENZIG, 1957). The investigation of this color center which is stable only at low temperatures with the method of paramagnetic resonance shows, that the molecule-ion-model ( $X_2^-$ ) gives a good description of its ground state properties.  $V_K$  centers or self-trapped holes are generated (e.g. by X-ray irradiation at low temperatures) by binding together two adjacent lattice anions with closed rare-gas shells to form a singly negative molecule-ion  $F_2^-$ ,  $Cl_2^-$ ,  $Br_2^-$  or  $I_2^-$ . The original distance between the two halogen nuclei in the unperturbed lattice is reduced. The  $V_K$  center shows axial symmetry, the axis corresponding very closely to the  $\langle 110 \rangle$  direction in the crystal.

Optical absorption spectra have been investigated mainly by DELBECQ, SMALLER and YUSTER (1958) and DELBECQ, HAYES and YUSTER (1961). Recent measurements have been carried out by MURRAY (1965) on NaI and RbI, by JONES (1966) on NaF as well as by DELBECQ, GILBERT, HAYES and YUSTER (private communication) on the series of the chlorides.

The spectra include several bands. The short-wave band is dominant. A preferential orientation in one of the six face diagonals may be obtained by polarized light down to LHT. This is expressed by a strong dichroism which may be destroyed optically by

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<sup>3)</sup> Detailed information on the  $V_K$  center may be found in SCHULMAN and COMPTON (1962, Chapter 4), PICK (1965), SEIDEL and WOLF (1965). An important paper is due to GILBERT (1966).

absorption of light in the long-wave band. By bleaching with ultraviolet light or by increasing temperature the  $V_K$  centers disappear irreversibly by electron-hole-recombination.

The empirical relation (GUCKER and CHOQUARD, 1966) between the ultraviolet absorption energies of  $V_K$  centers and the  $\beta R$  parameters of JANSEN (LOMBARDI and JANSEN, 1964) – to be discussed in the next chapter – is analogous to a wellknown MOLLWO- (MOLLWO, 1931) or IVEY- (IVEY, 1947) relationship for other kinds of color centers. This suggests that the molecule-ion-model is inadequate to describe the optical phenomena. This conjecture has been confirmed experimentally by the results of MURRAY (1965) as well as by recent measurements of DELBECQ, GILBERT, HAYES and YUSTER (private communication) on the series of the chlorides.

## 2. Experimental Correlation between $\lambda(V_K)_{UV}$ and $\beta R$

The lattice constant may be regarded as a useful parameter to classify certain properties of alkali halide crystals when the detailed structure of the ions forming the crystal is not important, so that they may be considered as singly positive and singly negative lattice-particles.

As an example we may recall a wellknown MOLLWO-IVEY-relation for  $F$  centers which relates the spectral position of the  $F$ -band at a given temperature with the lattice constant (MOLLWO, 1931; IVEY, 1947; SCHULMAN and COMPTON, 1962, Chapter 3; WOOD, 1965).

For  $V_K$  centers such a simple relation does not exist. This is easily shown by plotting the wavelengths  $\lambda(V_K)_{UV}$  versus the lattice constant  $a$  or the ratio of the ionic radii  $R^-/R^+$  or even versus any combination of these parameters, such as the parameter  $2R\sqrt{2}/a$  characterizing the degree of overlap of adjacent halide-ions as used by MURRAY (1965) for stability considerations.

The use of JANSEN's  $\beta R$  parameter (LOMBARDI and JANSEN, 1964), however, produces a remarkable regularity (Figure 1). The reciprocal value of  $\beta$  measures the

Table 1

Crystal	$a$ Å	$\beta R$	$\beta' R$	$\lambda(V_K)_{UV}$ m $\mu$	$E(V_K)_{UV}$ eV
LiF	4.017	1.88	5.22	$348 \pm 0.5$	3.56
NaF	4.62	2.16	2.68	366	3.39
LiCl	5.13	1.44	6.66	$401 \pm 0.5$	3.09
NaCl	5.628	1.57	3.27	$381 \pm 0.5$	3.25
KCl	6.28	1.75	2.25	$367 \pm 0.5$	3.38
RbCl	6.54	1.83	1.96	$365 \pm 0.5$	3.40
KBr	6.59	1.58	2.37	$385 \pm 0.5$	3.22
NaI	6.46	1.35	3.75	$432 \pm 7$	2.87
KI	7.05	1.48	2.53	$400 \pm 0.5$	3.10
RbI	7.33	1.54	2.20	$405 \pm 5$	3.06

width of a GAUSSIAN charge distribution for each type of ion and  $R$  stands for the nearest neighbour distance. The quantity  $\exp(-[\beta R]^{-2})$  is used because of its physical meaning rather than  $\beta R$  only, since this exponential factor appears in the expression of the classical vibration frequency of the electron in the oscillator approximation. In Figure 1 the seven "triangle-points" are more reliable, since the absorption wavelengths for these substances have been measured by the same investigators, under the same conditions and with greater accuracy. Contrary to the parameter  $\beta$  characterizing the negative ions the parameter  $\beta'$  associated with the positive ions produces no regularity at all.

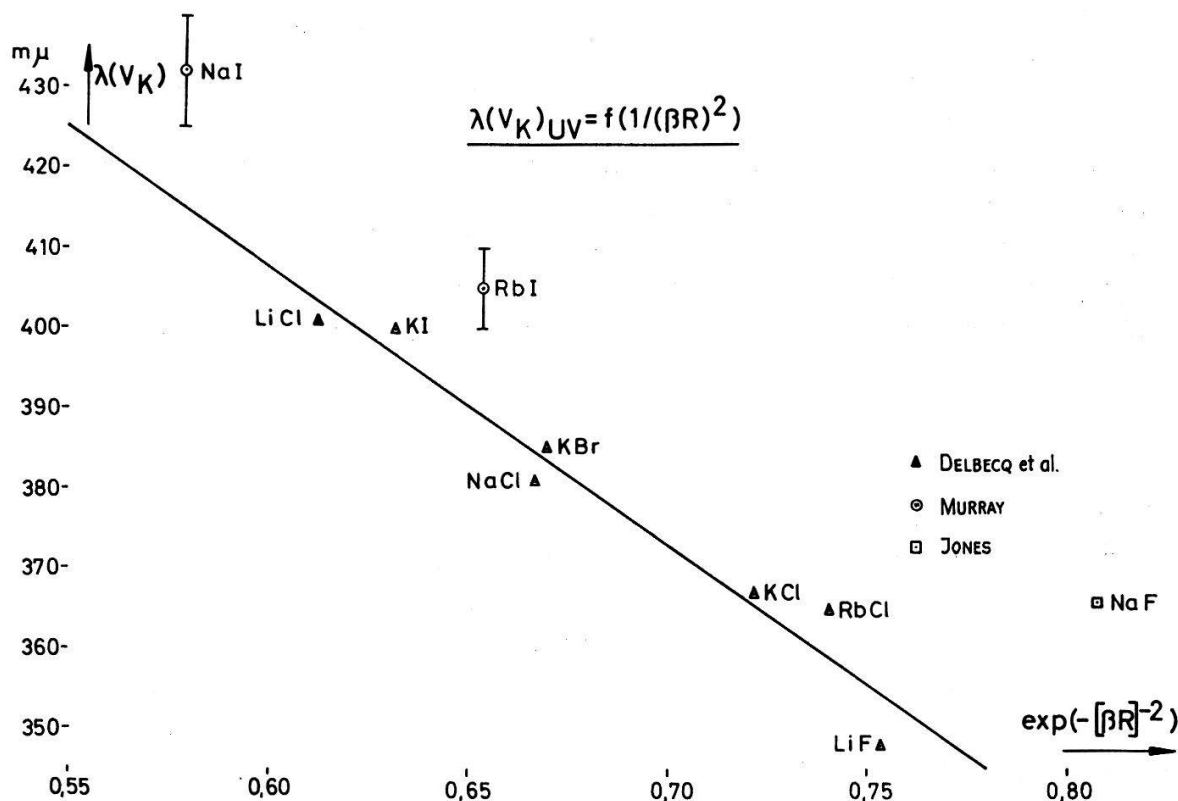


Figure 1

Correlation between the ultraviolet absorption wavelengths of the  $V_K$  center and JANSEN'S  $\beta R$  parameters.

Table 1 shows the numerical values of the lattice constants, the  $\beta R$  and  $\beta' R$  parameters, the UV absorption wavelengths  $\lambda(V_K)_{UV}$  and the corresponding energy values  $E(V_K)_{UV}$ .

### 3. General Outline of the Problem

We investigate the influence of the lattice on the ultraviolet absorption of the  $V_K$  center restricting our considerations to alkali halide crystals with sodium chloride structure. KCl will serve as an example without loss of generality.

We shall define the  $V_K$  center for our purpose as made up of different parts and give the form of the energy operator to be introduced into the Schrödinger equation.



### 3.1 Definition of the $V_K$ center

The singly charged lattice  $G^+$  resulting from the removal at low temperature of a valence electron  $e^-$  belonging to a  $\text{Cl}^-$  ion embedded in an ideal  $\text{KCl}$ -crystal  $G^0$  can be used to define the  $V_K$  center

$$G^0 - e^- = G^+ = V_K. \quad (3.1)$$

This system can be decomposed into a neutral  $\text{Cl}_2^0$  molecule, the valence electron  $e^-$  belonging in common to both  $\text{Cl}^0$  atoms forming the  $\text{Cl}_2^0$  molecule and in the remaining doubly charged lattice  $G^{++}$  which may be called the residual-lattice

$$V_K = \text{Cl}_2^0 + e^- + G^{++}. \quad (3.2)$$

### 3.2 Dynamical equation and potential energy of the electron

The  $V_K$  center defined by (3.2) represents a very complicated system of electrons and nuclei from the atomic point of view. We can, however, avoid considering them individually, since we are interested in the optical properties of the  $V_K$  center which are related essentially to the  $e^-$  electron of (3.2).

The motion of this electron in the field of the lattice-particles (ions of the crystal lattice and the two  $\text{Cl}^0$  atoms) is described in the static approximation which leaves the lattice-particles fixed at their equilibrium positions by the following Schrödinger equation

$$\left[ -\frac{\hbar^2}{2m} \sum_{\mu=1}^3 \frac{\partial^2}{\partial x_\mu^2} + V_{e-G}(\mathbf{x}, A) \right] \phi = E \phi(\mathbf{x}, A), \quad (3.3)$$

where  $m$  is the electron mass,  $x_\mu$  the coordinates of the electron,  $\phi(\mathbf{x}, A)$  the wavefunction of the electron and  $V_{e-G}$  the potential energy of the electron in the field of all lattice-particles.

This equation only contains the equilibrium parameters  $A$  of the lattice and so describes the electron for a fixed lattice configuration. We call it the electron equation.

In this tentative model the eigenvalues of the electron equation yield information about the energy levels of the electron and therefore the absorption energies of the  $V_K$  center.

The potential energy of the electron  $V_{e-G}$  in (3.3) contains according to (3.2) the following two terms

$$V_{e-G} = V_{e-\text{Cl}_2^0} + V_{e-G^{++}}, \quad (3.4)$$

$V_{e-\text{Cl}_2^0}$ : Energy of interaction of the electron  $e^-$  with the neutral  $\text{Cl}_2^0$  molecule (which takes into account the stable molecule-ion  $\text{Cl}_2^-$ ),

$V_{e-G^{++}}$ : Energy of interaction of the electron  $e^-$  with the doubly positively charged residual-lattice  $G^{++}$ .

In the following two simple models will be developed for the residual-lattice  $G^{++}$  and the molecule  $\text{Cl}_2^0$  in order to compute the potential energies  $V_{e-\text{Cl}_2^0}$  and  $V_{e-G^{++}}$  which are to be introduced in the Schrödinger equation (3.3).

### 3.3 Approximations

Besides the above mentioned simplification of condensing the ions and atoms into fixed lattice-particles, the ions of the residual-lattice  $G^{++}$  will be taken at the positions of the unperturbed ideal crystal. Lattice distortions in the immediate neighbourhood

of the molecule-ion and relaxation effects will be considered as small perturbations compared with the influence of the "ideal-lattice" and therefore ignored. This rather crude model will be subjected to a critical discussion in the last chapter on the basis of the results obtained.

#### 4. Lattice-Model

We begin with the computation of the potential energy of the electron  $e^-$  in the residual-lattice  $G^{++}$ , i.e. with the second term  $V_{e--G^{++}}$  of (3.4).

The residual-lattice may be described as resulting from an arbitrary ideal crystal containing two kinds of ions when the defect is produced by extraction of two adjacent negative ions from the crystal. The potential energy  $V_{e--G^{++}}$  of the electron  $e^-$  is thus obtained by subtracting the contribution of the two ions.

##### 4.1 Formalism for the ideal crystal

We shall base our calculations on JANSEN's effective-electron model (JANSEN, 1965) in taking extended charges instead of point charges for the ions of the ideal crystal. If the charge distribution of the effective electrons is chosen to be of GAUSSIAN form characterized by the parameters  $\beta$ , the total charge density of the crystal may be expressed as

$$\varrho(\mathbf{r}) = \sum_j e_j \left( \frac{\beta_j}{\sqrt{\pi}} \right)^3 e^{-\beta_j^2 (\mathbf{r}_j - \mathbf{r})^2}, \quad (4.1)$$

where

$$\begin{aligned} \mathbf{r}_j: & \quad \text{radius vector of the } i^{\text{th}} \text{ ion,} \\ e_j: & \quad \text{its charge (+ } e \text{ or } -e), \\ \beta_j = & \begin{cases} \beta & \text{for negative ions} \\ \beta' & \text{for positive ions.} \end{cases} \end{aligned}$$

This statement is obvious, since the parameters  $\beta R$ , which have lead to our correlation (chapter 2) enter thereby directly into the calculations as we shall see in the following.

POISSON's equation giving the relation between the electrostatic potential and the charge density may be solved by Fourier expansion with the periodicity of the lattice. This yields the result

$$\varphi(\mathbf{r}) = \frac{4\pi}{\Omega_0} \sum_n \sum_{\boldsymbol{\tau}} e_n \frac{1}{|\boldsymbol{\tau}|^2} e^{-i\boldsymbol{\tau} \cdot (\mathbf{r}_n - \mathbf{r})} e^{-|\boldsymbol{\tau}|^2/4\beta_n^2}, \quad (4.2)$$

( $\Omega_0$ : volume of the elementary cell,

$\boldsymbol{\tau}$ : vector of the reciprocal lattice).

The summation over  $n$  runs over the  $n$  lattice-particles of the elementary cell only.

If we make use of the special geometrical configuration of the rock-salt lattice, our general result (4.2) can be transformed in

$$\varphi(\mathbf{r}) = - \frac{4e}{a\pi} \sum_{\boldsymbol{\tau}_0} \Phi(\beta_{\boldsymbol{\tau}_0}^2) e^{i\boldsymbol{\tau}_0 \cdot \mathbf{r}} \quad (4.3)$$

with

$$\Phi(\vartheta_{\mathbf{r}_0}^2) = \frac{1}{\vartheta_{\mathbf{r}_0}^2} (e^{-\Gamma^2 \vartheta_{\mathbf{r}_0}^2} - (-1)^{\sigma_{\mathbf{r}_0}} e^{-\Gamma'^2 \vartheta_{\mathbf{r}_0}^2}), \quad (4.4)$$

$$\Gamma = \frac{\pi}{2\beta R}, \quad \Gamma' = \frac{\pi}{2\beta' R}, \quad (4.5)$$

$$\vartheta_{\mathbf{r}_0}^2 = 3 \sum_{i=1}^3 \tau_i^2 - 2 \sum_{i < j}^3 \tau_i \tau_j, \quad (4.6)$$

$$\sigma_{\mathbf{r}_0} = \sum_{i=1}^3 \tau_i, \quad (4.7)$$

$e$ : positive electron charge,

$a$ : lattice constant,

$R$ : nearest neighbour distance ( $= a/2$ ).

The vector  $\mathbf{r}_0 = (\tau_1, \tau_2, \tau_3)$  stands symbolically for the triple of integers  $\tau_1, \tau_2, \tau_3$ .

#### 4.2 Generation of the defect

The two adjacent anions to be removed from the crystal contribute to the total charge density

$$\tilde{\varrho}(\mathbf{r}) = -e \left( \frac{\beta}{\sqrt{\pi}} \right)^3 \{ e^{-\beta^2(\mathbf{r}-\mathbf{R}_0)^2} + e^{-\beta^2(\mathbf{r}+\mathbf{R}_0)^2} \}, \quad (4.8)$$

where  $\mathbf{R}_0$  is a vector of length  $a\sqrt{2}/4$  connecting the origin chosen between the two adjacent ions with their nuclei (with alternate sign).

With the wellknown solution of POISSON's equation

$$\chi(\mathbf{r}) = \int \frac{\tilde{\varrho}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3r' \quad (4.9)$$

one finds after some calculation the result

$$\chi(\mathbf{r}) = -e \left\{ \frac{\operatorname{erf}(\beta|\mathbf{r}-\mathbf{R}_0|)}{|\mathbf{r}-\mathbf{R}_0|} + \frac{\operatorname{erf}(\beta|\mathbf{r}+\mathbf{R}_0|)}{|\mathbf{r}+\mathbf{R}_0|} \right\}, \quad (4.10)$$

where the error function

$$\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x dt e^{-t^2} \quad (4.11)$$

has been introduced.

#### 4.3 Potential in the residual-lattice

The potential in the residual-lattice  $G^{++}$  is obtained by subtracting (4.10) from (4.3)

$$\tilde{\varphi}(\mathbf{r}) = \varphi(\mathbf{r}) - \chi(\mathbf{r}). \quad (4.12)$$

Multiplication by  $e$  gives the potential energy

$$V_{e^{--}G^{++}} = V_{e^{--}G^0} - V_{e^{--}2X^-}. \quad (4.13)$$

For the two terms we get from (4.3) and (4.10)

$$V_{e^{-}-G^0} = \frac{4e^2}{a\pi} \sum_{\mathbf{r}_0} \Phi(\vartheta_{\mathbf{r}_0}^2) e^{i\mathbf{r}\mathbf{r}} \quad (4.14)$$

and

$$V_{e^{-}-2X^{-}} = e^2 \beta \left\{ \frac{\operatorname{erf}(\beta|\mathbf{r}-\mathbf{R}_0|)}{\beta|\mathbf{r}-\mathbf{R}_0|} + \frac{\operatorname{erf}(\beta|\mathbf{r}+\mathbf{R}_0|)}{\beta|\mathbf{r}+\mathbf{R}_0|} \right\}. \quad (4.15)$$

In order to get an idea of the shape of the potential energy according to (4.13) expressions (4.14) and (4.15) have been used to compute numerical values along the three axis of an orthogonal coordinate system. The origin is chosen in the center of symmetry of the  $V_K$  center, the  $x$ -axis joins anions along a face diagonal, the  $y$ -axis cations and the  $z$ -axis goes through the centers between four ions of each ionic layer in the third dimension. The result is shown in Figure 2 for the case of KCl. The curves  $V(x)$ ,  $V(y)$  and  $V(z)$  are drawn in the same plane for comparison. They represent the potential energy of the electron  $e^{-}$  in the three perpendicular directions  $x$ ,  $y$  and  $z$ . Other data of this Figure will be discussed later in connection with Figure 5.

Figure 3 shows the curves of constant electrostatic potential in the  $xy$ -plane. One notices two characteristic features, the saddle point at the origin and the two maxima on the  $y$ -axis near the positive potassium ions.

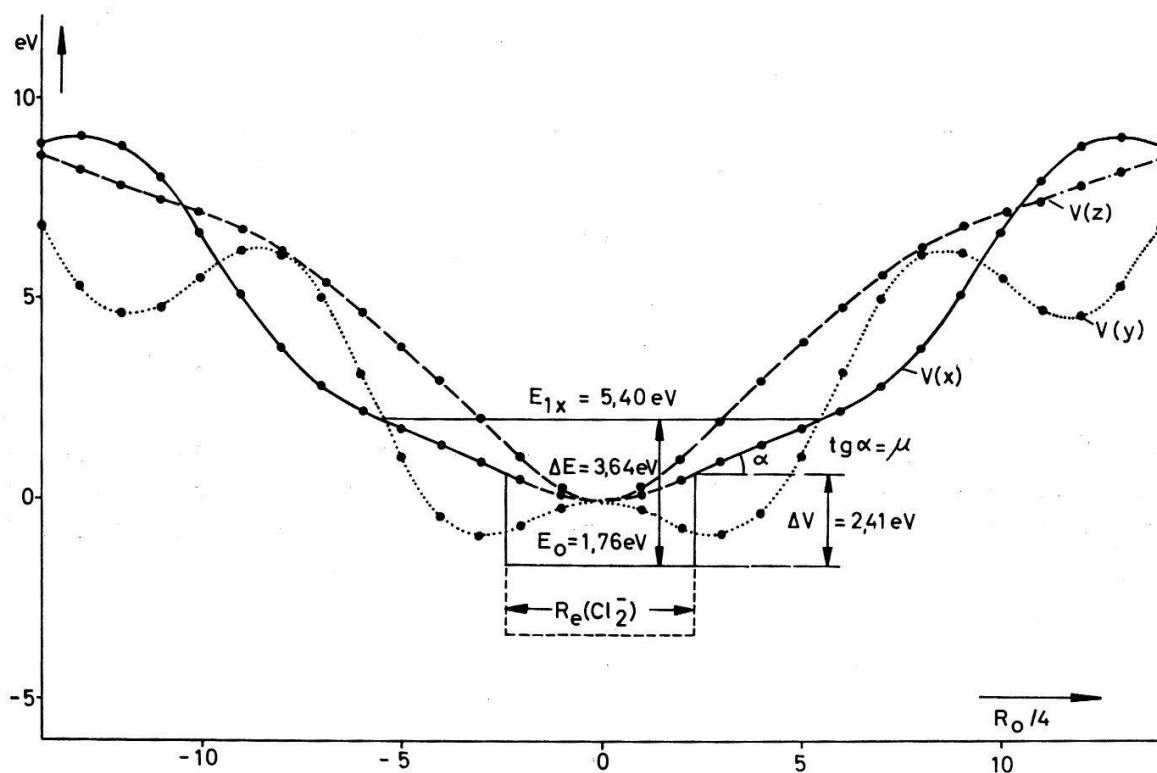


Figure 2

Potential energy  $V_{e^{-}-G^{++}}$  of the electron in the residual-lattice in the three perpendicular directions  $x$ ,  $y$  and  $z$  through the center of the defect.

#### 4.4 Absorption energy in lattice approximation

Before discussing the necessary model for the molecule we consider the absorption energies of the  $V_K$  center obtained by taking into account the influence of the "ideal" residual-lattice  $G^{++}$  only.

The Schrödinger equation (3.3) cannot be solved analytically, since the form of the potential energy (4.13) to be inserted doesn't allow separation of the variables. So we must restrict to an estimation of the relative energy levels for the main directions  $x$ ,  $y$ ,  $z$ . This one-dimensional procedure can be made plausible by the experimental fact that the absorption of the  $V_K$  center is strongly anisotropic.

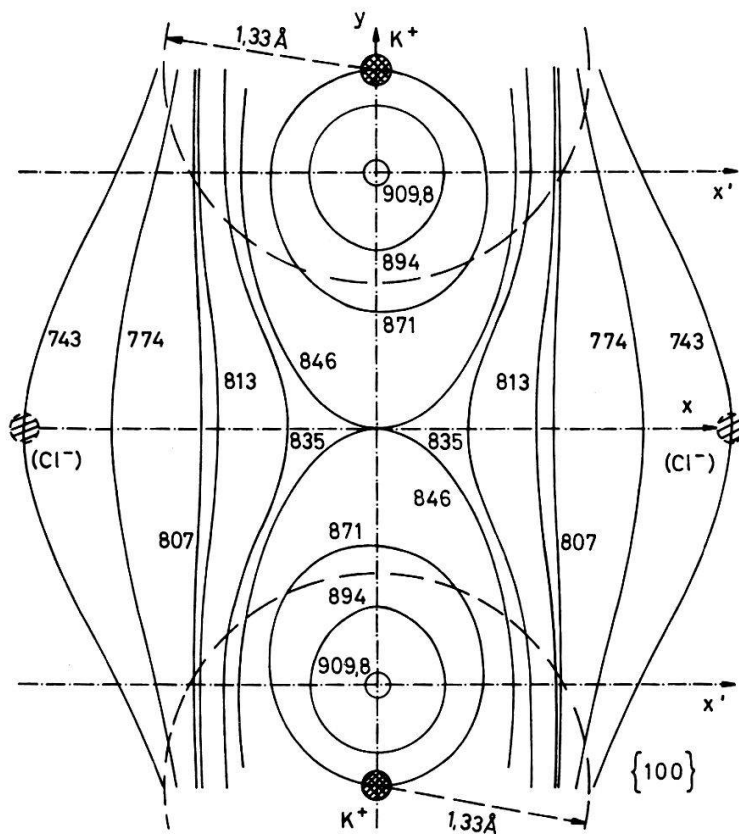


Figure 3

Curves of constant electrostatic potential of the residual-lattice in the  $xy$ -plane. (Arbitrary units).

In order to get approximate numerical values the BOHR-SOMMERFELD quantum condition has been used. The curves  $V(x)$  and  $V(z)$  have been replaced by families of parabolas and the curve  $V(y)$  by fragments of parabolas. The results are listed in Table 2.

Table 2

Direction	Absorption energies	
	Experimental values (YUSTER and coworkers)	Theoretical values (lattice approximation)
	eV	eV
$x$	3.38	1.65
$y$	1.65	2.15
$z$	1.65	2.75

The comparison with the experimental results (Table 2) shows bad agreement and opposite tendency. This leads to the following conclusions:

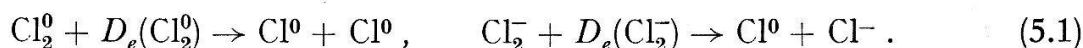
The "ideal" residual-lattice alone cannot describe the absorption phenomena in a satisfactory manner. That the molecular part (1st term of (3.4)) has to be taken into account is not surprising: The molecule-ion model is an adequate description of the ground state of the  $V_K$  center and the absorption process starts of course from the ground state.

## 5. Molecule-Model

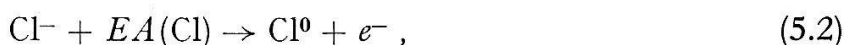
In order to take into account the two neutral chlorine atoms we should compute the term  $V_{e-\text{Cl}_2^0}$  in detail considering the interaction of the electron with the two chlorine nuclei and with the different electron shells of the two chlorine atoms. We shall choose in our approximation, however, a simple model for the molecular part derived from the interaction potential curves of the  $\text{Cl}_2^0$  molecule and the  $\text{Cl}_2^-$  molecule-ion.

### 5.1 Interaction potentials

The following relations hold for the dissociation of the  $\text{Cl}_2^0$  molecule and the  $\text{Cl}_2^-$  molecule-ion ( $D_e(\text{Cl}_2^0)$  resp.  $D_e(\text{Cl}_2^-)$  are the corresponding dissociation energies<sup>4)</sup>)



With the electron affinity  $EA$  of the chlorine defined by the relation



the important connexion



can be used where  $\Delta V$  is standing for

$$\Delta V = D_e(\text{Cl}_2^-) + EA(\text{Cl}) - D_e(\text{Cl}_2^0) . \quad (5.4)$$

We shall take (5.3) as a basis for our molecule-ion model (Figure 4) represented in the simple form of a potential box.  $\Delta V$  is the difference of energy according to (5.3) between the ground state of the molecule-ion  $\text{Cl}_2^-$  and the "ionized" state  $\text{Cl}_2^0 + e^-$ . The width of the potential box in the  $x$ -direction is chosen as the equilibrium distance  $R_e(\text{Cl}_2^-)$  between the two nuclei of the molecule-ion which yields reasonable electron densities due to the penetration of the wave function into the potential wall at the position of the nuclei (Figure 5). For the other two directions  $y$  and  $z$  which are identical because of symmetry a width of half the equilibrium distance  $R_e(\text{Cl}_2^-)$  may be chosen.

The numerical values are due to DOUGLAS, MØLLER and STOICHEFF (1963) for the  $\text{Cl}_2^0$  molecule, to GILBERT and WAHL (private communication) and PERSON (1963) for the  $\text{Cl}_2^-$  molecule-ion and to BERRY and REIMANN (1963) for the electron affinity. These important data (also for the other molecule-ions) are listed in Table 3.

<sup>4)</sup>  $D_e$  can be taken in place of  $D_0^0 = D_e - 1/2 \omega_e$  on account of the smallness of the fundamental quantum  $\omega_e$  (order 0.01 eV).

Table 3

$X_2^-$	$D_e(X_2^0)^a)$ eV	$D_e(X_2^-)$ eV	$EA(X)^e)$ eV	$\Delta V^f)$ eV	$R_e(X_2^0)^a)$ Å	$R_e(X_2^-)$ Å	Matrix	$\lambda(V_K)_{IR}$ m $\mu$	$E(V_K)_{IR}$ eV
$F_2^-$	1.56	$\sim 0.8^b)$	$3.448 \pm 0.005$	$\sim 2.69$	1.42	1.90 <sup>d)</sup>	LiF	$\sim 750^g)$	$\sim 1.65$
$Cl_2^-$	2.48	$1.2 \pm 0.5^c)$ $1.28 \pm 0.3^d)$	$3.613 \pm 0.003$	2.33 2.41	1.99	$2.6 \pm 0.1^c)$ $2.65 \pm 0.1^d)$	LiCl NaCl KCl RbCl	$\sim 750^h)$ $\sim 750^h)$ 750 <sup>g)</sup> $\sim 750^h)$	$\sim 1.65$ $\sim 1.65$ 1.65 $\sim 1.65$
$Br_2^-$	1.97	$1.0 \pm 0.5^c)$	$3.363 \pm 0.003$	2.39	2.28	$2.8 \pm 0.1^c)$	KBr	750 <sup>g)</sup>	1.65
$I_2^-$	1.54	$0.7 \pm 0.3^c)$	$3.063 \pm 0.003$	2.22	2.67	$3.15 \pm 0.1^c)$	NaI KI RbI	$880 \pm 10^i)$ 800 <sup>g)</sup> $793 \pm 5^i)$	1.41 1.55 1.56

a) Data from T. L. CORRELL, The Strengths of Chemical Bonds, Butterworths, London, 1958, Table 11.5.1

b) According to the rough rule:  $D_e(X_2^-) \approx \frac{1}{2} D_e(X_2^0)$ , since no reliable value is known

c) W. B. PERSON, J. Chem. Phys. 38, 109 (1963)

d) T. L. GILBERT, private communication

e) R. S. BERRY and C. W. REIMANN, J. Chem. Phys. 38, 1540 (1963)

f) According to equation (5.4):  $\Delta V = -D_e(X_2^0) + D_e(X_2^-) + EA(X)$

g) C. J. DELBECQ, W. HAYES and P. H. YUSTER, Phys. Rev. 121, 1043 (1961)

h) C. J. DELBECQ, private communication

i) R. B. MURRAY, private communication



### 5.2 Three-dimensional potential box

The three-dimensional potential box used for the molecule-ion contains the energy level we have fixed as giving the ground state. In order to exhibit the influence of the lattice on the excited states our calculation must rely on the fact that no further energy levels can exist within the potential box. This has now to be shown.

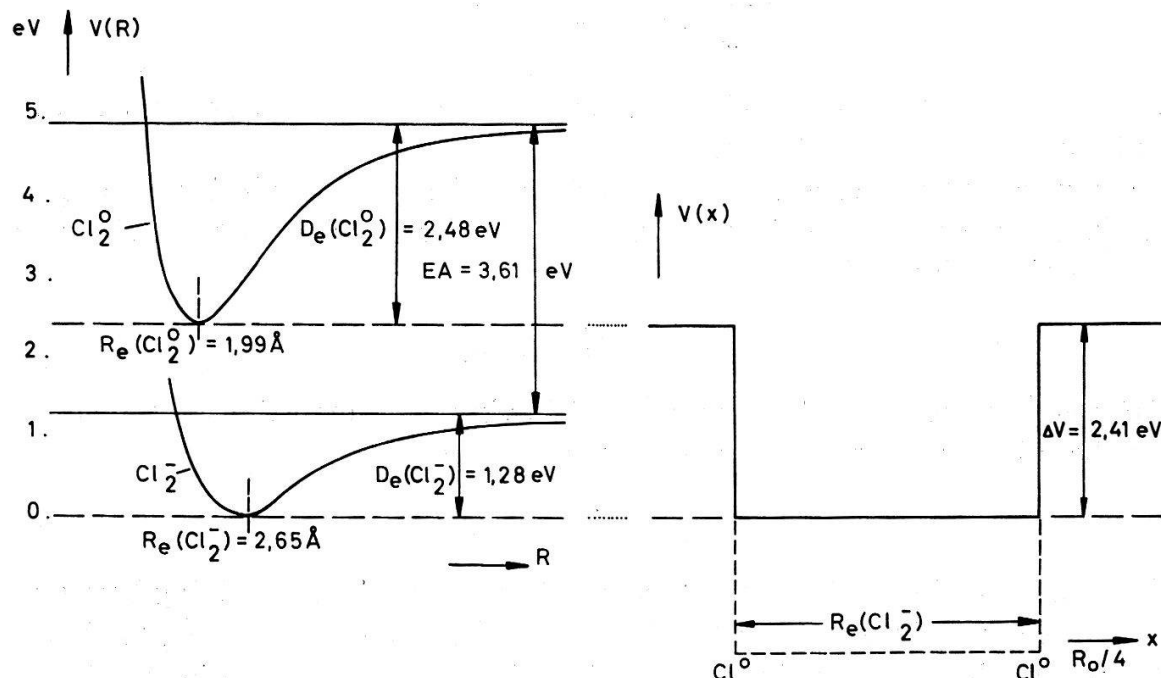


Figure 4

Construction of the molecule-ion-model from the interaction potential curves of the  $\text{Cl}_2^0$  molecule and the  $\text{Cl}_2^-$  molecule-ion.

The potential energy of a three-dimensional rectangular finite potential box with sides  $2\xi$ ,  $2\eta$  and  $2\zeta$  is of the form

$$V(x, y, z) = -V_0 \Theta_x \Theta_y \Theta_z \quad (5.5)$$

with

$$\Theta_x = \begin{cases} 1 & \text{if } |x| < \xi \\ 0 & \text{if } |x| > \xi \end{cases}, \quad \Theta_y = \begin{cases} 1 & \text{if } |y| < \eta \\ 0 & \text{if } |y| > \eta \end{cases}, \quad \Theta_z = \begin{cases} 1 & \text{if } |z| < \zeta \\ 0 & \text{if } |z| > \zeta \end{cases}. \quad (5.6)$$

This potential energy, despite its relatively simple form, does not lead to a separable Schrödinger equation.

To overcome this difficulty the criterion of the RAYLEIGH-quotient (ZURMUEHL, 1961, chapter 4, § 15) may be used in connexion with potentials of spherical symmetry.

In the three-dimensional square well potential with

$$V(r) = \begin{cases} -V^0 & \text{if } r < a \\ 0 & \text{if } r > a \end{cases} \quad (5.7)$$

there is one bound state for the electron if

$$\frac{\pi^2 \hbar^2}{8m} < V^0 a^2 < \frac{9\pi^2 \hbar^2}{8m}, \quad (5.8)$$

(SCHIFF, 1955, chapter 4, § 15). This is true for the case with zero angular momentum, the only one of interest in this context.

We now consider the inscribed sphere  $S_i$  and the circumscribed sphere  $S_c$  of the prism  $P$ . By means of the RAYLEIGH-quotients for the different cases one easily finds the series of inequalities

$$|E_i^0| < |E_P^0| < |E_c^0| \quad (5.9)$$

for the energy values of the lowest states,  $V^0$  having the same value in each case.

On the other hand the same given value  $|E^0|$  yields

$$V_i^0 > V_P^0 > V_c^0. \quad (5.10)$$

We can, from the results (5.8), draw conclusions for the prism lying between the two extreme cases of the inscribed and circumscribed spheres according to (5.10). An approximate value of  $V_P^0$  is obtained for the sphere  $S_P$  of radius  $a_P$  having the same volume as the prism  $P$ .

The characteristic values of the different cases are listed in Table 4

Table 4

Sphere	$a$ 10 <sup>-8</sup> cm	$V^0$ 10 <sup>-12</sup> erg	$V^0 a^2$ 10 <sup>-28</sup> ergcm <sup>2</sup>
$S_i$	0.68	49.3	22.78
$S_P$	1.05	25.2	27.95
$S_c$	1.64	14.1	37.72
$S_L$	4.98	5.5	136.40

In Table 4 are given additional values corresponding to the limiting case  $S_L$  for which there exists just a second energy level within the potential well (for  $l = 0$ ).

The comparison of the values of the fourth column of Table 4 with the criterion (5.8) which gives the quantitative limits

$$15.06 \cdot 10^{-28} \text{ ergcm}^2 < V^0 a^2 < 135.54 \cdot 10^{-28} \text{ ergcm}^2 \quad (5.11)$$

clearly shows, that in our potential well only one energy level does exist. This is an interesting and satisfactory result.

## 6. Lattice-Molecule-Model

Following the outline of chapter 3 we have now to combine the molecular part of chapter 5 with the lattice part of chapter 4 to get the necessary lattice-molecule-model. This can be expressed as follows

$$V_{e-Cl_2^0} + V_{e-G^{++}} = V_{e-(Cl_2^0+G^{++})}. \quad (6.1)$$

The three-dimensional Schrödinger equation (3.3) will be reduced as stated before to the one-dimensional problem responsible for the ultraviolet absorption, that is the  $x$ -direction.

### 6.1 Absorption energy in the "cup-like" potential

It can be seen from Figure 2, that the potential energy in the  $x$ -direction has the form of a pot in the central part and that the curve immediately joining on the potential well can be approximated by a straight line with a slope  $\mu = \tan \alpha$ .

The way to solve this problem is in principle the same as the one of the ordinary potential well with finite step (SCHIFF, 1955, chapter 2, § 9).

The solutions in the inner domain are cos- and sin-functions, and the Schrödinger equation for the outer domain is solved by the AIRY functions (ABRAMOWITZ and STEGUN, 1964). It is most convenient to solve the implicit equations for the energy eigenvalues graphically.

In this way the energy difference  $\Delta E$  between the first two levels corresponding to the ultraviolet absorption has been found to be 3.64 eV (Fig. 5 and Fig. 2). The comparison with the experimental value of 3.38 eV yields a difference of about 8%.

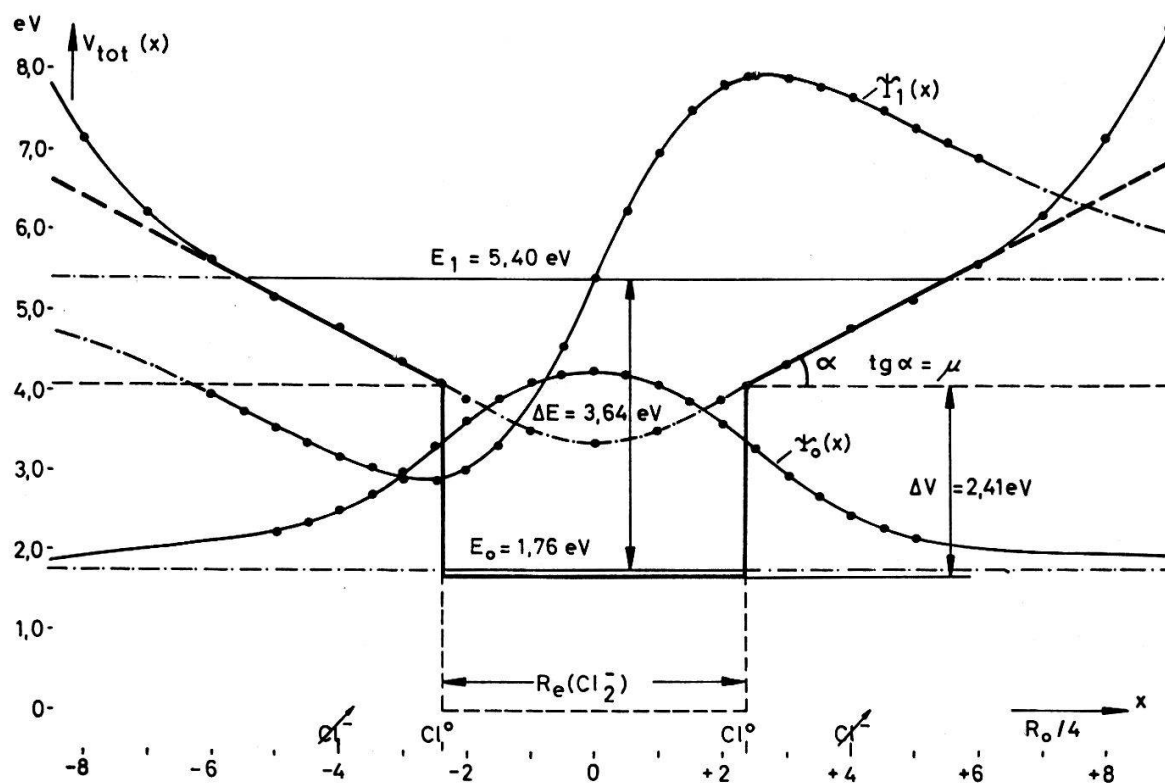


Figure 5

Energy levels and unnormalized wave functions of the ground state and the first excited state in the "cup-like" potential.

The unnormalized wave functions for the two states have been computed numerically and are sketched in Figure 5.

### 6.2 Variation of the energy levels with the flank slope $\mu$

The change in the energies  $E_0$ ,  $E_1$  and  $\Delta E$  with the slope  $\mu$  of the flanks has been investigated, since we expect according to the model that the difference for the various chlorides may be due to a different flank slope  $\mu$ .

We vary the flank slope  $\mu$  starting from the KCl value by a factor 10 in both directions. As may be seen from Figure 6 the energy of the ground state remains practically constant in a large interval. This corresponds to the fact that the ground state is fixed by the molecule-ion alone. On the other hand the energy of the first excited state and with it the difference  $\Delta E$  vary considerably. This produces a lattice effect on the optical phenomena of the  $V_K$  center.

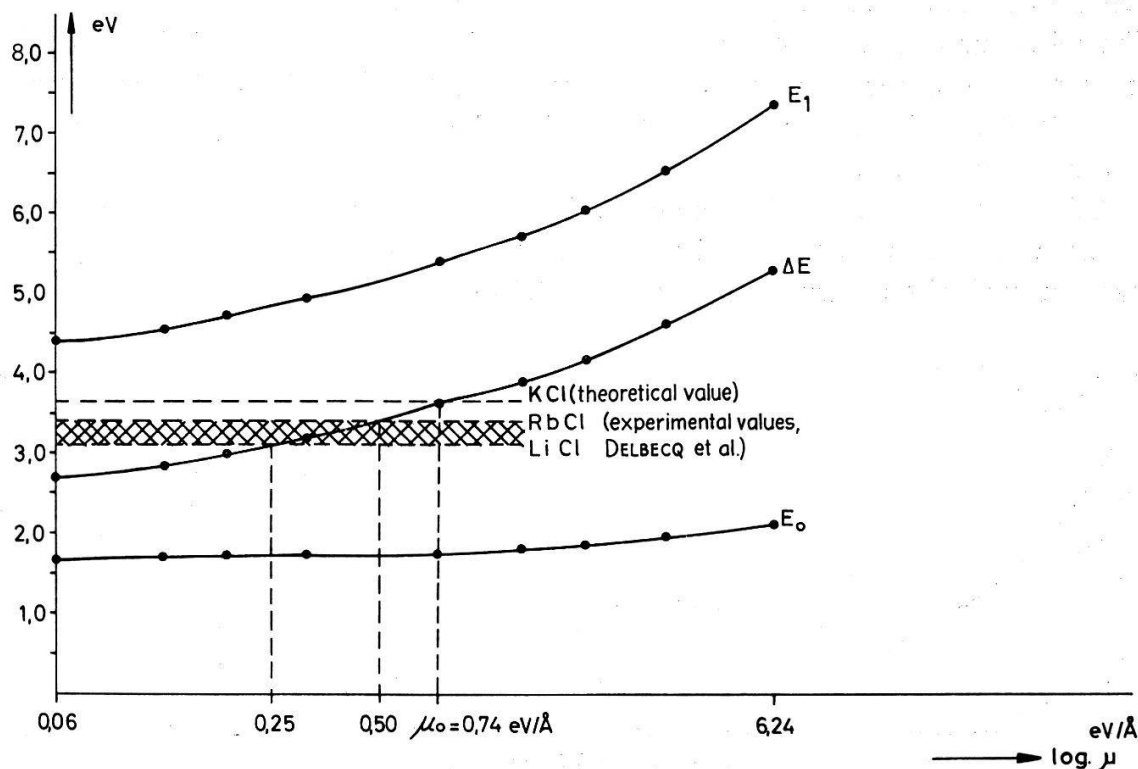


Figure 6

Variation of the energy eigenvalues  $E_0$ ,  $E_1$  of the first two states as well as of their difference  $\Delta E$  (UV absorption energy) with the flank slope  $\mu$  for the series of the alkali chlorides.

Figure 6 shows that the  $\mu$  values corresponding to the limits of the experimentally determined interval of the absorption energies for the chloride series differ by a factor of 2.

We shall now try to survey the situation for the whole chloride series.

A very simple method to determine approximately the flank slope  $\mu$  to be evaluated for the chlorides, can be derived from Figure 7. The resulting potential energy  $V_{e^- - G^{++}}$  composed of the two parts  $V_{e^- - G^0}$  and  $V_{e^- - 2Cl^-}$  is shown. The approximately linear

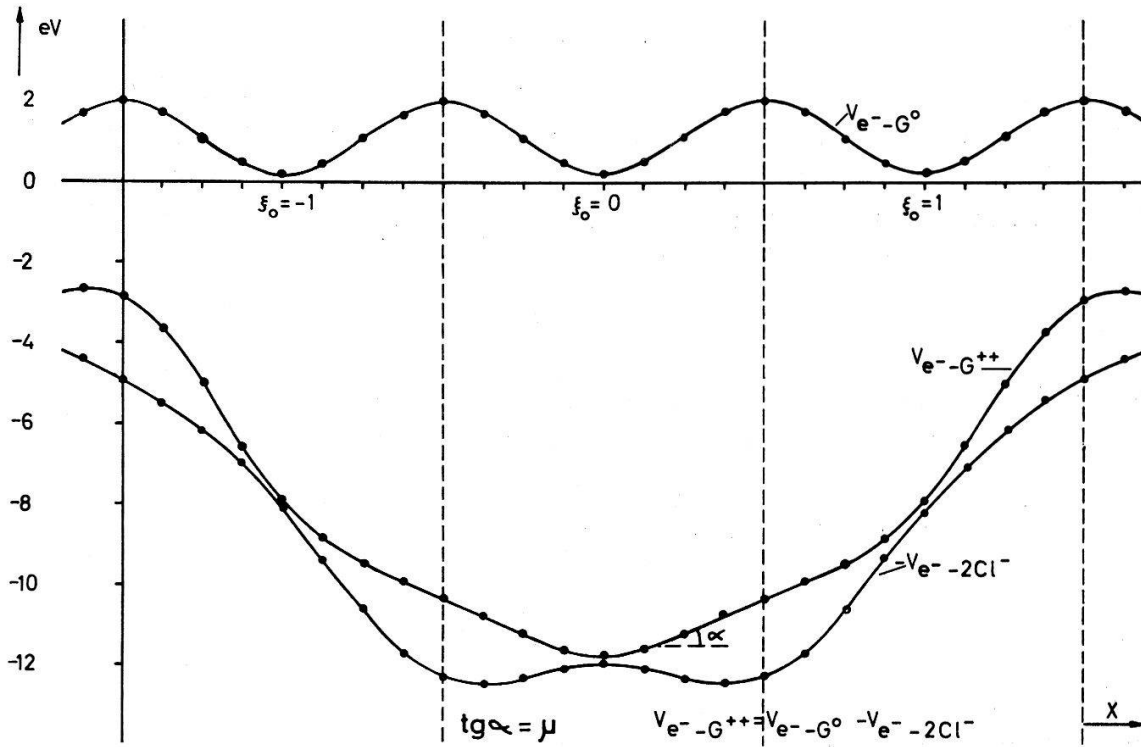


Figure 7

Generation of the potential energy of the electron in the residual-lattice ( $x$ -direction) from the two parts  $V_{e-G^0}$  and  $-V_{e-2Cl^-}$  in the case of GAUSSIAN charge distributions ("JANSEN" lattice)

shape with slope  $\mu$  is due to charge compensation. From the periodicity of the potential energy  $V_{e-G^0}$  we see that (Fig. 7) the difference

$$V_{e-G^{++}}(\xi_0 = 1) - V_{e-G^{++}}(\xi_0 = 0) \quad (6.2)$$

is independent of the contribution  $V_{e-G^0}$  and consequently equal to the difference

$$V_{e-2Cl^-}(\xi_0 = 0) - V_{e-2Cl^-}(\xi_0 = 1), \quad (6.3)$$

$\xi_0$  being a parameter along the  $x$ -axis. This leads to an upper approximation for  $\mu$

$$\mu^u = \frac{V_{e-2Cl^-}(0) - V_{e-2Cl^-}(1)}{a/\sqrt{2}}, \quad (6.4)$$

a lower approximation

$$\mu^l = \frac{V_{e-2Cl^-}(0) - V_{e-2Cl^-}(7/8)}{a/\sqrt{2}} \quad (6.5)$$

and the mean value

$$\bar{\mu} = \frac{1}{2} (\mu^u + \mu^l). \quad (6.6)$$

This gives for the "JANSEN" lattice by (4.15)

$$\bar{\mu}_\beta = 2 \frac{e^2}{a^2} \left\{ 3 \operatorname{erf} \left( \frac{\beta a}{2\sqrt{2}} \right) - \frac{1}{3} \operatorname{erf} \left( \frac{3\beta a}{2\sqrt{2}} \right) - \frac{4}{3} \operatorname{erf} \left( \frac{3\beta a}{8\sqrt{2}} \right) - \frac{4}{11} \operatorname{erf} \left( \frac{11\beta a}{8\sqrt{2}} \right) \right\}. \quad (6.7)$$

Before evaluating this expression numerically in connexion with the chloride series it is interesting to compare our results with the simple point lattice predictions.

## 6.3 Point lattice

The question arises, whether the GAUSSIAN charge distribution ( $\beta$  parameters) have to be considered as fundamental for the calculation, or if the simple point lattice would lead to a similar result.

The point lattice can be treated in analogy to the "JANSEN" lattice with a charge distribution given now by  $\delta$ -functions

$$\varrho(\mathbf{r}) = \sum_j e_j \delta(\mathbf{r}_j - \mathbf{r}), \quad (6.8)$$

corresponding to the limit  $\beta \rightarrow \infty$ ,  $\beta' \rightarrow \infty$ . The formulas corresponding to (4.14) and (4.15) with the notation of chapter 4 are for the  $x$ -direction:

$$V_{e^-G^0}(\xi_0) = \frac{4e^2}{a\pi} \sum_{\mathbf{r}_0} \frac{(-1)^{\tau_2}}{\vartheta_{\mathbf{r}_0}^2} e^{2\pi i \tau_2 \xi_0} [1 - (-1)^{\sigma \tau_0}] \quad (6.9)$$

and

$$V_{e^-2Cl}(\xi_0) = e^2 \left\{ \frac{1}{(a/\sqrt{2}) |\xi_0 - 1/2|} + \frac{1}{(a/\sqrt{2}) |\xi_0 + 1/2|} \right\}, \quad (6.10)$$

$\xi_0$  being a parameter along the  $x$ -axis.

In analogy to the case of the "JANSEN" lattice we shall use the "geometrical ratio" to determine  $\mu$ -values. Corresponding to (6.7) we get for the point lattice with (6.6) and (6.10)

$$\bar{\mu}_P = \frac{64}{33} \frac{e^2}{a^2}. \quad (6.11)$$

The numerical values are listed in Table 5 together with the energy values  $\Delta E$  taken from Figure 6. The experimental absorption energies  $\Delta E_{exp}$  are given in the last column for comparison.

Table 5

Crystal	$\bar{\mu}_\beta$ eV Å <sup>-1</sup>	$\bar{\mu}_P$ eV Å <sup>-1</sup>	$\Delta E(\bar{\mu}_\beta)$ eV	$\Delta E(\bar{\mu}_P)$ eV	$\Delta E_{exp}$ eV
LiCl	0.97	1.06	3.77	3.82	3.09
NaCl	0.85	0.88	3.70	3.72	3.25
KCl	0.72	0.71	3.62	3.60	3.38
RbCl	0.67	0.65	3.57	3.56	3.40

Comparison of  $\bar{\mu}_\beta(\text{KCl}) = 0.72 \text{ eV Å}^{-1}$  with the accurate value  $\mu_\beta(\text{KCl}) = 0.74 \text{ eV Å}^{-1}$  (Fig. 6) shows good agreement, so that the values  $\bar{\mu}_\beta$  can be considered as a good approximation.

The difference between the values  $\bar{\mu}_\beta$  and  $\bar{\mu}_P$  (column 2 and 3 of Table 5) is very small (2 till 9%); the values for the point lattice vary somewhat more from RbCl to LiCl.

From the preceding calculations we can conclude that the formula

$$\mu \approx 2e^2/a^2 \quad (6.12)$$

gives a convenient rough value of the flank slope  $\mu$  (with an accuracy of 10%).

### 6.4 Absorption energies of the chlorides

The absorption energies corresponding to different  $\mu$  values can be read off from the representation  $\Delta E(\log \mu)$  of Figure 6. They are listed in column 4 and 5 of Table 5. Comparison with the experimental absorption energies (column 6) shows order of magnitude agreement of our theoretical results (mean deviation 12%). The variation in energy from LiCl to RbCl, however, is opposite, as may be seen by comparing columns 4 and 5 with column 6 of Table 5. A discussion of this result will be given in the last chapter.

### 6.5 Comparison between the "JANSEN" lattice and the point lattice

Considering the small difference between the values  $\bar{\mu}_\beta$  and  $\bar{\mu}_P$  and therewith between  $\Delta E(\bar{\mu}_\beta)$  and  $\Delta E(\bar{\mu}_P)$  (Table 5) the "JANSEN" model and the point-charge model seem to be almost equivalent in the central zone ( $|\xi_0| < 1$ ) (Fig. 7). In this zone the shape of the potential energy  $V_{e-G^{++}}$  is probably nearly independent of the chosen static model.

The estimations for the point lattice are not accurate because of the very slow convergence of the triple lattice sum. We shall, however, not insist further on the central zone, since an essential difference can be observed for the outer zone ( $|\xi_0| > 1$ ).

In the case of the "JANSEN" lattice (Fig. 7) the "linear continuation" for the potential energy ("cup"-model Fig. 5) beyond the zone  $|\xi_0| < 1$  is justified, since the difference with the real shape of  $V_{e-G^{++}}$  is not important for the energy levels of the ground and first excited state. The situation is quite different in the case of the point lattice. Here the increase of the potential energy is much stronger for  $|\xi_0| > 1$  and tends to infinity for  $|\xi_0| = 3/2$ . At this point the wave functions of all stationary states have already decayed to zero. Consequently the energy levels are shifted upwards considerably. This leads of course to higher absorption energies in disagreement with experiment.

## 7. Discussion of Results and Concluding Remarks

The main result of the investigation of the lattice-molecule-model developed in chapters 4, 5 and 6 is to show the influence of the lattice on the ultraviolet absorption of the  $V_K$  center. This can be considered as an extension of the well-known molecule-ion model which allows to describe the ground state alone. Our calculations support the fact that the state excited by ultraviolet absorption is not so strongly localized at the position of the molecule-ion as the ground state. They describe in an approximate way the influence of the surrounding crystal lattice, as experimentally shown by the results of MURRAY (1965) on the iodides and by the recent measurements of DELBECQ, GILBERT, HAYES and YUSTER on the chloride series.

Another result which must be pointed out is the order of magnitude agreement found in sections 6.1 and 6.4 and Table 5 between the theoretical ultraviolet absorption energies for the chloride series based on the "JANSEN" lattice and the corresponding experimental values.

The parameters  $\beta$  suggested by the empirical correlation (chapter 2) and describing the ionic charge distributions have not only turned out to be useful for the conver-



gence of the lattice sum<sup>5)</sup>, but they seem to be of fundamental importance, since the computation with point charges does not lead to satisfactory results as shown at the end of section 6.5.

The lattice-molecule-model leads to a complicated three-dimensional problem which cannot be solved by simple methods. In accord with this approximate model used we have simplified the calculations by treating the one-dimensional problem. This can be justified by the anisotropy of the absorption of the  $V_K$  center in the  $x$ ,  $y$  and  $z$  directions.

In order to draw the limits of the present model it may be of interest to evaluate the absorption energies corresponding to the  $y$  and  $z$  directions, where experimentally  $\pi$ -polarized transitions in the infrared with energies of about 1.65 eV are found (DELBECQ, HAYES and YUSTER, 1961). A rough estimate yields for the  $y$ -direction an absorption energy of about 2 eV and for the  $z$ -direction a value greater than 4 eV as may be seen from Figure 2 assuming a box width of about  $\frac{1}{2} R_e(\text{Cl}_2^-)$ . While for the  $y$ -direction the present model seems to give the right order of magnitude, the ultra-violet absorption resulting for the  $z$ -direction does not correspond to any known experimental observation. This clearly stresses the simplified nature of the present model and its limitations in describing as complicated a system as the  $V_K$  center.

A further weakness of the present calculations appears in studying the variation within the chloride series. As a consequence of our static lattice model it follows that the computed absorption energy  $\Delta E$  increases with decreasing lattice constant, since this leads to a steeper potential shape (columns 4 and 5 of Table 5). This typical behaviour corresponds to a generally observable tendency for many optical absorption phenomena in alkali halide crystals (e.g. for  $F$  centers and other color centers, SCHULMAN and COMPTON, 1962, chapter 3). The inverse tendency of the experimental ultraviolet absorption energies of the  $V_K$  center for the series of chlorides and iodides appears to be an anomaly from the point of view of the "pure" static lattice. This anomaly cannot be explained by the present calculations. A more realistic investigation should take into account the interaction between the molecule and the lattice which has not been considered so far. This should include relaxation effects leading to lattice deformation in the immediate neighbourhood of the defect and polarization effects of the molecule-ion in the crystal field. Such effects could suggest a criterion for the coupling of the molecular part of the potential energy to the lattice, which is rather artificial for the moment.

The variation of the absorption energy for the different molecule-ions for fixed cation can be reproduced correctly by our model by choosing for the width of the potential well the equilibrium distance  $R_e(X_2^-)$ . The explanation of the variation for the fixed anion, i.e. for the same molecule-ion in different alkali halide crystals is left to future investigation.

A more accurate calculation would probably lead to a more complex relation involving the parameters  $\beta$  and  $\beta'$ .

We must notice that the parameter  $\beta'$  characteristic of the positive ions does not play any role in the correlation of chapter 2. It occurs, however, together with the parameter  $\beta$  in the proposed formalism (chapter 4).  $\beta'$  contributes to the potential

<sup>5)</sup> The convergence of the triple sum over the indices  $\tau_1, \tau_2, \tau_3$  is such for the values  $\beta R$  and  $\beta' R$  of KCl, that the sum could be limited to the first 26 terms.

energy of the ideal crystal (periodic part). But the term  $V_{e-2Cl-}$  and the "ratio" used to determine approximately the slope  $\mu$  are independent of  $\beta'$ . We can thus think of the influence of  $\beta'$  to be small. This is confirmed by the following accurate computation (Table 6).

Table 6

	$\beta'$ $10^8 \text{ cm}^{-1}$	$\mu$ $\text{eV } \text{\AA}^{-1}$	$\Delta E$ $\text{eV}$
Li <sup>+</sup>	2.60		
K <sup>+</sup>	2.12	0.678	3.59
in	1.04	0.680	3.59
KCl	0.718 <sup>6)</sup>	0.727	3.62
	0.625	0.773	3.65
Rb <sup>+</sup>	0.600		

<sup>6)</sup> Value for K<sup>+</sup> computed by LOMBARDI and JANSEN (1964).

$\beta'$  has been varied for the case of KCl between reasonable wide limits. The variation of the corresponding absorption energy, however, is only of the order of 1%. (The specific values of  $\beta'$  for K<sup>+</sup> are chosen for convenience in numerical computation only).

We shall conclude our remarks in giving the numerical accuracy of the calculations carried out in the present work:

1. The accuracy of computation will lie within 5–10%.
2. Concerning the parameters  $\beta$ , JANSEN pointed out in his papers only to be interested in the stability behaviour in function of  $\beta$  and not in the precise  $\beta$  values.
3. The molecular data  $D_e(X_2^0)$ ,  $R_e(X_2^0)$  as well as the electronic affinity  $EA(X)$  are known with good accuracy.
4. Concerning the molecule-ion GILBERT (private communication) believes that the internuclear distance  $R_e(Cl_2^-)$  is accurate to within a few percent, but he would not trust the binding energy  $D_e(Cl_2^-)$  to better than about twenty or thirty percent.

For the rest the known inaccuracies are listed in Table 3.

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