Non Radiative Electronic Transitions in Ionic Crystals I*

Crystal model and calculation of states

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The theory of non radiative electronic transitions is represented in two papers. In the first of these we calculate wavefunctions, energies, matrix-elements etc. In the second we discuss the general reaction mechanism and apply the theory to two examples. The wavefunction of a crystal volume containing one defect is calculated on the base of a microscopic theory. For our numerical discussion we used as an example an anion vacancy in MgO, LiF, NaCl, NaBr, KCl, KBr, KJ. The results are collected in Table 1 and 2. As far as experimental data have been available they agree completely with our results.

Introduction

We have the intention to calculate transition probabilities for conduction electrons of an ionic crystal for falling back to the valence-band without emitting radiation. These quenching processes do disturb many reactions of the crystal as e.g. conduction of current, phosphorescence, luminescence. To have a measure for their magnitude one defines the quantum efficiency or quantum yield as the ratio of emitted to absorbed photons. But comparing numerical results for transition probabilities, calculated for some special quenching center, we have to regard that radiationless decay is only one of many possible radiationless electronic reactions (e.g. conversion of F to F′ centers). Stumpf[1] first established a reasonable model on a microscopic theory of the crystal to describe the decay process (double Franck-Condon process). In the meantime we have been able, firstly to calculate the wave functions of the crystal with very high accuracy[2], secondly to give a new more strict description of the reaction mechanism[3]. On the base of this progress we have been able to derive conditions when radiationless transitions should be possible.

The calculations are outlined within two papers. In the first of these, we derive all things necessary to describe the reaction mechanism: appropriate wave functions for the crystal, energy eigenvalues, normal coordinates, matrix elements. In the second we describe the formalism to evaluate transition probabilities. Though there remain some uncertainties with regard to the quantities calculated, we have been able to describe the reaction process for a radiationless transition. Applying the general formulae to the example of an anion vacancy as trapping center, we get significant results depending on the host crystal: In MgO the probability for a radiationless electronic transition is much greater than for an optical transition. On the other hand in KCl the anion vacancy does not quench optical transitions as it is well known by experimentalists. To get results quantitatively comparable with phenomenological equations of experimentalists, we propose to treat the ensemble of independent impurity processes by means of the theory of Markov's chains.

Reduction of the Many Particle Problem

A crystal as used for experiments does contain a great number of different defects. But even if the defect concentration is very large (10^{-3} defects per regular lattice point) we can, in a first approximation, consider the processes at different defects being independent. The total crystal then can be treated as a statistical ensemble of independent small blocks ("microblocks") each containing one defect. The quantum mechanical calculation then can be confined to that of a microblock's wave function. Neglecting spin and other relativistic effects the hamiltonian K^* of one microblock is (within this paper atomic units are used $\hbar = m = e = 1$)[4]:

$$K^* = T_g + T_e + V^* \qquad (1.1)$$

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[1] H. Stumpf, Quantentheorie der Ionenrealkristalle, Springer-Verlag, Berlin 1961.

[2] A. Löffler, Z. Naturforsch. **22 a**, 1771 [1967].

[3] H. Rampacher, Z. Naturforsch. **23 a**, 401 [1968].

where

$$T_{\mathrm{e}} = -\frac{1}{2} \sum_{i_\alpha} \Delta_{i_\alpha} = -\frac{1}{2} \sum_{i_\alpha} \frac{\partial^2}{\partial r^2_{i_\alpha}} \tag{1.2}$$

means the kinetic energy of the electrons and

$$T_{\mathrm{g}} = -\frac{1}{2} \sum_i \frac{1}{M_i} \Delta_i = -\frac{1}{2} \sum_i \frac{\partial^2}{M_i \, \partial R_i^2} \tag{1.3}$$

the kinetic energy of the nuclei of the lattice.

The Coulomb interaction energy is:

$$V^*(r, R) = \frac{1}{2} \sum_{\substack{i_\alpha, j_\beta \\ i_\alpha \neq j_\beta}} \frac{1}{|r_{i_\alpha} - r_{j_\beta}|} + \frac{1}{2} \sum_{\substack{i,j \\ i \neq j}} \frac{e_i e_j}{|R_i - R_j|} - \sum_{i, j_\alpha} \frac{e_i}{|R_i - r_{j_\alpha}|} . \tag{1.4}$$

In the adiabatic approximation[5,6] the many particle problem is divided into one part for the electrons and another for the nuclei. This approximation corresponds to the following trial solution for the wave function:

$$\hat{\varphi}^n_m(r, R) = \psi^n(r, R) \, \varphi^n_m(R) . \tag{1.5}$$

where ψ^n is an eigenfunction of the hamiltonian K_{e}:

$$\begin{aligned} K_{\mathrm{e}} \psi^n(r, R) &= [T_{\mathrm{e}} + V^*(r, R)] \, \psi^n(r, R) \\ &= U_n(R) \, \psi^n(r, R) . \end{aligned} \tag{1.6}$$

The eigenvalues $U_n(R)$ depending on R as parameters define the potential energy of the hamiltonian K^n_{g}, which describes the lattice motion:

$$K^n_{\mathrm{g}} \varphi^n_m(R) = [T_{\mathrm{g}} + U_n(R)] \, \varphi^n_m(R) = E^n_m \, \varphi^n_m(R) . \tag{1.7}$$

Electronic Wave Function

We first treat the electronic Eq. (1.6) by means of a Hartree-Fock product wave function

$$\psi^n(r) \sim \sum_{\lambda_1, \dots, \lambda_N} (-1)^p \, \psi^n_1(r_{\lambda_1}) \cdots \psi^n_N(r_{\lambda_N}) \tag{1.8}$$

[the sum is extended over all permutations of the N electrons, and the one electron functions are assumed to be orthonormalized:

$$(\psi^n_{i_\alpha}(r_k), \psi^n_{j_\beta}(r_k)) = \delta_{i_\alpha, j_\beta}] . \tag{1.9}$$

With help of (1.8) we get from (1.6) the energy expectation value as a functional of the one electron wave functions and the parameters R. We now assume, that except for few electrons, located in the surrounding of the defect, the $\psi^n_{i_\alpha}$ could be represented by a linear combination of the free ion's ground state wave functions $\tilde{\psi}^0_{i_\alpha}$ and the first excited states[2,8,9] $\tilde{\psi}^\nu_{i_\alpha}$:

$$\psi^n_{i_\alpha} \sim \tilde{\psi}^0_{i_\alpha} + \sum_\nu f^\nu_{i_\alpha} \tilde{\psi}^\nu_{i_\alpha} . \tag{1.10}$$

The $f^\nu_{i_\alpha}$ can be related to the polarization of the ions[2]. We then get $U_n(R)$ as a function of the polarization dipoles m_k. As an example we consider a F-center, where it seems sufficiently accurate to calculate only the trapped electron's wave function $\psi^n_1(r_1)$ explicitly:

$$\begin{aligned} U_n(\psi^n_1, m_k, R) = {} & \left(\psi^n_1 \left[-\frac{1}{2} \Delta_1 - \sum_{k>1} \left(\frac{a_{\mathrm{k}}}{|r_1 - R_k|} + \frac{m_{\mathrm{k}}(r_1 - R_k)}{|r_1 - R_k|^3}\right)\right] \psi^n_1\right) \\ & + \frac{1}{2} \sum_{\substack{i \\ i \neq 1}} \frac{m_i^2}{\alpha_i} + \frac{1}{2} \sum_{\substack{i,k \\ i \neq k \\ i,k \neq 1}}{}' m_i \nabla_{R_i} \frac{m_{\mathrm{k}}(R_k - R_i)}{|R_k - R_i|^3} + \sum_{\substack{i,k \\ i \neq k \\ i,k \neq 1}}{}' a_k \frac{m_i(R_k - R_i)}{|R_k - R_i|^3} + \frac{1}{2} \sum_{\substack{i,k \\ i,k \neq 1}}{}' \frac{a_i a_k}{|R_i - R_k|} + \frac{1}{2} \sum_{\substack{i,k \\ i,k \neq 1}}{}' \frac{b}{|R_i - R_k|^1} \end{aligned} \tag{1.11}$$

(α_i is the polarizability of the ion i, α_i the charge of the ion at R_i; for all details we refer to)[2].

According to the principles of quantum mechanics the eigenfunctions $\psi^n_{i_\alpha}$ should make U_n a minimum. This gives the conditions:

(A)
$$\frac{\delta}{\delta \psi^n_1} \left(\psi^n_1, \left[-\frac{1}{2} \Delta_1 - \sum_{k>1} \left(\frac{a_{\mathrm{k}}}{|r_1 - R_k|} + \frac{m_k(r_1 - R_k)}{|r_1 - R_k|^3}\right)\right] \psi^n_1\right) \overset{!}{=} 0 , \tag{1.12}$$

(B)
$$m_i + \alpha_i \nabla_{R_i} [\Phi^n_{\mathrm{s}} + \Phi_m] \overset{!}{=} 0 . \tag{1.13}$$

In (1.13) we use a decomposition of the static Coulomb potential $\Phi^n(R_j)$ of the microblock, where

$$\Phi_m(R_j) := \sum_{k>1} \frac{m_k(R_j - R_k)}{|R_j - R_k|^3} \tag{1.14}$$

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[4] The following notation is used: R the totality of all nuclei coordinates R_i; r the totality of all electronic coordinates r_{j_α}, where r_{j_α} denotes the α-th electron at the j-th nucleus. M_i is the mass and e_i the charge of the nucleus i.

[5] M. Born u. K. Huang, Dynamical Theory of Crystal Lattices, Oxford Univ. Press, London 1954.

[6] H. Rampacher, Dissertation, München 1967.

[7] F. Wahl, Z. Naturforsch. **19 a**, 620 [1964].

[8] F. Wahl, Ann. Phys. Leipzig **11**, 151 [1963].

[9] H. Rampacher, Z. Naturforsch. **17 a**, 1057 [1962].

is the potential built up by the polarization dipoles m_k.

$\Phi_0(R_j)$ is the Coulomb potential of the regular lattice:

$$\Phi_0(R_j) := \sum_{k \geqq 1} \frac{a_k}{|R_j - R_k^0|} \qquad (1.15)$$

(1.15) is used to define the potential of the disturbance $\Phi_s^n(R_j)$, depending on the trapped electron's state ψ_1^n:

$$\Phi^n(R_j) = \Phi_0(R_j) + \Phi_s^n(R_j) + \Phi_m(R_j). \qquad (1.16)$$

The conditions (A) and (B) are to be fulfilled for every choice of the coordinates R_j. This could be done using our knowledge about the ionic crystal:

At absolute zero temperature the ions are approximately located at the equilibrium positions R_k^n which minimize the potential energy $U_n(R)$

$$\text{(C)} \qquad \nabla|_{R_k = R_k^n} U_n(R_k) = 0. \qquad (1.17)$$

For temperatures not too high, the ions then oscillate about these equilibrium positions. We therefore expand (A) and (B) about these R_k^n into a Taylor series fulfilling them step by step. We denote by $\alpha = (\alpha_+ + \alpha_-)/2$ the average polarizability of the ions, by d their nearest neighbour

	MgO	LiF	NaCl	NaBr
d [Å]	2.10	2.01	2.81	2.98
$\beta_0^{1s} \cdot d$	1.5	1.46	1.70	1.71
$\beta_0^{2p} \cdot d$		1.96	2.29	2.33
$[U_{2p}(R^{2p}) - U_{1s}(R_1{}^s)]_{ber.}$ [eV]		2.23 ?	1.77	1.68
$[U_{2p}(R^{2p}) - U_{1s}(R^s)]_{exp.}$ [eV]	[5.0]	[5.10]	1.92	
(1, 0, 0)		+ 3.1, 0.0, 0.0.	− 0.8, 0.0, 0.0	− 0.8, 0.0, 0.0
(1, 1, 0)		− 0.4, − 0.4, 0.0	− 0.4, − 0.4, 0.0	− 0.4, − 0.4, 0.0
(1, 1, 1)		− 0.3, − 0.3, − 0.3	− 0.0, − 0.0, − 0.0	− 0.1, − 0.1, − 0.1
(2, 0, 0)		− 0.7, 0.0, 0.0	− 1.1, 0.0, 0.0	− 1.3, 0.0, 0.0
(2, 1, 0)		− 0.8, − 0.9, 0.0	− 0.9, − 0.3, 0.0	− 1.0, − 0.4, 0.0
(2, 1, 1)		− 1.5, − 1.2, − 1.2	− 0.7, − 0.2, − 0.2	− 0.8, − 0.3, − 0.3

	KCl	KBr	KJ
d [Å]	3.14	3.29	3.53
$\beta_0^{1s} \cdot d$	1.80	1.81	1.82
$\beta_0^{2p} \cdot d$	2.41	2.43	2.47
$[U_{2p}(R^{2p}) - U_{1s}(R_1{}^s)]_{ber.}$ [eV]	1.61	1.47	1.30
$[U_{2p}(R^{2p}) - U_{1s}(R^s)]_{exp.}$ [eV]	1.78	1.51	1.35
(1, 0, 0)	− 2.0, 0.0, 0.0	− 2.1, 0.0, 0.0	− 2.2, 0.0, 0.0
(1, 1, 0)	− 0.4, − 0.4, 0.0	− 0.3, − 0.3, 0.0	− 0.3, − 0.3, 0.0
(1, 1, 1)	+ 0.0, + 0.0, + 0.0	+ 0.0, + 0.0, + 0.0	− 0.1, − 0.1, − 0.1
(2, 0, 0)	− 0.9, 0.0, 0.0	− 1.0, 0.0, 0.0	− 1.3, 0.0, 0.0
(2, 1, 0)	− 0.5, + 0.1, 0.0	− 0.5, + 0.1, 0.0	− 0.7, + 0.1, 0.0
(2, 1, 1)	− 0.4, − 0.1, − 0.1	− 0.4, − 0.1, − 0.1	− 0.6, − 0.1, − 0.1

Table 1. Parameters and results of the static calculations (at 0 °K). d next neighbour distance of the ions. $\beta_0^n = \beta^n(R^n)$ variational parameter for the one electron functions. For trapped electrons $\beta^n \cdot d$ is approximately constant[2]. β^{1s} and β^{2p} have been calculated by SCHMIDHAMMER[17] regarding displacements of the ions up to neighbours of order 10. The relation between the energies $U_n(R_k^n)$ calculated by SCHMIDHAMMER and experimental zero phonon absorption and emission energies E_{abs}, E_{em} are given by $U_{2p}(R_k^{2p}) - U_{1s}(R_k^{1s}) = E_{em} + \frac{1}{2}(E_{abs} - E_{em})$. Experimental values after MARKHAM[18]. For MgO and LiF no emission bands are known[19]. The absorption energy of an F-center in MgO is assumed to be 5.0 eV. This band seems to result from superposition of several bands[20]. The energies in [ ] are absorption energies. The spherical symmetric displacements for the ground state have been calculated by SCHMIDHAMMER up to neighbours of order 10; they are given in percent of d.

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[17] E. SCHMIDHAMMER, Diplomarbeit, Universität München, in Vorbereitung.

[18] J. J. MARKHAM, Solid State Physics, Sup. 8, Academic Press, New York 1966.

[19] B. HENDERSON et al., Preprint A. E. R. E. Harwell, Didcot, Berks 1967.

[20] Y. CHEN et al., Preprint, Solid State Division, Oak Rigde National Laboratory, Tennessee 1967.

distance, and define as a measure of average polarizability

$$\gamma = -4\pi\,\alpha/d^3 \tag{1.18}$$

then a solution of condition (B) is given by [2, 9]

$$\Phi_m(R_j) = \frac{\gamma}{1-\gamma}\,\Phi_{\mathrm{s}}^n(R_j) \tag{1.19}$$

or

$$m_i = \frac{\alpha_i}{1-\gamma}\,\nabla|_{R_i}\,\Phi_{\mathrm{s}}^n(R_j)\,. \tag{1.20}$$

Inserting this into (A) and (C) we realize that the polarization of the lattice ions can follow immediately the motion of the nuclei and the trapped electron's changes of state. By means of a Green's function[1, 10] condition (C) can be treated. It can be solved simultaneously with condition (A), which becomes an algebraic one, if we use Ritz‘s variational method. This principle to be applied, one has to specify a class of test functions.

For a radiationless recombination of a conduction-band-electron at an anion vacancy the following states will prove to be important:

1. the conduction band state: characterized by a vacancy which is free from electrons; a conducting microblock (but without a current); the lattice in the thermal equilibrium,
2. the F-center state: an electron trapped at the vacancy; zero resistivity of the microblock, no current; arbitrary excitation of the lattice oscillations,
3. the valence band state: no electrons trapped at the vacancy; zero conductivity of the microblock; and arbitrary excitations of lattice oscillations.

For these states we assume the following one-electron functions as trial solutions:

1. for the conduction band state: a Bloch-function at the lower band edge

$$\psi_1^{\mathrm{c}}(r_1) \sim u_c(r_1)\,e^{ikr_1}\,, \quad k \cong 0\,, \tag{1.21}$$

2. for the trapped state: for spherical symmetric defects, with positive defect charge in approximately isotropic crystals, hydrogen wave functions. Especially with the ground state

$$\psi_1^{\mathrm{s}}(r_1) \sim \beta^{3/2}\,e^{-\beta r_1}\,, \tag{1.22}$$

3. for the valence band state: a Bloch function

$$\psi_1^{\mathrm{v}}(r_1) \sim u_v(r_1)\,e^{ikr_1}\,. \tag{1.23}$$

For practical calculations we take $u_c(r_1)$ and $u_v(r_1)$ to be constants properly orthonormalized (because we can exclude by energetical reasons direct radiationless electronic transitions from the conduction band to the valence band, it is no great error not to regard the orthogonality of (1.19) and (1.20)). The numerical results for the static wavefunction ψ_1^{s} are given in Table 1. The two functions orthogonal to ψ_1^{s} are then

$$\psi_1^{\mathrm{c}} = \psi_1^{\mathrm{v}} = \mathrm{const}\cdot\Big\{\Omega^{-1/2}\,\Theta\Big(\frac{a}{2}-|x_1|\Big)\,\Theta\Big(\frac{a}{2}-|y_1|\Big)\,\Theta\Big(\frac{a}{2}-|z_1|\Big) - S\,\psi_1^{\mathrm{s}}(r_1)\Big\}\,, \tag{1.24}$$

[10a]

$$r_1^2 = x_1^2 + y_1^2 + z_1^2\,,$$

where $\Omega = a^3$ is the volume of the microblock and S the overlap integral

$$S = \Omega^{-1/2}\int_\Omega \psi_1^{\mathrm{s}}(r_1)\,d^3r_1 \approx \frac{8\cdot\pi^{1/2}}{(\Omega\,\beta^3)^{1/2}}\,. \tag{1.25}$$

The normalization constant is approximately 1 for localized states:

$$\mathrm{const} = (1 - S^2) \approx 1\,. \tag{1.26}$$

Now, before treating the dynamical dependence of the trapped electron on lattice oscillations, we investigate the lattice vibrations, described by the hamiltonian (1.7).

Lattice Dynamics [11]

Using the adiabatic approximation, we geot for the hamiltonian of the lattice motion

$$K_{\mathrm{g}}^n = T_{\mathrm{g}} + U_n(R)\,. \tag{2.1}$$

For temperatures not too high, we describe the lattice in the harmonic approximation, i.e. we expand $U_n(R)$ into a Taylor series and neglect the anharmonic terms of third and higher order, which are considered to be a perturbation

$$U_n(R) = U_n(R^n) + \frac{1}{2}\sum_{i,j}(R_i - R_i^n)\,\frac{\partial^2 U_n}{\partial R_i\,\partial R_j}\,(R_j - R_j^n) + \cdots. \tag{2.2}$$

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[10] L. Kern-Bausch, Z. Naturforsch. **21 a**, 798 [1966].

[10a] Where $\Theta(x) = \begin{cases} 0 & \text{for } x < 0\,. \\ 1 & \text{for } x \geqslant 0\,, \end{cases}$

[11] e.g. G. Leibfried, Hdb. d. Physik VII/1, Springer-Verlag, Berlin 1955. — W. Ludwig, Ergebn. Exakt. Naturwiss., Springer-Verlag, Berlin 1964, Bd. 35. — W. Ludwig, Springer Tracts in Modern Physics, Bd. 43, Springer-Verlag, Berlin 1967.

The potential $U_n(R)$ and therefore the expansion coefficients

$$G^n_{ij} := \frac{\partial^2 U_n}{\partial R_i \, \partial R_j} \tag{2.3}$$

depend on the special defect model and the state of the trapped electron.

For weak perturbations one can replace the coupling matrix G^n by that of the regular lattice G^0.

Though in principle one knows how to treat the eigenvalue problem of G^n exactly[3, 11], this has not been done until now with sufficient accuracy and completeness. Until those calculations will be extended, we use the following approximation:

$$G^n \approx G^0 . \tag{2.4}$$

The eigenvalue problem of G^0 can be solved easily because of the translational symmetry of the lattice. For non primitive lattices with L different particles per elementary cell, we get for every possible polarization vector k, $3L$ eigenfrequencies and eigenvectors. Such a spectrum is given in Fig. 1a. We simplify this spectrum somewhat more as shown in Fig. 1b. This approximation was used by MÄRTL[12], whose results upon the anharmonic interactions will be used.

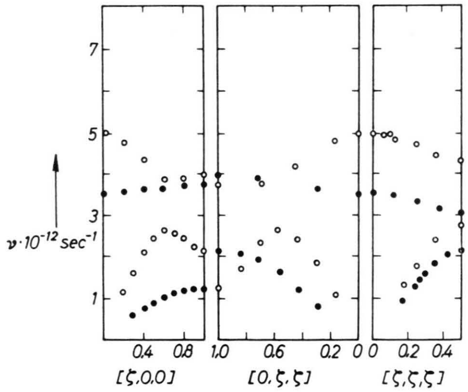

Fig. 1a. Experimental dispersion curves for optical and acoustical branches of the phonon spectrum of potassium bromide at 90 °K, after WOODS et al.[22].

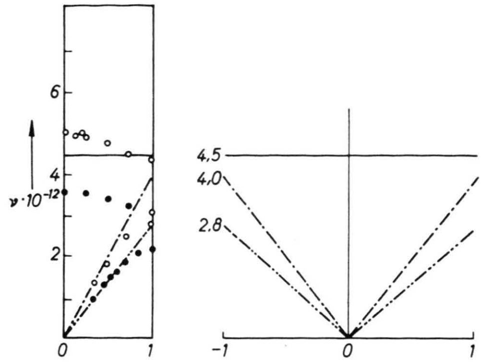

Fig. 1b. Approximation of 1a as used by MÄRTL[12]

An arbitrary deviation from the equilibrium positions R^n can be expanded with respect to the orthonormalized system $\xi^{\nu t}$ of eigenvectors of G^0

$$R - R^n = \sum_{\substack{t=1\\ \nu=a,o}}^{3M/2} \xi^{\nu t} Q^n_{\nu t} , \tag{2.5}$$

where we distinguish between the eigenvectors of the optical part of the spectrum and the acoustical eigenvectors by an additional index $\nu = a$, o. With respect to this coordinate frame we get, up to an unimportant constant, a sum of uncoupled harmonic oscillator hamiltonians:

$$\overset{\circ}{K}{}^n_{\mathrm{g}} = U_n(R^n) + \sum_{t,\nu}\left(-\frac{1}{2M_\nu}\,\frac{\partial^2}{\partial Q^{n2}_{\nu t}} + \frac{1}{2}\,\bar{M}_\nu\,\omega^2_\nu (Q^n_{\nu t})^2\right), \tag{2.6}$$

where $\bar{M}_{\mathrm{a}} = M_+ + M_-$ and $\bar{M}_{\mathrm{o}} = M_+ \cdot M_- / \bar{M}_{\mathrm{a}}$.

The eigenfunctions of $\overset{\circ}{K}{}^n_{\mathrm{g}}$ are given by

$$\varphi^n_m(Q^n) = \prod_{\substack{t=1\\ \nu=a,o}}^{3M/2} \varphi^n_{m_{\nu t}}(Q^n_{\nu t}) \tag{2.7}$$

and the energy eigenvalues by

$$E^n_m = U_n(R^n) + \sum_{\substack{t=1\\ \nu=a,o}}^{3M/2} \omega_{\nu t}(m_{\nu t} + \tfrac{1}{2}) . \tag{2.8}$$

We are specially interested in ionic crystals with NaCl-structure. For these lattices, every point is an inversion center of the total lattice. Regarding the limit of long waves, one knows[13], that the motion of the cell's center of mass is not coupled at the relative motion of the ions with opposite charge. Hence in the long wave limit the relative motion corresponds to the optical branch and the center of mass motion to the acoustical branch.

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[12] H. G. MÄRTL, Diplomarbeit, Universität München 1967 (to be published). This is no serious restriction; our calculations would give identical results, if we would assume only the longitudinal optical branch in the long wave limit to be degenerated.

[13] G. LEIBFRIED, in Encyclopedia of Physics, Springer-Verlag, Berlin 1955, pp. 193.

Dynamical Electron Lattice Coupling

The electronic energy expectation value $U_n(R)$ consists of one part $u_n(R)$ corresponding to the electron-lattice interaction energy (including the kinetic energy of the electron) and a rest $V(R)$ depending solely on lattice coordinates

$$U_n(R) = u_n(R) + V(R), \tag{2.9}$$

$$u_n(R) = \left(\psi_1^n, \left[-\frac{1}{2}\Delta_1 - \sum_{k>1}\left(\frac{a_k}{|r_1 - R_k^0|} + \frac{1}{1-\gamma}\left(\frac{a_k}{|r_1 - R_k|} - \frac{a_k}{|r_1 - R_k^0|}\right)\right)\right]\psi_1^n\right). \tag{2.10}$$

Expanding $u_n(R)$ into a Taylor series about the equilibrium positions $R_{j_u}^n$, the linear term causes dynamical electron lattice coupling in lowest order

$$u_n(R) = u_n(R^n) + \sum_{j=1}^{M} \frac{\partial u_n}{\partial R_j}(R_j - R_j^n) + \cdots. \tag{2.11}$$

The coordinate frame best adapted to describe the coupling of states at the lattice vibrations is defined by the eigenvectors ${}^n\xi^{\nu t}$ of the dynamical matrix. With (2.5) we get from (2.11)

$$u_n(R) = u_n(R^n) + \sum_{t,\nu} C_{\nu t}^n \cdot Q_{\nu t}^n + \cdots \tag{2.12}$$

with

$$C_{\nu t}^n = \sum_j \frac{\partial u_n}{\partial R_j}\, {}^n\xi_j^{\nu t}, \quad \nu = a, \mathrm{o}. \tag{2.13}$$

Since we don't know the eigenvectors exactly we have to look for another way to calculate the projections (2.13). To this aim we remember the special features of the vibrational spectrum of crystals having NaCl-structure[5, 13].

Since for such lattices, regarding the limit of long waves, the relative motion of the ions corresponds to the optical modes and the motion of the center of mass to the acoustical modes, we transform (2.11) to relative and center of mass coordinates

$$X_{\mathrm{o}j} = (R_{2j} - R_{2j}^n) - (R_{2j+1} - R_{2j+1}^n), \tag{2.14}$$

$$X_{\mathrm{a}j} = \frac{M_-}{M_\mathrm{a}}(R_{2j} - R_{2j}^n) + \frac{M_+}{M_\mathrm{a}}(R_{2j+1} - R_{2j+1}^n) \tag{2.15}$$

and (2.12) becomes

$$u_n(R) = u_n(R^n) + \sum_k X_{\mathrm{o}k}\left(\frac{M_+}{M_\mathrm{a}}\frac{\partial u_n}{\partial R_{2\mathrm{k}}} - \frac{M_-}{M_\mathrm{a}}\frac{\partial u_n}{\partial R_{2k+1}}\right) + \sum_k X_{\mathrm{a}k}\left(\frac{\partial u_n}{\partial R_{2k}} + \frac{\partial u_n}{\partial R_{2k+1}}\right). \tag{2.16}$$

The interaction energy of the center of mass motion with the electron can be neglected compared with the strong electron — dipole interaction with the relative motion. Further regarding

$$\left(\frac{M_+}{M_\mathrm{a}}\frac{\partial u_n}{\partial R_{2j}} - \frac{M_-}{M_\mathrm{a}}\frac{\partial u_n}{\partial R_{2j+1}}\right) = -\frac{1}{1-\gamma}\int \psi_1^{n*}(r_1)\left[\frac{M_+}{M_\mathrm{a}}\frac{(r_1 - R_{2j})}{|r_1 - R_{2j}|^3} + \frac{M_-}{M_\mathrm{a}}\frac{(r_1 - R_{2j+1})}{|r_1 - R_{2j+1}|^3}\right]\psi_1^n(r_1)\,\mathrm{d}^3 r_1 \tag{2.17}$$

one observes that this expression for deep electronic states (where the wave function ψ_1^n has only a few zeros) varies only slightly for adjacent cells. Therefore in (2.12) only those $C_{\nu t}^n$ will be essentially different from zero, which correspond to optical modes in the long wave limit. Regarding this limit we use the arguments given by PEKAR[14] to neglect the coupling to the transversal optical modes. Hence the sum (2.12) can be restricted to the longitudinal optical branch. This means that $\partial u_n / \partial R_j$ can be expressed by a linear combination of the eigenvectors of the longitudinal optical branch. The vibrational spectrum of the longitudinal optical phonons is quasi degenerated, hence, assuming it to be completely degenerated, $\partial u_n / \partial R_j$ itself is an eigenvector, and can be used as a basevector if properly normalized.

$$\eta^{n1} = (C^n)^{-1}\left(\frac{\partial u_n}{\partial R_1}, \cdots, \frac{\partial u_n}{\partial R_M}\right), \tag{2.18}$$

$$(C^n)^2 = \sum_j \left(\frac{\partial u_n}{\partial R_j}\frac{\partial u_n}{\partial R_j}\right). \tag{2.19}$$

By appropriate linear combinations of the ${}^n\xi^{\nu t}$ this can be completed to give a new base in lattice configuration space:

$$\eta^{n1}, \eta^{n2}, \ldots, \eta^{n3M}. \tag{2.20}$$

With respect to this base we get for (2.5)

$$R_j - R_j^n = \sum_t \eta_j^{nt} Q_t^n \tag{2.21}$$

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[14] S. I. PEKAR, Untersuchung über die Elektronentheorie der Kristalle, Akademie-Verlag, Berlin 1954, pp. 58.

	MgO	LiF	NaCl	NaBr	KCl	KBr	KJ
ω_1 $[10^{13}\,\mathrm{sec}^{-1}]$	11.0	8.6	4.0	3.4	3.2	2.6	2.1
$\hat{\omega}$ $[10^{13}\,\mathrm{sec}^{-1}]$	14.0	12.0	5.0	3.9	4.0	3.1	2.6
$\hbar\omega_1$ $[10^{-2}\,\mathrm{eV}]$	6.9	5.7	2.6	2.2	2.1	1.7	1.3
C^{s} $[10^{-4}\,\mathrm{dyn}]$	11.3	6.63	3.18	2.24	2.28	2.32	1.85
B_1^{s} $[10^{14}\,\mathrm{cm}^{-2}]$	9.0	10.1	4.1	2.7	7.7	2.6	2.0
α $[\cdot 10^{-2}]$	101.3	166.0	72.4	48.3	139.1	45.3	36.2
$M_0 \cdot \omega_1^2$ $[10^4\,\mathrm{erg} \cdot \mathrm{cm}^{-2}]$	17.8	6.29	3.73	3.45	3.18	2.96	2.88
$(\hbar\omega_1/M_0 \cdot \omega_1^2)^{1/2}$ [Å]	7.88	12.0	10.6	10.2	10.3	9.6	9.4
$(C^{\mathrm{s}})^2/M_0 \cdot \omega_1^2$ $[\mathrm{eV}]_{\mathrm{ber}}$	4.5	4.4	1.7	0.9	1.0	1.1	0.99
$(C^{\mathrm{s}})^2/M_0 \cdot \omega_1^2$ $[\mathrm{eV}]_{\mathrm{gem}}$			1.65		1.04	1.09	1.01
$2\,S_{\mathrm{HR}}$	65	77	65	41	48	65	45

Table 2. Dynamical Results. We assume effective frequency after MÄRTL[12]. $\hat{\omega}$ frequency of the longitudinal optical branch for $k \to 0$ after KITTEL[21]. The norm C^{s} and $B_1{}^{\mathrm{s}}$ have been calculated by means of a computer. To do this ions with opposite charge have been collected to give a spherically symmetric arrangement of elementary cells and then the sum was taken over all cells. From C^{s} and $M_0\omega_1{}^2$ one obtains polarization energies known as Stokes-shift of absorption and emission band. Once the energies known one obtains the Huang-Rhys-Factor, which can be determined by the temperature dependence of the absorption band, too[18].

and (2.12) becomes

$$u_n(R) = u_n(R^n) + C^n \cdot \eta^{n1} \sum_t \eta^{nt} Q_t^n \qquad (2.22)$$
$$= u_n(R^n) + C^n \cdot Q_1^n .$$

If the eigenvectors are known the considerations following (2.13) are superfluous and we can confine ourselves for further calculations to (2.12) and (2.13) Though our numerical calculations did start with (2.22) we use in the following the more general formula (2.12).

With this knowledge it is not very difficult to describe the dependence of the electron's state on the lattice vibrations. If the electron's wave function is adapted to the symmetry conditions, and the variational parameter can be expanded in a Taylor series with respect to the Q_j^n

$$\beta^n(R) = \beta^n(R^n) + \sum_{j=1}^{3M} \frac{\partial\beta^n}{\partial Q_j^n} Q_j^n + \cdots \qquad (2.23)$$

we only have to calculate the dynamical coupling coefficients $\partial\beta^n/\partial Q_j^n =: B_j^n$. This is done by minimizing $U_n(R)$ with respect to $\beta^n(R)$ for every position R. Expanding $\partial u_n/\partial\beta^n$ into a Taylor series we find

$$\frac{\partial u_n}{\partial\beta^n} = \frac{\partial u_n}{\partial\beta^n}(R^n) \qquad (2.24)$$
$$+ \sum_{j=1}^{3M} \left(\frac{\partial^2 u_n}{\partial\beta^n\,\partial Q_j^n} + \frac{\partial^2 u_n}{(\partial\beta^n)^2} \frac{\partial\beta^n}{\partial Q_j^n} \right) \cdot Q_j^n + \cdots \overset{!}{=} 0 .$$

Since $\partial u_n/\partial\beta^n(R^n)$ is made to vanish by the static calculations, we get for the coupling coefficients B_j^n

$$B_j^n \frac{\partial^2 u_n}{(\partial\beta^n)^2} + \frac{\partial^2 u_n}{\partial\beta^n\,\partial Q_j^n} = 0 \qquad (2.25)$$

because $\partial u_n/\partial\beta^n$ must vanish for every choice of the Q_j^n. For localized states

$$\frac{\partial^2 u_n}{(\partial\beta^n)^2} =: N_n \qquad (2.26)$$

can be evaluated numerically by summing over the lattice points. Then we get for the coupling parameters from (2.25) with (2.12)

$$B_j^n = -\frac{1}{N_n} \frac{\partial}{\partial\beta^n} C_j^n . \qquad (2.27)$$

Accepting the approximations made above we get from (2.22)

$$B_1^n = -\frac{1}{N_n} \frac{\partial}{\partial\beta^n} C^n , \qquad (2.28)$$
$$B_j^n = 0 \quad \text{for} \quad j \geqq 2 .$$

The numerical values for B_1^n, C^n and N_n for the example of a F-center electron are collected in Table 2.

Relations between Normal Coordinates

From (2.5), (2.7), and (2.8) we see that the normal coordinates defined above depend on the electronic state. Hence one has to know the relations between them. For that purpose we write the cartesian coordinates R_j with respect to two different frames:

$$R_j - R_j^n = Y_j^n = \sum_t \eta_j^{nt} Q_t^n , \qquad (2.29)$$

$$R_j - R_j^{n'} = Y_j^{n'} = \sum \eta_j^{n't} Q_t^{n'} . \qquad (2.30)$$

With respect to the coordinate system η^{nt} we get for the displacement caused by an electronic

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[21] G. KITTEL, Introduction to Solid State Physics, J. Wiley, New York 1967.

transition

$$R_j^{n'} - R_j^n = \sum_t \eta_j^{nt} A_t^{nn'} . \qquad (2.31)$$

Inserting (2.31) into (2.30) we have by comparison

$$\sum_t \eta_j^{nt} Q_t^n = \sum_t \eta_j^{n't} Q_t^{n'} + \sum_t \eta_j^{nt} A_t^{nn'} \qquad (2.32)$$

and since the η^{nt} are orthonormalized:

$$Q_r^n = \sum_t (\eta^{nr} \eta^{n't}) Q_t^{n'} + A_r^{nn'} . \qquad (2.33)$$

For weak perturbations, with eigenfrequencies and eigenvectors depending only weakly on the electronic state, we can simplify (2.33) somewhat more: We use for both states one common eigenvector system $\eta^1, \ldots, \eta^{3M}$ not depending on the electron's state, then (2.33) reduces to:

$$Q_r^n = Q_r^{n'} + A_r^{nn'} . \qquad (2.34)$$

$R_j^{n'}$ and R_j^n are known by the static calculations, therefore in principle one finds $A_j^{nn'}$ from (2.31), if the eigenvectors η^{nt} (or η^t) are known. Since in most cases the eigenvectors are not known accurately, we give an alternative method basing upon some reasonable assumptions about the frequency spectrum of weakly perturbed lattices.

From (2.9) and (2.12) we get

$$U_n(R) = u_n(R^n) + \sum_t C_t^n Q_t^n + V(R) \qquad (2.35)$$

on the other hand we use the expansion (2.2) and find

$$U_n(R) = U_n(R^n) + \tfrac{1}{2} \sum_t (\omega_t^n)^2 (Q_t^n)^2 + \cdots . \qquad (2.36)$$

Now we eliminate $U_n(R)$ and get the relation:

$$0 = u_n(R^n) - U_n(R^n) + \sum_t (C_t^n Q_t^n - \tfrac{1}{2} (\omega_t^n)^2 (Q_t^n)^2) + V(R) . \qquad (2.37)$$

Since $V(R)$ does not depend on the electronic state n, we eliminate it from (2.43) by writing this equation for the second electronic state n' being of interest:

$$\begin{aligned} &U_n(R^n) - u_n(R^n) + \sum_t (\tfrac{1}{2} (\omega_t^n)^2 (Q_t^n)^2 - C_t^n Q_t^n) \\ &\quad = V(R) = U_{n'}(R^{n'}) - u_{n'}(R^{n'}) + \sum_t (\tfrac{1}{2} (\omega_t^{n'})^2 (Q_t^{n'})^2 - C_t^{n'} Q_t^{n'}) . \end{aligned} \qquad (2.38)$$

(2.38) does hold for an arbitrary choice of the Q_t^n and $Q_t^{n'}$. If in addition we assume relation (2.34) to hold, we get from (2.38)

$$\begin{aligned} &U_n(R^n) - u_n(R^n) - U_{n'}(R_{n'}) + u_{n'}(R_{n'}) - \sum_t C_t^n A_t^{nn'} \\ &\quad - \sum_t (C_t^n - C_t^{n'}) Q_t^{n'} + \sum_t (\omega_t^n)^2 A_t^{nn'} Q_t^{n'} + \tfrac{1}{2} \sum_t ((\omega_t^n)^2 - \omega_t^{n'})^2) (Q_t^{n'})^2 \equiv 0 \end{aligned} \qquad (2.39)$$

which must hold identically in $Q_t^{n'}$ and therefore

$$(\omega_t^n)^2 = (\omega_t^{n'})^2 \qquad (2.40)$$

and

$$(\omega_t^n)^2 A_t^{nn'} = C_t^n - C_t^{n'} . \qquad (2.41)$$

In the preceding section we assumed the optical vibrations to be completely degenerated which led to $C_t^n = 0$ for $t \neq 1$ for the trapped electron's state. If in addition for the conduction and the valence electron we neglect the dynamical coupling at the lattice vibrations we get:

$$A^{nn'} := A_1^{nn'} = C^n/(\omega_t^n)^2 . \qquad (2.42)$$

With (2.42) we have completed the calculations about the crystal states. From the static calculations we know the wave functions and approximately the energies (the numerical results are collected in Table 1) and from the dynamic calculations the dynamical coupling coefficients B_j^n and the relations between the normal coordinates. But the latter results depend on a precise knowledge of the normal mode coupled at the electron's state. Since these calculations have not been finished we use the frequencies as calculated by MÄRTL[12] from next neighbour interaction. By means of these calculated frequencies and our numerical values for C^n we could establish an excellent agreement with the numerical values for the polarization energies which are easily determined from the absorption and emission energies of the electron

$$U_{\text{abs}} - U_{\text{em}} = \bar{M}_0 \, \omega^2 (A^{nn'})^2 \qquad (2.43)$$

as can be seen from Table 2.

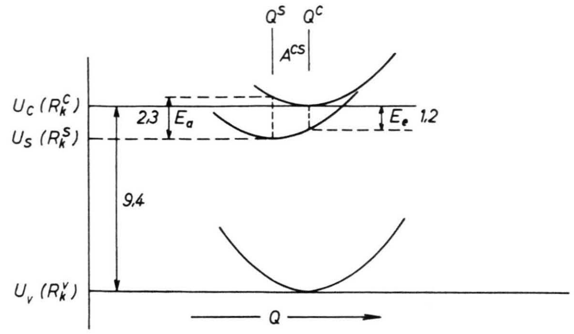

Fig. 2a. Energy depending on one normal mode for 3 electronic states for KCl. The F-absorption energy is 2.3 eV, the emission energy 1.3 eV. The normal coordinate in arbitrary units.

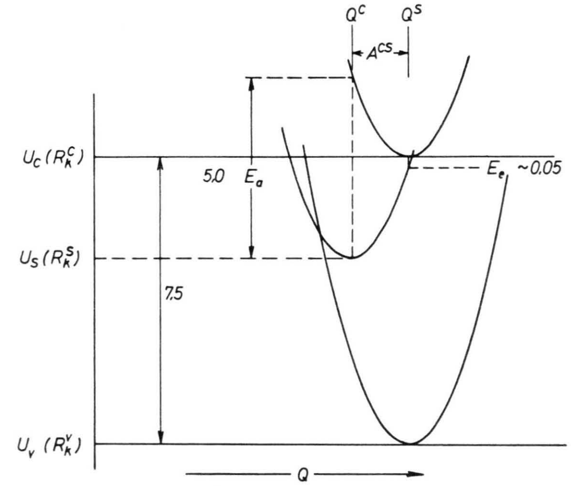

Fig. 2b. As Fig. 2a but for MgO. One observes the F-emission energy to be approximately zero.

Summary

1. Statics

The eigenvalue problem of the microblock K^* has been separated into one for the electrons and a second for the lattice motion. The coupling of the defect electron at the other electrons is expressed by means of the polarization calculations. The hamiltonian of the electron depends on the lattice coordinates as parameters and is first solved for the equilibrium positions R_j^n.

Results:

Static energy: $U_n(R^n)$

Static electronic wave function: $\psi^n(r, \beta^n(R^n))$ (2.44)

with variational parameter $\beta^n(R^n)$.

2. Dynamics

By means of normal coordinates Q^n, the dynamical dependence of the wave function on lattice oscillations can be quantitatively described. Only a few coordinates are needed:

Energy-expansion:

$$U_n(R) = u_n(R^n) + \sum_\nu C_\nu Q_\nu^n + V(R);$$

Variational Parameter:

$$\beta^n(R) = \beta^n(R^n) + \sum_\nu B_\nu^n Q_\nu^n; \qquad (2.45)$$

Electronic wave function:

$$\psi^n(r, \beta^n, R) = \psi^n(r; \beta^n(R^n) + \sum_\nu B_\nu^n Q_\nu^n).$$

A very simple relation between different normal coordinate frames is established.

$$Q_j^n = Q_j^{n'} + A_j^{nn'}. \qquad (2.46)$$

The lattice oscillation problem is only treated in a rough approximation assuming the disturbance of the frequency spectrum beeing weak. The results are demonstrated in Figs. 2a and 2b for MgO and KCl.

Matrix Elements for Radiationless Transitions

At the beginning of a theoretical investigation the fundamental problem is the definition of the unperturbed hamiltonian, the eigenstates of which should be at least metastable states. We use the adiabatic and a Hartree-Fock-approximation to reduce the many particle problem, and the harmonic approximation to simplify the lattice hamiltonian. If we neglect the possible transitions which are caused by the assumption of the one-electron approximation we have two perturbation operators. The first, K^t, corresponds to the nonadiabatic interactions, which result from the electrons' being unable to follow the ionic motion immediately:

$$K^{\mathrm{t}}\,\psi^n(r)\prod_{j=1}^{3M}\varphi^n_{m_j}(Q^n_j) = -\tfrac{1}{2}\sum_j\left(\frac{\partial^2}{\partial Q_j^{n\,2}}\,\psi^n\right)\prod_{k=1}^{3M}\varphi^n_{m_k}(Q^n_k) - \sum_j\left(\frac{\partial}{\partial Q^n_j}\,\psi^n\right)\left(\frac{\partial}{\partial Q^n_j}\,\varphi^n_{m_j}(Q^n_j)\right)\prod_{\substack{k=1\\k\neq j}}^{3M}\varphi^n_{m_k}(Q^n_k) \tag{3.1}$$

and the second from the anharmonic terms (of which we write only the third order terms[15]):

$$K^{\mathrm{a}}\,\psi^n(r)\prod_{j=1}^{3M}\varphi^n_{m_j}(Q^n_j) = \psi^n(r)\,\frac{1}{3!}\sum_{i,k,l}G^n_{i,k,l}\,Q^n_i\,Q^n_k\,Q^n_l\prod_{j=1}^{3M}\varphi^n_{m_j}(Q^n_j)\,. \tag{3.2}$$

The anharmonic terms have been discussed by MÄRTL[12] and RAMPACHER[3].

Since their investigations will be published in a later paper, we refer here only to their results as far as needed.

The matrix elements of K^{t} which will prove to give rise to radiationless electronic transitions, will be discussed in this section for the example of a F-center as quenching center.
The microblock‘s wave function is following the preceding chapters:

$$\psi^n(r)\prod_{j=1}^{3M}\varphi^n_{m_j}(Q^n_j) = \hat{\psi}^n_m\,. \tag{3.3}$$

For the F-electron in the groundstate we found especially

$$\psi^{\mathrm{s}}_1(r_1) = \pi^{-1/2}\,\beta^{\mathrm{s}\,3/2}\exp(-\,\beta^{\mathrm{s}}\cdot r_1) \tag{3.4}$$

with

$$\beta^{\mathrm{s}} = \beta^{\mathrm{s}}_0 + B^{\mathrm{s}}_1\,Q^{\mathrm{s}}_1 \tag{3.5}$$

and for the valence and conduction band state respectively (1.24)

$$\psi^{\mathrm{c}}_1 = \psi^{\mathrm{v}}_1 \simeq [\Omega^{-1/2}\,\Theta(\tfrac{1}{2}a - |x_1|)\,\Theta(\tfrac{1}{2}a - |y_1|)\,\Theta(\tfrac{1}{2}a - |z_1|) - S\,\psi^{\mathrm{s}}_1(r_1)]\,. \tag{3.6}$$

Hence (3.2) can be reduced to

$$K^{\mathrm{t}}\,\hat{\psi}^{\mathrm{s}}_m = -\tfrac{1}{2}\left[\left(\frac{\partial^2}{\partial Q_1^{\mathrm{s}\,2}}\,\psi^{\mathrm{s}}\right)\varphi^{\mathrm{s}}_{m_1}(Q^{\mathrm{s}}_1) + 2\,\frac{\partial\psi^{\mathrm{s}}_1}{\partial Q^{\mathrm{s}}_1}\cdot\frac{\partial\varphi^{\mathrm{s}}_{m_1}}{\partial Q^{\mathrm{s}}_1}\right]\prod_{j=2}^{3M}\varphi^{\mathrm{s}}_{m_j}(Q^{\mathrm{s}}_j) \tag{3.7}$$

from (3.7) we find for the matrixelements

$$(c, l, l(q), K^{\mathrm{t}}\,s, m, m(q)) = K^t_{c,\,l_1,\,\ldots,\,l_{3M};\,s,\,m_1,\,\ldots,\,m_{3M}}$$

$$= -\frac{1}{2}\Big\{\int dQ^{\mathrm{s}}_1\int d^3r_1\left[\psi^{\mathrm{c}}_1\,\frac{\partial^2}{(\partial Q^{\mathrm{s}}_1)^2}\,\psi^{\mathrm{s}}_1\right]\varphi^{\mathrm{c}}_{l_1}(Q^{\mathrm{s}}_1)\cdot\varphi^{\mathrm{s}}_{m_1}(Q^{\mathrm{s}}_1) \tag{3.8}$$

$$+\,2\int dQ^{\mathrm{s}}_1\int d^3r_1\left[\psi^{\mathrm{c}}_1\,\frac{\partial}{\partial Q^{\mathrm{s}}_1}\,\psi^{\mathrm{s}}_1\right]\varphi^{\mathrm{c}}_{l_1}(Q^{\mathrm{s}}_1)\,\frac{\partial}{\partial Q^{\mathrm{s}}_1}\,\varphi^{\mathrm{s}}_{m_1}(Q^{\mathrm{s}}_1)\Big\}\times\prod_{j=2}^{3M}\int dQ^{\mathrm{s}}_j[\varphi^{\mathrm{c}}_{l_j}(Q^{\mathrm{s}}_j)\,\varphi^{\mathrm{s}}_{m_j}(Q^{\mathrm{s}}_j)]\,.$$

With the relations (2.40) for the normal coordinates

$$Q^{\mathrm{c}}_1 = Q^{\mathrm{s}}_1 + A^{\mathrm{cs}}_1,\qquad Q^{\mathrm{c}}_j = Q^{\mathrm{s}}_j,\qquad j \geqq 2 \tag{3.9}$$

we get for the harmonic oscillator eigenfunctions:

$$\varphi^{\mathrm{c}}_{m_1}(Q^{\mathrm{c}}_1) = \varphi^{\mathrm{c}}_{m_1}(Q^{\mathrm{s}}_1 + A^{\mathrm{cs}}_1) = \varphi_{m_1}(Q_1 + A^{\mathrm{cs}}_1)\,,\qquad \varphi^{\mathrm{c}}_{m_j}(Q^{\mathrm{c}}_j) = \varphi^{\mathrm{c}}_{m_j}(Q^{\mathrm{s}}_j) = \varphi_{m_j}(Q^{\mathrm{s}}_j)\,,\qquad j \geqq 2 \tag{3.10}$$

and therefore (3.8) becomes

$$K^{\mathrm{t}}_{\mathrm{c},\,l_1,\,\ldots,\,l_{3M};\,\mathrm{s},\,m_1,\,\ldots,\,m_{3M}} = -\,\Big\{\frac{1}{2}\int dQ^{\mathrm{s}}_1\left[I^{\mathrm{cs}}_1(Q^{\mathrm{s}}_1)\,\varphi_{l_1}(Q^{\mathrm{s}}_1 + A^{\mathrm{cs}}_1)\,\frac{\partial}{\partial Q^{\mathrm{s}}_1}\,\varphi_{m_1}(Q^{\mathrm{s}}_1)\right]$$

$$+\int dQ^{\mathrm{s}}_1\,[I^{\mathrm{cs}}_2(Q^{\mathrm{s}}_1)\,\varphi_{l_1}(Q^{\mathrm{s}}_1 + A^{\mathrm{cs}}_1)\,\varphi_{m_1}(Q^{\mathrm{s}}_1)]\Big\}\times\prod_{j=2}^{3M}\delta_{l_j,\,m_j}\,. \tag{3.11}$$

In (3.11) the functions I^{cs}_1 and I^{cs}_2 are defined by

$$I^{\mathrm{cs}}_1(Q^{\mathrm{s}}_1) = \int d^3r_1\left[\psi^{\mathrm{c}}_1(r_1)\,\frac{\partial}{\partial Q^{\mathrm{s}}_1}\,\psi^{\mathrm{s}}_1(r_1)\right] = \frac{\partial}{\partial Q^{\mathrm{s}}_1}\,S = -\,\frac{3}{2}\,\frac{B^{\mathrm{s}}_1}{\beta^{\mathrm{s}}}\cdot S \tag{3.12}$$

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[15] For perfect lattices with NaCl-structure the third order terms vanish identically, but not for disturbed lattices.

and
$$I_2^{\mathrm{cs}}(Q_1^{\mathrm{s}}) = \int d^3 r_1 \left[\psi_1^{\mathrm{c}}(r_1) \frac{\partial^2}{(\partial Q_1^{\mathrm{s}})^2} \psi_1^{\mathrm{s}}\right] = \frac{9}{2}\left(\frac{B_1^{\mathrm{s}}}{\beta^{\mathrm{s}}}\right)^2 \cdot S \,. \tag{3.13}$$

For simplicity we introduce the coordinates

$$Q^{\mathrm{s}} := \left(\frac{M_0 \cdot \omega_1{}^2}{\hbar\,\omega_1}\right)^{1/2} \cdot Q_1^{\mathrm{s}} \tag{3.14}$$

and get
$$\alpha := \left(\frac{\hbar\omega_1}{M_0 \cdot \omega_1{}^2}\right)^{1/2} \cdot \frac{B_1^{\mathrm{s}}}{\beta_0^{\mathrm{s}}} \,. \tag{3.15}$$

The parameter α gives a measure for the dynamical coupling of the electronic state ψ^{s} at the lattice vibrations. The oscillator wave functions with respect to the new coordinates are:

$$\Phi_m(Q^{\mathrm{s}}) := \left(\frac{\hbar\,\omega_1}{M_0 \cdot \omega_1{}^2}\right)^{1/4} \varphi_m\left(\left(\frac{\hbar\,\omega_1}{M_0 \cdot \omega_1{}^2}\right)^{1/2} Q^{\mathrm{s}}\right). \tag{3.16}$$

We then have for (3.11)

$$\begin{aligned} K^{\mathrm{t}}_{\mathrm{c},l;\,\mathrm{s},m} = -\frac{\hbar\,\omega_1}{2} \Bigg\{ &\int dQ^{\mathrm{s}} \left[\Phi_l(Q^{\mathrm{s}} + A^{\mathrm{cs}})\, \frac{9}{2}\, \frac{\alpha^2}{(1+\alpha\, Q^{\mathrm{s}})^2} \cdot S\, \Phi_m(Q^{\mathrm{s}})\right] \\ &+ \int dQ^{\mathrm{s}} \left[\Phi_l(Q^{\mathrm{s}} + A^{\mathrm{cs}}) \cdot 3\, \frac{\alpha}{1+\alpha\, Q^{\mathrm{s}}} \cdot S\, \frac{\partial}{\partial Q^{\mathrm{s}}} \Phi_m(Q^{\mathrm{s}})\right]\Bigg\} . \end{aligned} \tag{3.17}$$

Expanding S and β^{s} into a power series about $Q^{\mathrm{s}} + A^{\mathrm{cs}}/2$ and collecting terms of equal powers of α the matrixelements become:

$$\begin{aligned} K^{\mathrm{t}}_{\mathrm{c},l;\,\mathrm{s},m} = &-\frac{\hbar\,\omega_1}{2} \cdot S_0 \cdot \left(\frac{\mathrm{d}^3}{\Omega}\right)^{1/2} \cdot \Bigg\{ \int \frac{3\,\alpha}{(1-\alpha)^{5/2}/A^{\mathrm{cs}}/2} \cdot \Phi_l(Q^{\mathrm{s}} + A^{\mathrm{cs}})\, \frac{\partial}{\partial Q^{\mathrm{s}}} \Phi_m(Q^{\mathrm{s}})\, dQ^{\mathrm{s}} \\ &- \int \frac{\alpha^2}{(1-\alpha)^{7/2}/A^{\mathrm{cs}}/2}\, \Phi_l(Q^{\mathrm{s}} + A^{\mathrm{cs}}) \left[\frac{9}{2} + \frac{15}{2}\left(Q^{\mathrm{s}} + \frac{A^{\mathrm{cs}}}{2}\right) \frac{\partial}{\partial Q^{\mathrm{s}}} \Phi_m(Q^{\mathrm{s}})\, dQ^{\mathrm{s}}\right. \\ &+ \int \frac{\alpha^3}{(1-\alpha)^{9/2}/A^{\mathrm{cs}}/2}\, \Phi_l(Q^{\mathrm{s}} + A^{\mathrm{cs}}) \left[\frac{63}{4}(Q^{\mathrm{s}} + A^{\mathrm{cs}}) + \frac{105}{8}(Q^{\mathrm{s}} + A^{\mathrm{cs}})^2\, \frac{\partial^2}{\partial Q^{\mathrm{s}2}} \Phi_m(Q^{\mathrm{s}})\, dQ^{\mathrm{s}} - + \cdots\right\} . \end{aligned} \tag{3.18}$$

We prefer this expansion about $A^{\mathrm{cs}}/2$, since we find the matrix elements to be symmetric in every power of α. The individual integrals can be reduced by algebraic relations (Appendix B) to one type, the so-called Franck-Condon-Integrals[16]

$$F_{n,\,m}(A) := \int \Phi_n(Q + A)\, \Phi_m(Q)\, dQ = \exp\{-A^2/4\} \left(\frac{A}{\sqrt{2}}\right)^{m-n} \sqrt{\frac{n!}{m!}}\, \mathscr{L}_n^{m-n}\left(\frac{A^2}{2}\right); \qquad m \geqq n \tag{3.19}$$

and because of $F_{n,\,m}(A) = F_{m,\,n}(-A)$ one gets a formula for $n > m$, too. In (3.19) $\mathscr{L}_n^{m-n}$ is a Laguerre polynomial.

With

$$G_{n,\,m}(A) = \sqrt{\frac{m}{2}}\, F_{n,\,m-1} - \sqrt{\frac{m+1}{2}}\, F_{n,\,m+1} \tag{3.20}$$

the matrix elements in first and second order of α are:

$$\begin{aligned} K^{\mathrm{t}}_{\mathrm{c},l;\,\mathrm{s},m} = &\frac{\hbar\,\omega_1}{2} \cdot S_0 \left(\frac{d^3}{\Omega}\right)^{1/2} \\ &\cdot \left\{ \frac{3\,\alpha}{(1-\alpha \cdot A^{\mathrm{cs}}/2)^{5/2}} \cdot G_{l,\,m}(A^{\mathrm{cs}}) - \frac{\alpha^2}{(1-\alpha \cdot A^{\mathrm{cs}}/2)^{7/2}} \left[\frac{9}{2} F_{l,\,m} + \frac{15}{2}\left(\frac{l-m}{A^{\mathrm{cs}}} G_{l,\,m} + \left(\frac{m-l}{(A^{\mathrm{cs}})^2} + \frac{1}{2}\right) F_{l,\,m}\right]\right\} . \end{aligned} \tag{3.21}$$

	MgO	LiF	NaCl	NaBr	KCl	KBr	KJ
S_0	7.72	8.03	6.40	6.34	5.87	5.82	5.78
$\alpha \cdot 10^2$	101.3	166.0	72.4	48.3	139.1	45.3	36.2
A^{cs}	8.05	8.8	8.05	6.4	6.9	8.05	6.7
$\hbar\omega_1 \cdot 10^{14}$ [erg]	11.1	9.1	4.2	3.6	3.4	2.7	2.2
K_0	0.84	0.72	0.26	0.22	0.19	0.15	0.12

Table 3. Parameters for matrix elements, $\hbar\omega_1$ energy of the normal mode coupled at the electron's state. α dynamical coupling parameter (3.15). S_0 overlap integral (1.25). $K_0 = 0.5 \cdot \hbar\omega_1 \cdot S_0 \cdot (d^3/\Omega)^{1/2}$ for $\Omega = (10 \cdot d)^3$.

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[16] M. WAGNER, Z. Naturforsch. **14 a**, 81 [1959].

This formula cannot be obtain by straight forward calculation, but by means of the relations of Appendix B. It has some advantages for numerical evaluation.

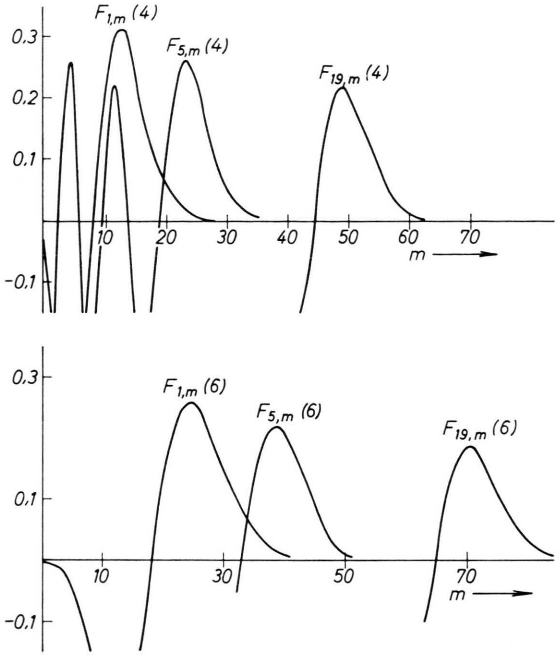

Fig. 3. Franck-Condon-Integrals $F_{n,m}(A)$ for $A = 4$ and $A = 6$. Only the last extrema have been plotted. One observes the last maximum going to greater m for growing A.

The Franck-Condon integrals have been numerically evaluated and tabulated and are given in Figs. 3a and 3b for some selected values of A, n and m. As a function of m the $F_{n,m}(A)$ oscillate up to one point $m = m_{\max}(A, n)$ depending on A and n and then decrease exponentially. Since this point is most interesting for the radiationless transition, we plotted in Fig. 4 $m_{\max}(A, n)$ for some values of A. For those values of A, $m = \max$, and n being of interest we approximate the diagrams of Fig. 4a by

$$m \approx \frac{1}{\ln(1 + 1/m)} = \frac{A^2}{2} + \frac{A}{2} \frac{1}{(\ln 1 + 1/n)}. \quad (3.22)$$

This approximation is shown in Fig. 4b. For an oscillator with frequency ω in thermal equilibrium with a heat reservoir of temperature T we expect to have n oscillator quanta excited

$$\frac{\hbar\omega}{kT} = \ln\left(1 + \frac{1}{n}\right). \quad (3.23)$$

By (3.23) we can reduce (3.22) to

$$m \approx \frac{A^2}{2} + \frac{A}{2} \frac{kT}{\hbar\omega}. \quad (3.24)$$

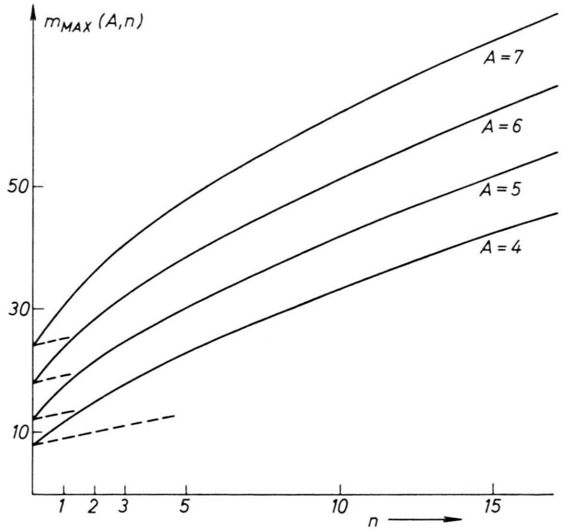

Fig. 4a. The Franck-Condon-Integrals $F_{n,m}(A)$ vanish for A fixed depending on n for $m > m_{\mathrm{MAX}}$. For $n = 0$: $m_{\mathrm{MAX}} = A^2/2$.

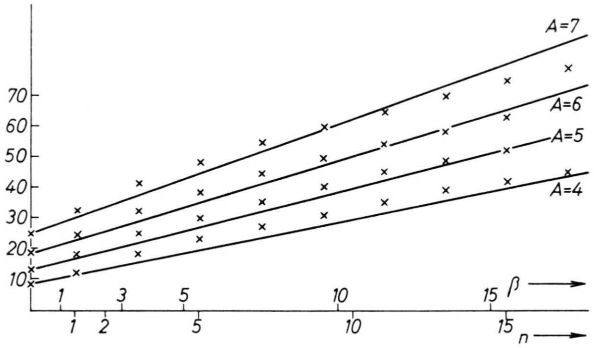

Fig. 4b. Approximation of Fig. 4a. For A not too large we have

$$\left[\ln\left(1 + \frac{1}{m_{\mathrm{MAX}}}\right)\right]^{-1} = \frac{A^2}{2} + \frac{A}{2}\left[\ln\left(1 + \frac{1}{n}\right)\right]^{-1}.$$

We plotted m_{MAX} against

$$\beta = \frac{kT}{\hbar\omega_1} = \left[\ln\left(1 + \frac{1}{n}\right)\right]^{-1}.$$

The deviation from Fig. 4a is marked by ×.

For n not too large this functional dependence is transmitted to that of the $K^{\mathrm{t}}_{\mathrm{c},n;\,\mathrm{s},m}$. The numerical values of $|K^{\mathrm{t}}_{\mathrm{c},n;\,\mathrm{s},m}|^2$ are plotted in Fig. 5 for two values of n.

Appendix A

Hermitian Symmetry of K^{t}

The unperturbed hamiltonian in the adiabatic and one-electron approximation has been construc-

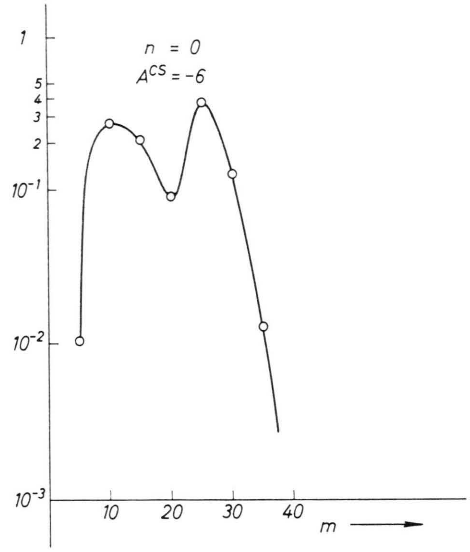

Fig. 5a. The square of the matrixelements in logarithmic measure. For a special defect the values have to be multiplied by

$$K_0^2 = \frac{d^3}{\Omega} \cdot S_0^2 \cdot \left(\frac{\hbar\,\omega_1}{2}\right)^2 .$$

The circles give the values calculated, the line an approximated average.

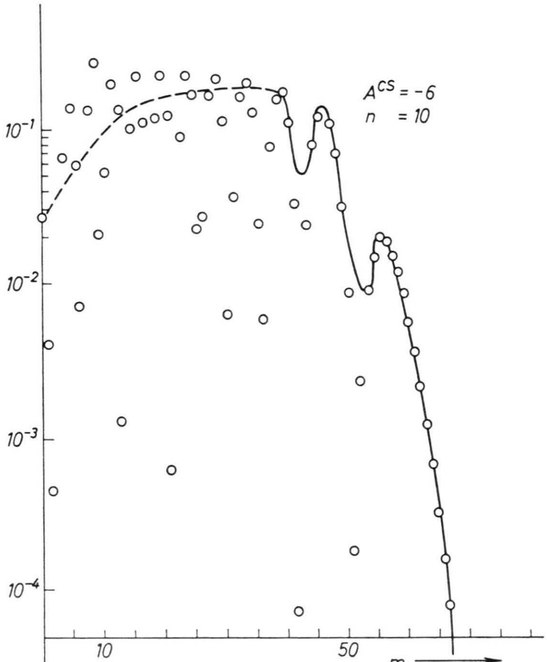

Fig. 5b. As Fig. 5a but for $n = 10$. One should observe the heavy oscillations of the values calculated.

ted by means of various, partially classical, considerations. We therefore have to discuss wether the perturbation K^{t} remains an hermitian operator. By means of partial integration one proves the symmetry of the matrix elements of K^{t}.

First we decompose K^t

$$K^{\mathrm{t}} = \sum_j K^{\mathrm{t}}_{(j)} \tag{A.1}$$

with

$$K^{\mathrm{t}}_{(j)}\,\hat{\psi}^n_m = -\frac{1}{2\,M_j}\left[\left(\frac{\partial^2}{\partial Q_j^{n2}}\,\psi_n\right)\varphi^n_{m_j}(Q^n_j) + 2\left(\frac{\partial}{\partial Q^{\mathrm{n}}_j}\,\psi^n\right)\left(\frac{\partial}{\partial Q^n_j}\,\varphi^n_{m_j}(Q^n_j)\right)\right]. \tag{A.2}$$

From (A.2) we get the matrix elements of $K^{\mathrm{t}}_{(j)}$ to be:

$$K^{\mathrm{t}}_{(j)\mathrm{s},l;\,\mathrm{c},m} = -\frac{1}{2\,M_j}\left\{\int \psi_{\mathrm{s}}\,\varphi^{\mathrm{s}}_l\left[\left(\frac{\partial^2}{\partial Q_j^2}\,\psi_{\mathrm{c}}\right)\varphi^{\mathrm{c}}_m + 2\left(\frac{\partial}{\partial Q_j}\,\psi_{\mathrm{c}}\right)\left(\frac{\partial}{\partial Q_j}\,\varphi^{\mathrm{c}}_m\right)\right]\mathrm{d}Q_j\,\mathrm{d}r\right\}. \tag{A.3}$$

By partial integration of the first term we find

$$\begin{aligned} K^{\mathrm{t}}_{(j)\mathrm{s},l;\,\mathrm{c},m} = \frac{1}{2\,M_j}\Bigg\{ & \int\left[\left(\frac{\partial}{\partial Q_j}\,\psi_{\mathrm{s}}\right)\varphi^{\mathrm{s}}_l\varphi^{\mathrm{c}}_m + \psi_{\mathrm{s}}\left(\frac{\partial}{\partial Q_j}\,\varphi^{\mathrm{s}}_l\right)\varphi^{\mathrm{c}}_m\right]\left(\frac{\partial}{\partial Q_j}\,\psi_{\mathrm{c}}\right)\mathrm{d}Q_j\,\mathrm{d}r \\ & + \int\left[\psi_{\mathrm{s}}\,\varphi^{\mathrm{s}}_l\left(\frac{\partial}{\partial Q_j}\,\psi_{\mathrm{c}}\right)\left(\frac{\partial}{\partial Q_j}\,\varphi^{\mathrm{c}}_m\right) - 2\,\psi_{\mathrm{s}}\,\varphi^{\mathrm{s}}_l\left(\frac{\partial}{\partial Q_j}\,\psi_{\mathrm{c}}\right)\left(\frac{\partial}{\partial Q_j}\,\varphi^{\mathrm{c}}_m\right)\right]\mathrm{d}Q_j\,\mathrm{d}r\Bigg\}. \end{aligned} \tag{A.4}$$

By means of a second integration and collecting equivalent terms we get

$$\begin{aligned} K^{\mathrm{t}}_{(j)\mathrm{s},l;\,\mathrm{c},m} = -\frac{1}{2\,M_j}\Bigg\{ & \int\psi_{\mathrm{c}}\left[\left(\frac{\partial^2}{\partial Q_j^2}\,\psi_{\mathrm{s}}\right)\varphi^{\mathrm{s}}_l\,\varphi^{\mathrm{c}}_m + \left(\frac{\partial}{\partial Q_j}\,\psi_{\mathrm{s}}\right)\left(\frac{\partial}{\partial Q_j}\,\varphi^{\mathrm{s}}_l\right)\varphi^{\mathrm{c}}_m\right]\mathrm{d}Q_j\,\mathrm{d}r \\ + \int\left[\left(\frac{\partial}{\partial Q_j}\,\psi_{\mathrm{s}}\right)\varphi^{\mathrm{s}}_l\left(\frac{\partial}{\partial Q_j}\,\varphi^{\mathrm{c}}_m\right) + \left(\frac{\partial}{\partial Q_j}\,\psi_{\mathrm{s}}\right)\left(\frac{\partial}{\partial Q_j}\,\varphi^{\mathrm{s}}_l\right)\varphi^{\mathrm{c}}_m\right] & \psi_{\mathrm{c}}\,\mathrm{d}Q_j\,\mathrm{d}r + \int\psi_{\mathrm{s}}\,\varphi^{\mathrm{s}}_l\left(\frac{\partial}{\partial Q_j}\,\psi_{\mathrm{c}}\right)\left(\frac{\partial}{\partial Q_j}\,\varphi^{\mathrm{c}}_m\right)\mathrm{d}Q_j\,\mathrm{d}r\Bigg\}. \end{aligned} \tag{A.5}$$

where the orthogonality of the wave functions has been used. Using the identity

$$\int\psi_{\mathrm{s}}\,\varphi^{\mathrm{s}}_l\left(\frac{\partial}{\partial Q_j}\,\psi_{\mathrm{c}}\right)\left(\frac{\partial}{\partial Q_j}\,\varphi^{\mathrm{c}}_m\right)\mathrm{d}Q_j\,\mathrm{d}r = -\int\left(\frac{\partial}{\partial Q_j}\,\psi_{\mathrm{s}}\right)\varphi^{\mathrm{s}}_l\,\psi_{\mathrm{c}}\left(\frac{\partial}{\partial Q_j}\,\varphi^{\mathrm{c}}_m\right)\mathrm{d}Q_j\,\mathrm{d}r \tag{A.6}$$

we find from (A.5)

$$K^{\mathrm{t}}_{(j)\mathrm{s},l;\,\mathrm{c},m} = -\frac{1}{2\,M_j}\int\left[\psi_{\mathrm{c}}\,\varphi^{\mathrm{c}}_m\left(\frac{\partial^2}{\partial Q_j^2}\,\psi_{\mathrm{s}}\right)\varphi^{\mathrm{s}}_l + 2\left(\frac{\partial}{\partial Q_j}\,\psi_{\mathrm{s}}\right)\left(\frac{\partial}{\partial Q_j}\,\varphi^{\mathrm{s}}_l\right)\right]\mathrm{d}Q_j\,\mathrm{d}r = K^{\mathrm{t}}_{(j)\mathrm{c},m;\,\mathrm{s},l}\,. \tag{A.7}$$

Appendix B

Algebraic Relations for Matrix Elements

In chapt. 3 we get an expansion of the matrix elements into a power series of the dynamical coupling parameter α. To find formulae easy to handle we express the expansion terms by means of creation and annihilation operators

$$a := \frac{1}{\sqrt{2}}\left(Q + \frac{\mathrm{d}}{\mathrm{d}Q}\right), \quad b := \frac{1}{\sqrt{2}}\left(Q + A + \frac{\mathrm{d}}{\mathrm{d}Q}\right),$$

$$a^+ := \frac{1}{\sqrt{2}}\left(Q - \frac{\mathrm{d}}{\mathrm{d}Q}\right), \quad b^+ := a^+ + \frac{A}{\sqrt{2}} \tag{B.1}$$

with the commutation rules:

$$[a, a^+] = [b, a^+] = [a, b^+] = [b, b^+] = 1$$

$$[a, b] = [a^+, b^+] = 0\,.$$

By straight forward calculation one obtains

$$\begin{aligned}
b^+b &= a^+a + A\left(\frac{A}{2} + Q\right),\\
\frac{1}{\sqrt{2}}\,(b^+ + b) &= \frac{1}{\sqrt{2}}\,(^+ + a) + A = Q + A\\
&= \frac{1}{A}\left(\frac{A^2}{2} + b^+b - a^+a\right),\\
\frac{1}{\sqrt{2}}\,(b - b^+) &= \frac{1}{\sqrt{2}}\,(a - a^+) = \frac{\mathrm{d}}{\mathrm{d}Q}\,, \qquad (\mathrm{B.2})\\
\frac{1}{\sqrt{2}}\,b^+b\,(a - a^+) &= \frac{1}{\sqrt{2}}\,a^+a\,(a - a^+)\\
&\quad + A\left(\frac{A}{2} + Q\right)\frac{\mathrm{d}}{\mathrm{d}Q}\,,
\end{aligned}$$

$$(b^+b - a^+a)\,(b^+b - a^+a) = A^2\left(\frac{A}{2} + Q\right)^2.$$

By means of the commutation rules we transform the expressions (B. 2) in such a way, that

1. only products b^+b remain (the operators b and b^+ are replaced by means of (B.1));
2. these products b^+b stand altogether at the left or the right hand side.

Having rearranged the operators in this way one uses the following relations

$$a\,\Phi_m(Q) = \sqrt{m}\,\Phi_{m-1}(Q)\,, \qquad b\,\Phi_m(Q + A) = \sqrt{m}\,\Phi_{m-1}(Q + A)\,,$$

$$a^+\Phi_m(Q) = \sqrt{m+1}\,\Phi_{m+1}(Q)\,, \qquad b^+\Phi_m(Q + A) = \sqrt{m+1}\,\Phi_{m+1}(Q + A)\,, \tag{B.3}$$

and gets easily some relations between the Franck-Condon-Integrals $F_{n,\,m}(A)$

$$F_{n,\,m}(A) := \int \Phi_n(Q + A)\,\Phi_m(Q)\,\mathrm{d}Q\,, \qquad G_{n,\,m}(A) := \sqrt{\frac{m}{2}}\,F_{n,\,m-1}(A) - \sqrt{\frac{m+1}{2}}\,F_{n,\,m+1}(A)\,, \tag{B.4}$$

where

$$G_{n,\,m}(A) = \left\langle \Phi_n(Q + A)\,\middle|\,\frac{\mathrm{d}}{\mathrm{d}Q}\,\middle|\,\Phi_m(Q)\right\rangle = -\left\langle \Phi_m(Q)\,\middle|\,\frac{\mathrm{d}}{\mathrm{d}Q}\,\middle|\,\Phi_n(Q + A)\right\rangle; \tag{B.5}$$

$$A\left\langle \Phi_n(Q + A)\,\middle|\,Q + \frac{A}{2}\,\middle|\,\Phi_m(Q)\right\rangle = (n - m)\cdot F_{n,\,m}(A) = A\left\langle \Phi_m(Q)\,\middle|\,Q + \frac{A}{2}\,\middle|\,\Phi_n(Q + A)\right\rangle \tag{B.6}$$

$$A\left\langle \Phi_n(Q + A)\,\middle|\left(Q + \frac{A}{2}\right)\frac{\mathrm{d}}{\mathrm{d}Q}\middle|\,\Phi_m(Q)\right\rangle = (n - m)\,G_{n,\,m} + \left(\frac{m - n}{A} + \frac{A}{2}\right)F_{n,\,m} \tag{B.7}$$

$$A\left\langle \Phi_m(Q)\,\middle|\left(Q + \frac{A}{2}\right)\frac{\mathrm{d}}{\mathrm{d}Q}\middle|\,\Phi_n(Q + A)\right\rangle = (m - n)\,G_{n,\,m} + \left(\frac{m - n}{A} - \frac{A}{2}\right)F_{n,\,m}\,. \tag{B.8}$$

By means of (B.4) to (B.7) one finds the matrix elements up to second order in α. If higher orders are needed one easily extends the procedure described above.

Appendix C

Numerical Calculation of Franck-Condon Integrals

WAGNER[16] found the Franck-Condon Integrals

$$F_{n,\,m}(A) := \int \Phi_n(Q + A)\,\Phi_m(Q)\,dQ \tag{C.1}$$

for $m \geqq n$ to have the form

$$F_{n,\,m}(A) = \exp(-A^2/4)\left(\frac{A}{\sqrt{2}}\right)^{m-n}\sqrt{\frac{n!}{m!}}\,\mathscr{L}\!\left(\frac{A^2}{2}\right) \tag{C.2}$$

For $n > m$ one takes the relation

$$F_{n,\,m}(A) = F_{m,\,n}(-A)\,. \tag{C.3}$$

$\mathscr{L}_n^{(k)}(x)$ means Laguerre's polynomial

$$\mathscr{L}_n^{(k)}(x) := \sum_{\nu=0}^{n} \binom{n+k}{n-\nu} \frac{(-1)^\nu}{\nu!} x^\nu =: \sum_{\nu=0}^{n} c_\nu x^\nu . \quad \text{(C.4)}$$

For numerical evaluation one must pay attention on the fact, that the known recurrence formulae give rather inexact results, since one uses differences of great numbers of equal order. Hence we calculate the $\mathscr{L}_n^{(k)}$ directly observing the recurrence formula for the coefficients c_ν.

$$c_{\nu+1} = - c_\nu \frac{(n-\nu)}{(\nu+1)(\nu+k+1)} \quad \text{(C.5)}$$

with the normalization

$$c_0 = \binom{n+k}{n} .$$

Using a symbolic notion we obtain the following ALGOL procedure.

```
   IF  n > m  THEN  BEGIN  h :=m;  m := n;
n := h; a := − a; END; s := c : (a/√2) ∗ (m − n)
∗ exp(− a∗a/4)∗sqrt(n!/m!)∗(m!/((m − n)!∗n!));
l := m − n;
x := a ∗ a/2;
FOR i := 0 STEP 1 UNTIL n − 1 DO
BEGIN
    c := − c ∗ a ∗ ∗ (n − i)/((i + 1) ∗ (i + l + 1));
    s := s + c;
END.
```

Non Radiative Electronic Transitions in Ionic Crystals II *

Reaction Formalism and Results

Alf Löffler

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(Z. Naturforsch. **24 a**, 530—539 [1969]; received 18 December 1968)

A general formalism to describe radiationless electronic decay (RED) is developed. Two conditions are derived that must be fulfilled to make RED possible. Using the data derived in part I of this paper the general formulae are applied to a F-center in KCl and MgO. In KCl the conditions for RED are not fulfilled while in MgO RED proves to be more probable than radiative decay. This is in complete agreement with experimental knowledge.

Introduction

To describe a quantum process it is necessary to calculate wave functions, energy eigenvalues and matrix elements in advance. This has been done in part I of this paper[1]. We did show that the dynamical coupling of the electronic state with the lattice vibrations could be expressed approximately by one normal mode with frequency ω_l. Recently Rampacher[2] did prove electronic decay processes to be possible if and only if the states are coupled with a system having a continuous energy spectrum. Since by the non adiabatic interactions of the electron with the lattice the discrete electronic levels are coupled with the discrete energy levels of a localized mode, decay seems impossible in contrast to experimental knowledge. The solution of the problem is given with regard to the fact, that anharmonic terms couple the discrete mode ω_l with the continuous acoustical frequencies.

We calculate transition probabilities by means of the resolvent method of Rampacher[2], which is slightly modified to get expressions that could be treated easier numerically. The general formulae then are discussed for two examples: The anion vacancy in MgO is shown to induce radiationless electronic decay (RED), whereas the same imperfection prefers optical transitions in KCl. These results are in best agreement with experimental knowledge: A F-center emission band in MgO until now has not been detected whereas in KCl the F-center emission band about 1.1 eV is well known. It is shown that the probability for RED at an anion vacancy depends on temperature, too. No attempt is made to derive the reaction formulae known from the phenomenological theories, what is kept for future work.

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* Thesis in partial fulfillment of the conditions for graduation at the „Mathematisch-naturwissenschaftliche Fakultät der Universität Tübingen".

[1] A. Löffler, Z. Naturforsch. (to be published) quoted hence forth by I.

[2] H. Rampacher, Z. Naturforsch. **23 a**, 401 [1968].