MOMENTS OF A→T ABSORPTION BAND IN ACTIVATED CRYSTALS

BY

JOHN FRANCIS KOGA

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This thesis is my original work and has not been presented for a degree in any other University

Signature_____

JOHN FRANCIS KOGA

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This thesis has been submitted for examination with my approval as University Supervisor

Signature_____

DR. T.S. DODD

DEPARTMENT OF PHYSICS
KENYATTA UNIVERSITY
P.O. BOX 43844
NAIROBI, KENYA

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ABSTRACT

On the basis of matrix formalism of method of moments developed by Perlin and Tsukerblat [20], we have calculated theoretically the second and third moments of A→T absorption band in U-centre of KBr and NaI. The electron-phonon interaction was expressed in a point-lattice model in linear approximation and the phonon sum appearing in the formulae for the moments was taken in Debye's approximation for acoustical and Einstein's approximation for optical phonons with cut off wave vector $\chi_D = \frac{(3\pi^2)^{1/3}}{a_0}$, where a_0 is the nearest neighbour distance. The calculated values of second moment, σ_2, are 8.01×10^{-3} eV^2 and 14.43×10^{-3} eV^2 at $7^{o}K$ and $78^{o}K$ respectively, and that of third moment, σ_3, which is temperature independent, is 10.30×10^{-5} eV^3 for KBr. While the experimental values for the second and third moments are $\sigma_2(7^{o}K)=(12.50\pm0.8)\times10^{-3}$ eV^2, $\sigma_2(78^{o}K)=(17.2\pm0.9)\times10^{-3}$ eV^2 and $\sigma_3=10.90\times10^{-5}$ eV^3 [34]. Similar calculations were done for NaI crystal and they are found to be $\sigma_2(7^{o}K)=7.18\times10^{-3}$ eV^2, $\sigma_2(78^{o}K)=12.82\times10^{-3}$ eV^2 and $\sigma_3=8.97\times10^{-5}$ eV^3. With the help of Edgeworth Series, where the band shape function is expressed in terms of Gaussian Curve as trial function and the moments of the spectrum, we have calculated the half-widths of the absorption spectra, which are found to be 0.21 eV and 0.28 eV at $7^{o}K$ and $78^{o}K$ respectively for KBr, while the corresponding

experimental values are 0.25eV and 0.30eV. For NaI crystal, the half-widths are found to be 0.20eV and 0.27eV at 7^{o}K and 78^{o}K respectively. These results show that the point-ion model for crystal field and the Extended Brillouin Zone scheme for phonon sum are applicable to the absorption spectrum by p-electron of U-centre in alkali halide crystals.

INTRODUCTION

The optical absorption spectra of impurity crystals and colour centres in crystal consist of a broad band shape unlike the discrete lines in the isolated atoms. The first theory of optical absorption in impurity crystal given in early fifties by Pekar [1,2], Huang Kun and A.R. Rhys [3] and Davidov [4,5] was based on the application of adiabatic approximation (separation of electronic motion of impurity centre from the nuclear motion of the surrounding crystal lattice), which is true for a system of two non-degenerate electronic levels. The inclusion of interaction of optical electrons with the lattice vibration of the surrounding atoms/ions, by these authors, could explain not only the appearance of broad band shape of the absorption spectra but also the novelty of the many-phonon absorption. Many-phonon band consists of superposition of lines, corresponding to the transitions from each electron-vibrational level of initial state to each level of the final state. Since the adiabatic approximation is applicable to find the electron-vibrational functions and energy states for the non-degenerate system, so the main problem of theory of optical transition between the singlet terms, which consists of quantum-statistical average of probability of initial state and summation over the final states, was solved in the above cited

papers [1,5]. In these papers [1,3], the dispersion and frequency effects of lattice vibrations were neglected and the optical absorption band so obtained, consists of equidistant absorption lines, separated by the frequency of lattice vibration ω (fig 1.). Ω_{ps} is the frequency of pure electronic transition.

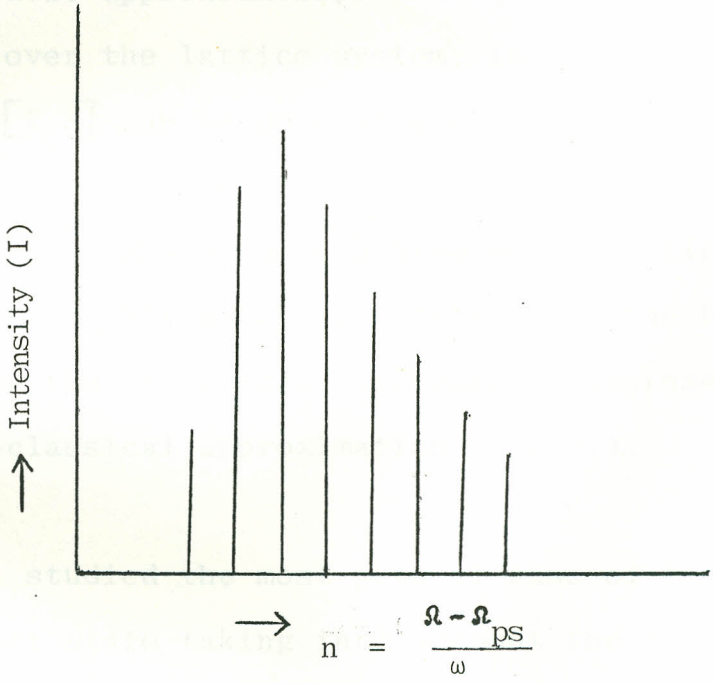


Fig. 1. Optical absorption spectrum on neglecting the dispersion of lattice vibrations

Taking into account the dispersion, the lines corresponding to n→n' transitions, are broadened forming a bell-shaped band, which is not symmetrical about its maximum, but at high temperature it transforms into a Gaussian Curve.

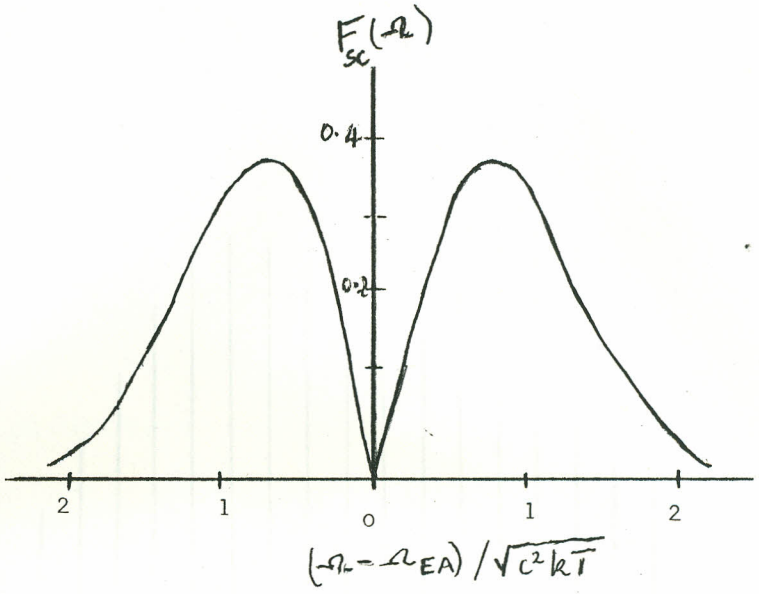
In the presence of electronic degeneracy, according to Jahn-Teller (JT) Theorem [6], the

symmetrical nuclear configuration is not stable and the JT stabilization energy is of the order of the energy of the lattice vibration involved in coupling. So the criterion of applicability of adiabatic approximation is not satisfied and hence electron-vibrational states cannot be determined on the basis of adiabatic approximation. But quantum-statistical average over the lattice system, in the presence of JT Effect [7,8] can be done in general form.

Toyozawa and Inoue [9] studied theoretically the singlet-multiplet A→E(e) and A→T(t) (in the brackets are shown the vibrational irreducible representation) in semi-classical approximation (fig 2.).

Cho [10] studied the most general case of transition to triplet state taking into account the interaction with symmetrical, tetragonal and trigonal lattice vibrations and also spin-orbit interaction. This semi-classical approximation is still adiabatic approximation and JT interaction is not very important.

Today we know some of the quantum mechanical calculation of band shape of optical transitions between the degenerate electronic state [11,12,13] and lines so obtained for each transition are replaced by Gaussian curves (see fig 3.). Thus the optical lines are expressed by envelopes of these lines.



(a)

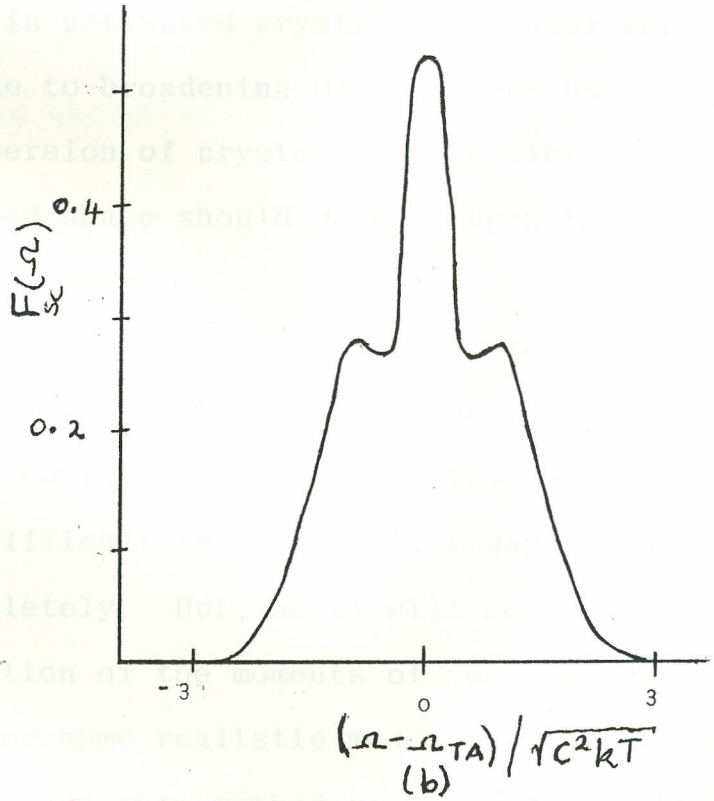


Fig. 2. Spectral curve for (a) A→E(e) transition (b) A→T(t) transition, in semiclassical approximation. c is coupling constant.

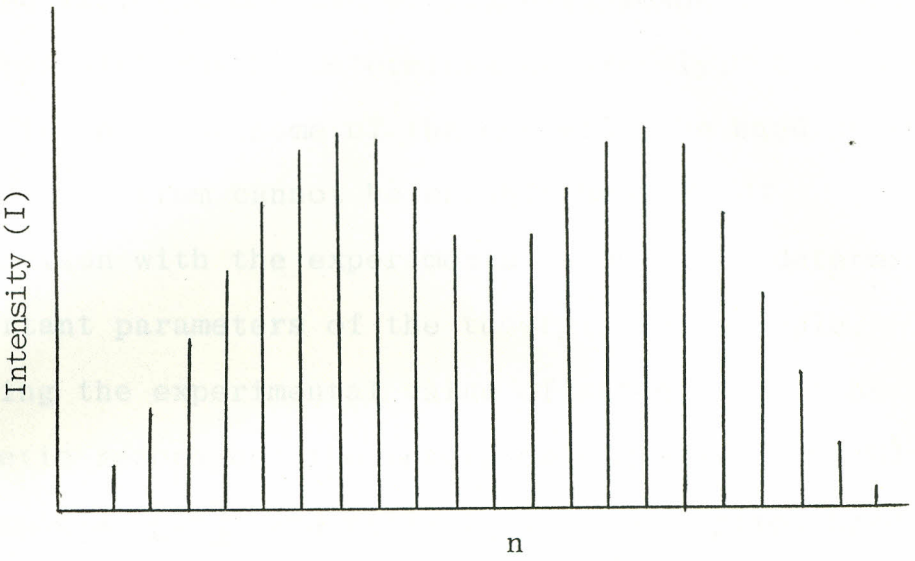


Fig. 3. Vibronic structure of A→E(e)

But the reason for the broad band shape of optical absorption in activated crystal and colour centres is not much due to broadening of the lines but more due to the dispersion of crystal lattice vibrations. Thus the band shape should depend upon the parameters of phonon-spectrum.

So summarizing all this we conclude that theoretical computation of the optical absorption band is a very difficult task and till today has not been solved completely. But, as it will be shown below, the calculation of the moments of spectral distribution function, for some realistic model of impurity centre, is possible, and this method of moments will be applied to study the optical absorption spectra of colour centres in crystals.

It was Van-Vleck [14] , who for the first time showed that the moments of magnetic resonance spectrum of crystals, can be determined accurately. Although, with the help of some of the moments, the band shape of the spectrum cannot be established, their comparison with the experiments helps us to determine important parameters of the theory. For example, knowing the experimental value of second moment of magnetic resonance, the interatomic distance (N-H) in ammonia [15] and half-width of absorption band of magnetic resonance in CaF_2 [16] can be determined. Later Lax [17] applied this technique of moments to the optical absorption due to singlet-singlet transition, where adiabatic approximation can be applied to determine the energy states of the system in which JT Effect has no role to play.

Henry, Schnatterly and Slichter developed the method of moments to analyse the effect of applied external fields on the optical properties of colour centres [18] . In 1975, Perlin and Tsukerblat [19,20] gave the matrix formalism of the method of moments which is based on the group theoretical knowledge, such that all the formulae for the moments and their changes under perturbation are put in a compact matrix form, which are easy and simpler to operate for any particular centre of some definite symmetry. Later this matrix formalism was extended to

the anisotropic centres in cubic crystal by Perlin et. al [21] .

CHAPTER I

BAND SHAPE FUNCTION OF IMPURITY CENTRES

§1. Hamiltonian of Impurity - Phonon System

Crystals which are made of its constituent atoms or ions are known as pure crystals e.g. C, CdS, NaCl. These crystals have definite characteristic properties. These characteristic properties may be changed by adding impurities of different elements. The impurity atoms can occupy two positions - interstitial or lattice site. These are known as interstitial impurity and substitutional impurity respectively.

The impurity atoms or ions in slightly doped crystals are usually considered as a gas of particles suspended in a condensed medium. The impurity atoms are found to absorb light in the visible region of the energy spectrum.

The total Hamiltonian of a crystal contains a very large number of space and momentum coordinates of all the electrons and atoms. But the Hamiltonian of impurity - phonon system can be constructed with the help of adiabatic approximation. In this approximation, the tightly bound electrons of the host crystals and core electrons of the impurity centre is considered a

fast subsystem, whose state does not change when the impurity optical transition takes place. While the weakly bound electrons of the impurity centre together with the nuclei form a slow subsystem. Under these assumptions the Hamiltonian of impurity-phonon system can be written as

$$H = H_e(\vec{r}) + H_L(\vec{q}) + H_{eL}(\vec{r},\vec{q}) \text{ ---------- } (1.1)$$

where,

H_e is the electronic Hamiltonian, including both the Hamiltonian of impurity electrons and the energy of their interaction with the static crystal surrounding i.e. crystal field,

H_L is the Hamiltonian of the free lattice vibrations of the host crystal, and

H_{eL} is the Hamiltonian of the interaction of the electrons of the impurity centre with the thermal lattice vibrations, known as electron-phonon interaction (EPI).

The crystal field in H_e possesses a lower symmetry than the spherical symmetry of the free atom and hence gives rise to an energy-level splitting.

For any system of n electrons each of mass m, and N nuclei of mass M_α, the classical non-relativistic Hamiltonian is,

$$\hat{H} = \sum_{i=1}^{n} \frac{\hat{P}_i^2}{2m} + \sum_{\alpha=1}^{N} \frac{\hat{P}_\alpha^2}{2M_\alpha} + \hat{V} \qquad \text{--- (1.2)}$$

where $\hat{P}_i$ and $\hat{P}_\alpha$ are the momenta of the ith electron and αth nucleus respectively, and V is the total potential energy. This is the sum of nucleus-electron attraction terms, electron-electron repulsion terms and nucleus-nucleus repulsion terms [22]. Thus

$$\hat{V} = \frac{1}{4\pi\varepsilon_0} \sum_{\alpha,\beta=1}^{N} \sum_{i,j=1}^{n} \left(\frac{Z_\alpha Z_\beta e^2}{|\vec{R}_\alpha - \vec{R}_\beta|} - \frac{Z_\alpha e^2}{|\vec{R}_\alpha - \vec{r}_i|} + \frac{e^2}{|\vec{r}_i - \vec{r}_j|} \right) \text{--- (1.3)}$$

where $Z_\alpha e$ is the positive charge of αth nucleus whose position vector is $\vec{R}_\alpha$, and $\vec{r}_i$ is the position vector of ith electron. Therefore the expression for electronic Hamiltonian H_e can be written as

$$\hat{H}_e = \sum_{i} \frac{\hat{P}_i^2}{2m} + \frac{1}{4\pi\varepsilon_0} \sum_{\alpha=1}^{N} \sum_{i,j=1}^{n} \left(\frac{e^2}{|\vec{r}_i - \vec{r}_j|} - \frac{Z_\alpha e^2}{|\vec{R}_\alpha - \vec{r}_i|} \right) \text{--- (1.4)}$$

In pure Harmonic Approximation, lattice vibrations are harmonic oscillators. The condition for harmonic motion to occur is the presence of a restoring force, which is proportional to the displacement, that acts to return the system to its equilibrium configuration when it is disturbed [24,25]. The Hamiltonian of harmonic oscillator is given by sum of kinetic energy and potential energy. Thus

$$\hat{H}_L = \frac{\hat{P}^2}{2m} + M\omega^2 R^2 \qquad \text{--- (1.5)}$$

where R is the displacement from equilibrium position and ω is the angular frequency of vibration. This can be expressed in terms of normal coordinates $q_{\vec{\kappa}}$ of harmonic lattice vibration, as follows

$$\hat{H}_L = \frac{1}{2} \sum_{\vec{\kappa}} \hbar \omega_{\vec{\kappa}} \left(q^2_{\vec{\kappa}} - \frac{\partial^2}{\partial q^2_{\vec{\kappa}}} \right) \qquad \text{(1.6)}$$

where $\vec{\kappa}$ is a wavevector of lattice vibration.

And in the language of second quantization [25], this can be expressed as

$$\hat{H}_L = \sum_{\vec{\kappa}} \hbar \omega_{\vec{\kappa}} \hat{c}^+_{\vec{\kappa}} \hat{c}_{\vec{\kappa}} \qquad \text{(1.7)}$$

where $\hat{c}^+_{\vec{\kappa}}$ and $\hat{c}_{\vec{\kappa}}$ are creation and annihilation phonon operators.

In first order approximation (linear approximation) the Hamiltonian H_{eL} is expressed as follows (see §4.)

$$\hat{H}_{eL} = \sum_{\vec{\kappa}} \hat{v}_{\vec{\kappa}}(\vec{r}) \hat{q}_{\vec{\kappa}} \qquad \text{(1.8)}$$

where, $\hat{v}_{\vec{\kappa}}(\vec{r})$ is electronic operator.
This H_{eL} gives rise to the well known optical manifestations: temperature shift and broadening of the spectral lines, appearance of the broad optical bands, and the optical phenomena arising from the JT Effect, which is the subject of our thesis.

§2: Absorption coefficient of light

Let $S(\Omega)$ be the spectral density of the emission flow of light frequency Ω, propagating along the Z-axis of a crystal. The attenuation of the intensity due to light absorption in the interval dz is given as

$$dS(\Omega, z) = -K(\Omega)\, S(\Omega, z)\, dz \qquad \text{---------} \quad (2.1)$$

where $K(\Omega)$ is the light-absorption factor.
Taking integration, we find

$$S(\Omega, z) = S(\Omega, 0)\, e^{-K(\Omega) z} \qquad \text{--------} \quad (2.2)$$

which is Lambert-Bugger rule.
The change in the spectral density of the emission flow is due to the absorption by the electrons of the impurity centre. If N is the number of absorbing centre per unit volume and each centre absorbs energy equal to

$$\hbar\Omega_{fi}$$

then N centres will absorb

$$N\hbar\Omega_{fi} \qquad \text{----------} \quad (2.3)$$

But absorption depends on the transition probability per second, $\omega_{i\to f}$, that such transition will take place and the depth of the centre from the surface of the crystal. Hence energy absorbed per unit time per unit

area through depth dz is given by

$$N\hbar\Omega_{if}\,\omega_{i\to f}\,dz \qquad \text{----------} \quad (2.4)$$

which should be equal to the change in spectral density of emission flow eq.. (2.1).

To find the expression for $\omega_{i\to f}$ we use conventional quantum electrodynamics methods. Assuming a media with dispersionless dielectric permeability ($\varepsilon_\infty = n^2$), the vector potential operator of the electromagnetic field (in the Coulomb gauge) is given by

$$\hat{A}(r,t) = \sum_{qp}\left(\frac{2\pi\hbar c^2}{V\Omega_q\varepsilon_\infty}\right)^{1/2}\vec{e}_p(q)\left\{\hat{a}_{qp}\,e^{i(\vec{q}\cdot\vec{r}-\Omega_p t)} + h.c\right\} \quad \text{---} \quad (2.5)$$

where V is the crystal volume

q and p are the photon wavevector and polarization index respectively.

$\vec{e}_p$ is the polarization unit vector

$\hat{a}^{+}_{qp}$ and $\hat{a}_{qp}$ are the photon creation and annihilation operators

and

$$\vec{e}_p \cdot \vec{q} = 0 \qquad \text{----------} \quad (2.6)$$

due to transversality of the electromagnetic excitations.

$$\Omega_q = \frac{c}{n}\,q \qquad \text{----------} \quad (2.7)$$

Equation (2.5) leads to the following relation for the

number of photons per unit crystal volume:

$$N_{phot} = \frac{2\pi^2 c^2 S(\Omega)}{V n^2 \hbar \Omega^3} \qquad \text{----------} \quad (2.8)$$

and for the probability (per second) of stimulated dipole optical transition, we have the expression

$$\omega_{i\to f} = \frac{4\Omega_{fi}^3}{3\hbar c^3} |d_{fi}|^2 n N_{phot} V \qquad \text{---------} \quad (2.9)$$

where $d_{fi} \equiv \langle f|\hat{d}|i\rangle$ matrix element of electric dipole moment $\vec{d} = -e.\vec{r}$ of electron between final $|f\rangle$ and initial state $|i\rangle$ states.

Equations (2.1) and (2.4) are equivalent, thus we get

$$K(\Omega_{if}) = \frac{N\hbar\Omega_{if}\omega_{i\to f}}{S(\Omega_{if})} \qquad \text{----------} \quad (2.10)$$

Using eqs. (2.8) and (2.9), the light absorption coefficient for i→f single transition is found to be:

$$K_{if}(\Omega_{fi}) = \frac{8\pi^2 \Omega_{fi} |d_{fi}|^2 N}{3\hbar c n} \qquad \text{--------} \quad (2.11)$$

For total absorption coefficient due to all transitions we have to sum over all the final states and average it over the initial states using the occupation probability of the initial states,

$$K = \sum_{if} \rho_i K_{if}(\Omega_{fi})$$

$$= \sum_{if} \rho_i \int K_{if}(\Omega)\, \delta(\Omega - \Omega_{fi})\, d\Omega \quad \text{---} \quad (2.12)$$

where ρ_i is the occupation probability of initial states [26] given as,

$$\rho_i = \frac{e^{-E_i/kT}}{\sum_i e^{-E_i/kT}} \quad \text{-----} \quad (2.13)$$

In the equation (2.12) we have ignored the effect of population of final states since

$$\hbar\Omega >> kT$$

for all available temperatures, where k is Boltzman constant.

Now let $$K = \int \chi(\Omega)\, d\Omega \quad \text{----------} \quad (2.14)$$

where $\chi(\Omega)$ is the spectral density of the absorption coefficient.

Then from equation (2.12)

$$\chi(\Omega) = \sum_{if} \rho_i K_{if}(\Omega)\, \delta(\Omega - \Omega_{if}) \quad \text{----} \quad (2.15)$$

Putting in the expression for $K_{if}(\Omega)$ (2.11), we get

$$\chi(\Omega) = \frac{8\pi^2 N \Omega}{3\hbar c n} \sum \rho_i |d_{fi}|^2\, \delta(\Omega - \Omega_{if}) \quad \text{--} \quad (2.16)$$

which is written as,

$$\chi(\Omega) = \frac{8\pi^2 N \Omega}{3\hbar c n} F(\Omega) \qquad \text{---(2.17)}$$

where

$$F(\Omega) = \sum \rho_i |\hat{d}_{fi}|^2 \delta(\Omega - \Omega_{if}) \qquad \text{-----} \quad (2.18)$$

is the so-called band-shape function. This band-shape function, $F(\Omega)$, of the electric-dipole transition characterises the absorption spectrum $\chi(\Omega)$ apart from Ω.

§3. Quantum Mechanical representation of shape function

Now let us represent the band-shape function by means of the time-correlation function. Substituting

$$\delta(\Omega - \Omega_{fi}) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i(\Omega - \Omega_{fi})t} \, dt$$

into equation (2.18), the band-shape function becomes

$$F(\Omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \sum_{if} \rho_i |\langle f | \hat{d} | i \rangle|^2 e^{i(\Omega - \Omega_{fi})t} \, dt \qquad \text{---(3.1)}$$

which can be written as

$$F(\Omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i\Omega t} I(t) \, dt \qquad \text{----} \quad (3.2)$$

where,

$$I(t) = \sum_{i,f} \rho_i \left| \langle f | \hat{d} | i \rangle \right|^2 e^{i(E_f - E_i)t/\hbar} \qquad \text{---(3.3)}$$

since $$\omega_{if} = \frac{E_f - E_i}{\hbar} \qquad \text{--------} \quad (3.4)$$

If the initial state is in thermodynamic equilibrium, then

$$\rho_i = \frac{e^{-E_i/kT}}{\sum_i e^{-E_i/kT}} = \frac{e^{-E_i/kT}}{Tr\, e^{-\hat{H}/kT}} = \frac{e^{-E_i/kT}}{Z} \qquad \text{--(3.5)}$$

E_i is the eigenvalue of $\hat{H}$, Z is the partition function of Impurity-phonon system. Converting I(t),

$$I(t) = \frac{1}{Z} \sum_{if} e^{-\frac{E_i}{kT}} \langle i | \hat{d}^+ | f \rangle \langle f | \hat{d} | i \rangle e^{\frac{i(E_f - E_i)t}{\hbar}} \qquad \text{--(3.6)}$$

into operator form

$$I(t) = \frac{1}{Z} \sum_{if} \langle i | e^{-\frac{\hat{H}}{kT}} \hat{d}^+ | f \rangle \langle f | e^{\frac{i\hat{H}t}{\hbar}} \hat{d} e^{-\frac{i\hat{H}t}{\hbar}} | i \rangle \qquad \text{--(3.7)}$$

which is rewritten as,

$$I(t) = \frac{1}{Z} \sum_{i} \langle i | e^{-\frac{\hat{H}}{kT}} \hat{d}^+ \hat{d}(t) | i \rangle \qquad \text{--(3.8)}$$

where

$$\hat{d}(t) = e^{\frac{i\hat{H}t}{\hbar}} \hat{d}\, e^{-\frac{i\hat{H}t}{\hbar}} \qquad \text{----(3.9)}$$

We can write equation (3.8) as

$$I(t) = \frac{1}{Z} \mathrm{Tr}\left[e^{-\hat{H}/kT}\, \hat{d}^{+}\, \hat{d}(t)\right] \qquad ---(3.10)$$

Therefore the band-shape function becomes,

$$F(\Omega) = \frac{1}{2\pi Z}\int_{-\infty}^{\infty} e^{i\Omega t}\, \mathrm{Tr}\left[e^{-\hat{H}/kT}\, \hat{d}^{+}\, \hat{d}(t)\right] dt \qquad ---(3.11)$$

But the quantum statistical average of an operator $\hat{A}$ [27] is given as

$$\langle \hat{A} \rangle = \frac{\mathrm{Tr}\left(e^{-\hat{H}/kT}\, \hat{A}\right)}{Z} \qquad ---(3.12)$$

Thus

$$F(\Omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{i\Omega t} \langle \hat{d}^{+}\, \hat{d}(t) \rangle\, dt \qquad ---(3.13)$$

Equation (3.13) has been derived under the assumption that the final excited states are empty. In particular, the correction connected with the stimulated emission is neglected. If we take into account this correction we have to multiply (3.13) by a factor $\left(1 - e^{-\frac{\hbar\Omega}{kT}}\right)$. Since for the optical region the inequality $\hbar\Omega \gg kT$ holds for all temperatures, this factor is replaced by unity and our equation (3.13) is a true equation.

§4. Theory of electron-phonon interaction

(Point-Ion Model)

The calculations of optical characteristics of electron-lattice system is possible only for some definite model for electron states and operator of electron-phonon interaction. Without going into the details of the electron states of impurity centre we devide the impurity centres into two categories: One - the impurity centers, whose effective radius of electronic state is greater than lattice constant, second - for which this effective radius is less than lattice constant. In the former case, the electron-phonon interaction operator is written in macroscopic approximation. The examples are the interaction operator of longitudinal optical lattice vibration with polarons. In the second case, the interaction of electron of impurity centre with lattice vibration is calculated on the basis of quasi-molecular model of crystal lattice. This model serves well for the p-, d- and f- electrons of the impurity centres. Here, we are considering the second case, which is known as the impurity centre of small radius.

In this case, it is supposed that the interaction of electrons of impurity-centres with lattice vibrations of the surrounding lattice atom/ions is due to a modulation of the crystal field by the lattice vibrations.

If

$$\hat{W}(\vec{r}_i \cdots \vec{R}_\alpha) = \sum_{i,\alpha} \left(\frac{1}{4\pi\varepsilon_0}\right) \frac{ee^*}{|\vec{r}_i - \vec{R}_\alpha|} \quad \text{----- (4.1)}$$

is the electrostatic potential energy of electrons of impurities with the lattice points of the surrounding, and

$$\Delta\vec{R}_\alpha = \vec{R}_\alpha - \vec{R}^0_\alpha \quad \text{---------- (4.2)}$$

is the displacements of αth lattice point from equilibrium position $\vec{R}^0_\alpha$, which is small as compared to lattice constant, then, for first order of displacements, the electron phonon interaction operator can be expressed as

$$\hat{H}_{eL} = \sum_{i,\alpha} \left(\frac{\partial \hat{W}(\vec{r}_i \cdots \vec{R}_\alpha)}{\partial R_\alpha} \Big|_{R_\alpha = R^0_\alpha}, \Delta\vec{R}_\alpha \right)$$

$$= \sum_{i,\alpha} \left(\vec{\nabla}_\alpha \frac{ee^*}{4\pi\varepsilon_0 |\vec{r}_i - \vec{R}_\alpha|} \Big|_{\vec{R} = \vec{R}^0_\alpha}, \Delta\vec{R}_\alpha \right) \text{------ (4.3)}$$

where e*- is the effective charge of the lattice point.

Similarly we can express $\hat{H}_{eL}$, in second order of displacements (which we are not considering in our case).

Using Group Theory, the actual displacement can be transformed into symmetrized displacement with the help of projection operator [28]. Considering the crystal

with an isolated centre as quasi-molecule with point-group symmetry G, we can transform the actual displacements to symmetrized displacements using, the following transformation: $\vec{Q}_{\bar{\Gamma}\bar{\gamma}} = \hat{P}^{(\bar{\Gamma})}_{\bar{\gamma}\bar{\gamma}} \vec{\Delta R}_\alpha$

where $\hat{P}^{(\bar{\Gamma})}_{\bar{\gamma}\bar{\gamma}}$ is the projection operator

$$\vec{Q}_{\bar{\Gamma}\bar{\gamma}} = \frac{g(\bar{\Gamma})}{g} \sum_{\vec{G}} D^{(\bar{\Gamma})}_{\bar{\gamma}\bar{\gamma}}(\hat{G})\, \hat{G}\, \vec{\Delta R}_\alpha \qquad \text{----} \quad (4.4)$$

$\bar{\Gamma}$ - irreducible representation for the lattice vibration

$\bar{\gamma}$ - index of row of $\bar{\Gamma}$

$\hat{G}$ - symmetry operator

$g(\bar{\Gamma})$ - dimension of $\bar{\Gamma}$

g - order of the group G

$D^{(\bar{\Gamma})}_{\bar{\gamma}\bar{\gamma}}(\hat{G})$ - matrix representation for the symmetry operation

$\vec{Q}_{\bar{\Gamma}\bar{\gamma}}$ - symmetrized displacements and are formed in the same way as the normal coordinates.

And finally eq. (4.3) H_{eL} can be expressed as

$$\hat{H}_{eL}(\vec{r}, \vec{q}) = \sum_{\bar{\Gamma}\bar{\gamma}} \hat{V}_{\bar{\Gamma}\bar{\gamma}}(\vec{r})\, \hat{Q}_{\bar{\Gamma}\bar{\gamma}} \qquad \text{----(4.5)}$$

where

$\hat{V}_{\bar{\Gamma}\bar{\gamma}}(\vec{r})$ are the electronic irreducible tensor operators of type $\bar{\Gamma}$ transforming like the corresponding symmetrized coordinates $\vec{Q}_{\bar{\Gamma}\bar{\gamma}}$ under the symmetry operations of the point group,

which are expressed as,

$$\hat{V}_{\bar{\Gamma}\bar{\gamma}} = \sum_{\alpha,i} \frac{\partial \hat{W}}{\partial R_{\alpha i}}\Big|_{R_\alpha = R_\alpha^0} \frac{\partial R_{\alpha i}}{\partial Q_{\bar{\Gamma}\bar{\gamma}}} = \sum_{\alpha,i} \frac{\partial \hat{W}}{\partial R_{\alpha i}} \cdot \frac{\partial Q_{\bar{\Gamma}\bar{\gamma}}}{\partial R_{\alpha i}} \quad ---(4.6)$$

$$\text{since } \frac{\partial R_\alpha}{\partial Q_{\bar{\Gamma}\bar{\gamma}}} = \frac{\partial Q_{\bar{\Gamma}\bar{\gamma}}}{\partial R_{\alpha i}} \quad ---(4.7)$$

On the other hand, $\vec{\Delta R}_\alpha$ which appear due to modulation of crystal field by the acoustical and optical normal modes of vibration, can be expanded in terms of the pure crystal normal modes with wavevectors $\vec{\kappa}$ and branch index ν [29]

$$\vec{\Delta R}_\alpha = \sum_{\vec{\kappa}\nu} \left(\frac{\hbar}{M\omega_{\vec{\kappa}\nu}}\right)^{1/2} \vec{e}_{\vec{\kappa}\nu} q_{\vec{\kappa}\nu} e^{-i\vec{\kappa}\vec{R}_\alpha^0} \quad ---(4.8)$$

where,

M - mass of crystal lattice

$\omega_{\vec{\kappa}\nu}$ - phonon frequency

$\vec{e}_{\vec{\kappa}\nu}$ - polarization vector

$q_{\vec{\kappa}\nu}$ - dimensionless normal coordinate of lattice vibration.

Due to the reality of Cartesian displacements $\vec{\Delta R}_\alpha$, it follows that $q_{\vec{\kappa}\nu} = q^*_{-\vec{\kappa}\nu}$ and $\vec{e}_{\kappa\nu} = \vec{e}_{-\kappa\nu}$

Putting the value of $\vec{\Delta R}_\alpha$, in equation (4.4) we can finally write

$$\vec{Q}_{\bar{\Gamma}\bar{\gamma}} = \sum_{\vec{\kappa}\nu} \left(\frac{\hbar}{M\omega_{\vec{\kappa}\nu}}\right)^{1/2} \vec{a}_{\vec{\kappa}\nu} q_{\kappa\nu} \quad -------(4.9)$$

where

$$\vec{a}_{\vec{\kappa}\nu} = \frac{g(\bar{r})}{g} \sum_{\hat{G}} D^{(\bar{r})}_{\bar{\gamma}\bar{\gamma}}(\hat{G})\, \hat{G} \times \vec{e}_{\vec{\kappa}\nu}\, e^{-i\vec{\kappa}\vec{R}^0_\alpha} \qquad ----(4.10)$$

which are known as Van-Vleck coefficients and satisfy the orthorgonality relation

$$\sum_{\Omega_{\vec{\kappa}}} \vec{a}_{\vec{\kappa}\nu}(\bar{r}\bar{\gamma})\vec{a}_{\vec{\kappa}\nu}(\bar{r}'\bar{\gamma}') = b_{\vec{\kappa}\nu}(\bar{r})\,\delta_{\bar{r}\bar{r}'}\delta_{\bar{\gamma}\bar{\gamma}'} \qquad --(4.11)$$

$$\sum_{\bar{r}\bar{\gamma}} \vec{a}_{\vec{\kappa}\nu}(\bar{r}\bar{\gamma})\,\vec{a}_{\vec{\kappa}\nu'}(\bar{r}\bar{\gamma}) = \delta_{\nu\nu'} \qquad ---(4.12)$$

where $\Omega_{\vec{\kappa}}$ means the integration w.r.t. the wavevector direction and averaging over the $\vec{e}$ direction.

The quantization of $\hat{H}_{eL}$ can be performed by introducing the creation and annihilation phonon operators $\hat{C}^{+}_{\vec{\kappa}\nu}$ and $\hat{C}_{\vec{\kappa}\nu}$,

$$\hat{Q}_{\vec{\kappa}\nu} = \frac{1}{\sqrt{2}}\left(\hat{C}^{+}_{\vec{\kappa}\nu} + \hat{C}_{\vec{\kappa}\nu}\right) \qquad -----(4.13)$$

As a result, the electron-phonon interaction Hamilitonian can be put as

$$\hat{H}_{eL} = \frac{1}{\sqrt{2}} \sum_{\vec{\kappa}\nu} \left(\hat{V}^{*}_{\vec{\kappa}\nu}\hat{C}_{\vec{\kappa}\nu} + \hat{V}_{\vec{\kappa}\nu}\hat{C}^{+}_{\vec{\kappa}\nu}\right) \qquad -----(4.14)$$

where

$$\hat{V}_{\vec{\kappa}\nu}(\vec{r}) = \sum_{\bar{r}\bar{\gamma}} \hat{V}_{\bar{r}\bar{\gamma}}(\vec{r}) \left(\frac{\hbar}{M\omega_{\vec{\kappa}\nu}}\right)^{1/2} \vec{a}_{\vec{\kappa}\nu} \qquad ------(4.15)$$

The Hamiltonian (4.14) is presented in conventional form of solid state theory and (4.15) enable us to devide this Hamiltonian into parts corresponding to irreducible representation of lattice vibration of quasi-molecule.

§5. Shape Function for optical transition from an adiabatic state: Non-degenerate to Degenerate transition

Further progress in the theory of band-shape is achieved by assuming that the initial electron-vibrational state $|i\rangle$ is adiabatic one. This means that both external and internal non-adiabaticities in this state are negligible. The former condition is achieved for the isolated electronic level, i.e. where the energy gap separating higher levels from the initial is larger relative to a typical phonon energy.

$$E_f - E_i \gg \hbar\omega \qquad \text{-------- (5.1)}$$

The latter condition is trivially satisfied for a non-degenerate electronic state.
Hence

$$\langle f | \hat{H}_{eL} | i \rangle = 0 \qquad \text{--------- (5.2)}$$

For the degenerate state, we assume that the non-adiabatic part of EPI Hamiltonian is sufficiently

small i.e.

$$\langle f | \hat{H}_{el} | f' \rangle \ll E_f - E_{f'} \quad \text{-------} \quad (5.3)$$

i.e. there does not exist the inter-multiplet vibronic mixing of the levels.

Thus, because of the unitary invariance of the trace of operator, we can write $F(\Omega)$ (Eq. 3.11) as follows:

$$F(\Omega) = \frac{1}{2\pi\hbar} \sum_{if} \int_{-\infty}^{\infty} e^{i\Omega t} dt \times \langle i | e^{-\frac{\hat{H}^i}{kT} + \frac{i\hat{H}^i t}{\hbar}} \hat{d}^+ | f \rangle \langle f | e^{-\frac{i\hat{H}^i t}{\hbar}} \hat{d} | i \rangle \quad \text{---} \quad (5.4)$$

where,

$\hat{H}^i$ is the initial Hamiltonian;

$|i\rangle$ and $|f\rangle$ are the initial and final eigenfunctions of this Hamiltonian respectively.

Since $\hat{d}$ operates on electron coordiantes, so it remains unchanged.

Considering the adiabatic case (ignoring non-adiabatic corrections to the energy and to the wavefunctions), the initial wavefunction can be written as

$$|i\rangle \simeq |A\rangle \prod_{\vec{n}} |n_{\vec{n}}\rangle \quad \text{-----} \quad (5.5)$$

$|A\rangle$ and $n_{\vec{n}}$ being the initial electronic wavefunction and the phonon occupation numbers respectively.

In this approximation we have

$$e^{\alpha \hat{H}} |i\rangle = e^{\alpha \hbar \Omega_i + \alpha \hat{H}_L} |i\rangle \qquad \text{---- (5.6)}$$

$$Z = \sum_i \langle i | e^{-\frac{\hat{H}}{kT}} | i \rangle = Z_L e^{-\frac{\hbar \Omega_i}{kT}} \qquad \text{---- (5.7)}$$

where $\hbar\Omega_i$ is an eigenvalue of the electronic Hamiltonian and

$$Z_L = \prod_{\vec{n}} \left(2 \sinh \frac{\beta_{\vec{n}}}{2}\right)^{-1}, \quad \beta_{\vec{n}} = \frac{\hbar \omega_{\vec{n}}}{kT} \qquad \text{----- (5.8)}$$

is the phonon partition function.

Further applying the spectroscopic stability principle, which is given as

$$\sum_f |f\rangle\langle f| = \sum_{f_0} |f_0\rangle\langle f_0| \qquad \text{----- (5.9)}$$

where $|f\rangle$ and $|f_0\rangle$ are the exact eigenfunctions of the Hamiltonians $\hat{H}^{(i)}$ and $\hat{H}_0^{(i)} = \hat{H}_e + \sum_{\vec{n}} \hbar \omega_{\vec{n}} \hat{C}_{\vec{n}}^{\dagger} \hat{C}_{\vec{n}}$ respectively, the wavefunction $|f_0\rangle$ is written as

$$|f_0\rangle = |\Gamma\gamma\rangle \prod_{\vec{n}} |n_{\vec{n}}^{(i)}\rangle \qquad \text{------- (5.10)}$$

where $|\Gamma\gamma\rangle$ is the wavefunction of the "non-self-consistent" or "Frank-Condon" excited electronic state. This wavefunction should be evaluated at a "frozen" nuclear configuration corresponding to its equilibrium position in the initial electronic state $|A\rangle$.

Since the phonon wavefunctions satisfy the requirement of functional completeness

$$\sum_{\vec{n}} |n_{\vec{n}}\rangle\langle n_{\vec{n}}| = 1 \qquad \text{------ (5.11)}$$

We can re-write the band-shape function (5.4) as

$$F(\Omega) = \frac{1}{2\pi} Av(A) \sum_{\Gamma\gamma} \int_{-\infty}^{\infty} dt\, e^{i(\Omega-\Omega_i)t} \times \langle\langle A| e^{\frac{i\hat{H}_L t}{\hbar}} \hat{d}^+ |\Gamma\gamma\rangle \times \langle\Gamma\gamma| e^{-\frac{i\hat{H}^i t}{\hbar}} \hat{d} |A\rangle\rangle_L \qquad \text{-- (5.12)}$$

where $\langle \cdots \rangle_L$ denotes the phonon average

Let us introduce the evolution operator [30] such that

$$e^{-\frac{i\hat{H}^i t}{\hbar}} = e^{-\frac{it}{\hbar}(\hat{H}_e^i + \hat{H}_L)} \hat{U}(t) \qquad \text{-- (5.13)}$$

This operator $\hat{U}(t)$ satisfies the equation of motion

$$i\hbar \frac{d\hat{U}(t)}{dt} = \hat{H}_{eL}(t)\, \hat{U}(t) \qquad \text{----- (5.14)}$$

The solution of this equation is written in the following form

$$\hat{U}(t) = T\, e^{-\frac{i}{\hbar}\int_0^t \hat{H}_{eL}(t_1)\, dt_1} \qquad \text{--- (5.15)}$$

where T is the time-ordering operator arranging the

time-dependent factors $\hat{H}_{eL}(t_1)$, $\hat{H}_{eL}(t_2)$....in chronological order $t_1 > t_2$

where

$$\hat{H}_{eL}(t) = e^{\frac{i\hat{H}_0 t}{\hbar}} \hat{H}_{eL} e^{-\frac{i\hat{H}_0 t}{\hbar}} \qquad -- \quad (5.16)$$

is the EPI operator in the interaction representation. Substituting equation (5.13) into equation (5.12) we obtain for the band-shape function

$$F(\Omega) = \frac{1}{2\pi} Av(A) \sum\sum \int_{-\infty}^{\infty} dt\, e^{i(\Omega - \Omega_{\Gamma A})t} \times \langle A|\hat{d}^+|\Gamma\gamma\rangle\langle\Gamma\gamma|\langle \hat{U}(t)\rangle_L |\Gamma'\gamma'\rangle\langle\Gamma'\gamma'|\hat{d}|A\rangle \qquad -- \quad (5.17)$$

where

$$\Omega_{\Gamma A} = \frac{\mathcal{E}_\Gamma - \mathcal{E}_A}{\hbar} \qquad ------ \quad (5.18)$$

is the frequency of Frank-Condon Transition, since the energy $\mathcal{E}_\Gamma$ is determined in fixed configuration $q_{\vec{n}}(A)$ of lattice subsystem.

Now let us use the limited basis, which includes all the excited states excluding the ground states whose Hamiltonian is written as $\hat{H}_e$. In this basis the matrix elements of $\hat{d}_\eta$ is to be replaced by one-column matrix, and Hamiltonian $\hat{H}_e$ and $\hat{H}_{eL}$ (including the evolution operator $\hat{U}(t)$) are expressed by square matrices. Shifting the origin for energy to $\mathcal{E}_\Gamma$, equation (5.17) can be written as

$$F_\eta(\Omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{i\omega t}\hat{d}_\eta^{+}\, e^{-\frac{i\hat{H}_e t}{\hbar}} \langle \hat{U}(t)\rangle_L \hat{d}_\eta\, dt \qquad (5.19)$$

where η is light polarization index .

Let us now include the external perturbation $\hat{W}$ to our electron phonon system, such that for further simplification, we express $\hat{H}_e$ as

$$\hat{H}_e = \hbar(\Omega_0 \hat{1} + \hat{W}) \qquad ----- \quad (5.20)$$

where $\hbar\Omega_0$ is the centre of gravity of the excited levels and is given by

$$\hbar\Omega_0 = \frac{Tr\,\hat{H}_e}{\sum [\Gamma]} \qquad ------ \quad (5.21)$$

$[\Gamma]$ - dimensions of irreducible representation Γ of excited state.

$\hat{W}$ - diagonal matrix such that Tr W=O.

The perturbation describes the splitting of the final excited state only. This perturbation involves both the internal interaction such as spin orbital, static crystal field as well as interaction with the external non-magnetic fields (electric and stress).

Thus, the shape function takes the form

$$F_{\eta}(\Omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dt\, e^{i(\Omega-\Omega_0)t} \times$$
$$\times \langle A|\hat{d}_{\eta}^{+} e^{-i\hat{W}t} \langle \hat{U}(t)\rangle_L \hat{d}_{\eta}|A\rangle \quad \text{---} \quad (5.22)$$

The transformation from coordinate representation, which was used to express the starting formulae, to matrix representation in limited basis, is not a unitary transformation and the commutative relation in coordinate representations are spoiled. For example, the operators $\hat{U}_{\vec{\kappa}}(\vec{r})$ which were commuting in coordinate representation, become now the non-commuting matrices. For computation of spectrum in above basis, we include only those excited states which are involved in the transition forming the said spectrum.

In terms of adiabatic approximation, the non-cummutatives of matrices $\hat{U}_{\vec{\kappa}}$ in limited basis means that the electronic wavefunction of excited state depends on phonon coordinates in zero order approximation. The problem becomes non-adiabatic, which does not allow the separation of electronic and nuclear motions, i.e. leads to JT effect in case of true degeneracy or to pseudo-JT effect for closely spaced levels. As discussed in the introduction that the analytical computation of absorption band is not possible in such cases, but at the same time, the formulae (5.22) allows us to get exact expressions for the moments.

CHAPTER II

MOMENTS OF OPTICAL BANDS

§6. Moments of optical bands: General formula

As discussed in the introduction, the analytical computation of the spectral bands is not possible for the degenerate electronic states of impurity-phonon system, but the integral characteristics of the band shape can be obtained by computing the moments of the spectral bands.

The moments of spectral distribution, $F(\omega)$, are defined as follows

The zeroth moment (band intensity) is given as

$$\langle \omega_0 \rangle = \int F(\omega)\, d\omega \qquad \text{--------} \quad (6.1)$$

First moment (centre of gravity) is expressed as

$$\langle \bar{\omega} \rangle = \frac{1}{\langle \omega_0 \rangle} \int \omega F(\omega)\, d\omega \qquad \text{---------} \quad (6.2)$$

Second moment which gives the half-width, is given by

$$\langle \omega_2 \rangle = \frac{1}{\langle \omega_0 \rangle} \int \omega^2 F(\omega)\, d\omega \text{----------} \quad (6.3)$$

The nth-order normalized moment is given as

$$\langle \Omega_n \rangle = \frac{1}{\langle \Omega_0 \rangle} \int \Omega^n F(\Omega)\, d\Omega \qquad \text{------ (6.4)}$$

If the moment is defined from the center of gravity, then the nth-order central normalized moment is defined as

$$\langle \Omega_n \rangle = \frac{1}{\langle \Omega_0 \rangle} \int F(\Omega)\, (\Omega - \bar{\Omega})^n\, d\Omega \qquad \text{------ (6.5)}$$

The integration in these equations (6.1)-(6.5) extends over the range $-\infty \leq \Omega \leq \infty$. Since light frequency $\Omega > 0$, the $F(\Omega)$ is assumed to be zero for $\Omega < 0$.

Substituting (5.22) for $F_\eta(\Omega)$ into equation (6.1) for the electric-dipole transition, we obtain the following expression for zeroth moment

$$\langle \Omega_0 \rangle_\eta = \sum_{\Gamma\gamma} \langle A | \hat{d}_\eta^{+} | \Gamma\gamma \rangle \langle \Gamma\gamma | \hat{d}_\eta | A \rangle = \hat{d}_\eta^{+} \hat{d}_\eta \qquad \text{----- (6.6)}$$

It is clear from equation (6.6) that band intensity does not depend on the perturbation.

Using the relation

$$\frac{1}{2\pi} \int_{-\infty}^{\infty} \Omega\, e^{i\Omega t}\, d\Omega = -i \frac{d}{dt} \delta(t) \qquad \text{---- (6.7)}$$

we get the following expression for first moment

$$\langle \bar{\Omega} \rangle_\eta = \Omega_0 + \Delta \bar{\Omega}_\eta \qquad \text{------ (6.8)}$$

where

$$\Delta \bar{\Omega}_\eta = \frac{1}{\langle \Omega_0 \rangle_\eta} \hat{d}_\eta^+ \hat{W} \hat{d}_\eta \qquad \text{------- (6.9)}$$

gives the change in the first moment due to the perturbation $\hat{W}$. These equations are valid for linear EPI, where $\langle \dot{\hat{U}}(0) \rangle_L = 0$. Thus, we see that the first moment does not involve phonon correction and turns out to be temperature independent. Phonon corrections of this kind appear through higher-order terms in the expansion of H_{eL} in nuclear displacements. [31].

And finally, the nth-order central moment is expressed as

$$\langle \Omega_n \rangle_\eta = \frac{1}{\langle \Omega^0 \rangle_\eta} \sum_{k=0}^{n} \binom{n}{k} \hat{d}_\eta^+ \left(\hat{W} - \Delta \bar{\Omega}_\eta \hat{1} \right)^{n-k} \times \hat{\sigma}_k \hat{d}_\eta \qquad \text{--- (6.10)}$$

where

$\binom{n}{k}$

are the binomial coefficients, and

$$\hat{\sigma}_k = i^k \frac{d^k}{dt^k} \langle \hat{U}(t) \big|_{t=0} \rangle_L \qquad \text{----- (6.11)}$$

The matrices $\hat{\sigma}_k$ determine the effect of the EPI on the band shape and its temperature dependence. They are known as the elementary moments of the unperturbed band shape. We notice that $\hat{\sigma}_0 = 1$ and $\hat{\sigma}_1 = 0$ for linear EPI. The higher order of moments are derived in next section.

§7. Second and Third moments

As said in §6, the phonon contribution to the first-order moment vanishes $(\hat{\sigma}_1 = 0)$ if we consider only the case of linear EPI. The higher order moments can be evaluated from equation (6.11). The kth-order derivative of evolution operator can be computed from (5.14) applying the differentiation rule for the Heisenberg operators (5.16). The second moment is written as (from eq. 6.11).

$$\hat{\sigma}_2 = i^2 \frac{d^2}{dt^2} \langle \hat{U}(t)|_{t=0} \rangle_L = - \langle \ddot{\hat{U}}(t)|_{t=0} \rangle_L \qquad \text{--- (7.1)}$$

Now from equation (5.14)

$$i\hbar \dot{\hat{U}}(t) = \hat{H}_{eL}(t) \hat{U}(t) + \dot{\hat{H}}_{eL}(t) \hat{U}(t) \qquad \text{--- (7.2)}$$

which leads

$$i\hbar \ddot{U}(t) = \hat{H}_{eL}(t) \frac{1}{i\hbar} \hat{H}_{eL}(t) \hat{U}(t) - \frac{i}{\hbar} [\hat{H}_0, \hat{H}_{eL}] \hat{U}(t) \qquad \text{--- (7.3)}$$

Therefore

$$\langle \ddot{U}(t)|_{t=0} \rangle_L = -\left\{ \frac{1}{\hbar^2} \langle \hat{H}_{eL}^2 \hat{U}(t)|_{t=0} \rangle_L + \frac{1}{\hbar^2} \langle [\hat{H}_0, \hat{H}_{eL}] \hat{U}(t)|_{t=0} \rangle_L \right\} \qquad \text{--- (7.4)}$$

Since $\hat{U}(t)\big|_{t=0} = 1$ and $\langle [\hat{H}_0, \hat{H}_{eL}] \rangle_L = 0$

for linear EPI, we get

$$\langle \ddot{\hat{U}}(t)\big|_{t=0} \rangle_L = -\frac{1}{\hbar^2} \langle \hat{H}_{eL}^2 \rangle \qquad \text{---- (7.5)}$$

Therefore the second moment is given by

$$\hat{\sigma}_2 = \frac{1}{\hbar^2} \langle \hat{H}_{eL}^2 \rangle_L \qquad \text{------- (7.6)}$$

Now expressing $\hat{H}_{eL}$ in second quantization language (eq. 4.14) and using the following relations for phonon average [32].

$$\langle \hat{C}_{\vec{\kappa}} \rangle = \langle \hat{C}_{\vec{\kappa}}^{+} \rangle = \langle \hat{C}_{\vec{\kappa}}^{2} \rangle = \langle \hat{C}_{\vec{\kappa}}^{+2} \rangle = 0 \qquad \text{---- (7.7)}$$

$$\langle \hat{C}_{\vec{\kappa}}^{+} \hat{C}_{\vec{\kappa}} \rangle = \bar{n}_{\vec{\kappa}}, \quad \langle \hat{C}_{\vec{\kappa}} \hat{C}_{\vec{\kappa}}^{+} \rangle = \bar{n}_{\vec{\kappa}} + 1 \qquad \text{---- (7.8)}$$

where $$\bar{n}_{\vec{\kappa}} = \frac{1}{e^{\frac{\hbar\omega_{\vec{\kappa}}}{kT}} - 1} \qquad \text{-------- (7.9)}$$

is the phonon occupation probability, we get

$$\hat{\sigma}_2 = \frac{1}{\hbar^2} \sum_{\vec{\kappa}} \hat{U}_{\vec{\kappa}}^{*} \hat{U}_{\vec{\kappa}} \coth \frac{\beta\vec{\kappa}}{2} \qquad \text{-------- (7.10)}$$

From equation (7.10) we see that the second moment is independent of the perturbation in first order.

Using the expansion (4.15) for the operators and applying orthogonality relation for $a_{\vec{n}\nu}$ (Eq. 4.11) we get,

$$\hat{\sigma}_2 = \frac{1}{2\hbar M}\sum_{\vec{n}\nu}\sum_{\vec{\Gamma}\gamma}\frac{b_{\vec{n}\nu}(\vec{\Gamma})}{\omega_{\vec{n}\nu}}\coth\frac{\beta\vec{n}}{2}\hat{V}^{+}_{\vec{\Gamma}\gamma}\hat{V}_{\vec{\Gamma}\gamma}$$

$$= \sum_{\vec{\Gamma}}\hat{\sigma}_2(\vec{\Gamma}) \qquad \text{----- (7.11)}$$

$$\hat{\sigma}_2(\vec{\Gamma}) = \frac{1}{2\hbar M}\sum_{\vec{n}\nu}\sum_{\vec{\gamma}}\frac{b_{\vec{n}\nu}(\vec{\Gamma})}{\omega_{\vec{n}\nu}}\coth\frac{\beta\vec{n}}{2}\hat{V}^{+}_{\vec{\Gamma}\vec{\gamma}}\hat{V}_{\vec{\Gamma}\vec{\gamma}} \qquad \text{---- (7.12)}$$

The total second moment is the sum of the contributions due to all $\vec{\Gamma}$ lattice vibrations. Further from equation (6.11), the third moment is

$$\hat{\sigma}_3 = -i^{\circ}\langle\dddot{\hat{U}}(t)\big|_{t=0}\rangle \qquad \text{---- (7.13)}$$

Now using equation of motion for $\hat{U}(t)$ (5.14), we get

$$\dddot{\hat{U}}(t) = \frac{i^{\circ}}{\hbar^3}\Big\{\big[\hat{H}_0,[\hat{H}_0,\hat{H}_{eL}]\big] - 2\big[\hat{H}_0,\hat{H}_{eL}\big]\hat{H}_{eL}$$

$$- \hat{H}_{eL}\big[\hat{H}_0,\hat{H}_{eL}\big] + \hat{H}^3_{eL}\Big\}\hat{U}(t) \qquad \text{---- (7.14)}$$

Taking the L-averaging on the right-hand side of equation (7.14) the terms containing odd powers of $\hat{H}_{eL}$ vanish. And using commutative properties of the phonon operators [33].

$$\big[\hat{C}_{\vec{n}},\hat{C}_{\vec{n}}\big] = \big[\hat{C}^{+}_{\vec{n}},\hat{C}^{+}_{\vec{n}}\big] = 0, \quad \big[\hat{C}_{\vec{n}},\hat{C}^{+}_{\vec{n}'}\big] = \delta_{\vec{n}\vec{n}'} \qquad \text{----- (7.15)}$$

and substituting

$$\hat{H}_0 = \hat{H}_L + \hbar\Omega_0 \hat{1} + \hbar\hat{W} \qquad \text{----- (7.16)}$$

where $\hbar\Omega_0$ is the center of gravity of the excited levels, we get

$$\hat{\sigma}_3 = \hat{\sigma}_3^{(1)} + \hat{\sigma}_3^{(2)} \qquad \text{--------- (7.17)}$$

where

$$\hat{\sigma}_3^{(1)} = \frac{1}{\hbar^2} \sum_{\vec{n}\nu} \omega_{\vec{n}\nu} \hat{U}_{\vec{n}\nu}$$

$$= \frac{1}{2\hbar M} \sum_{\vec{n}\nu} \sum_{\vec{r}\vec{r}'} b_{\vec{n}\nu}(\vec{r}) \hat{V}^{+}_{\vec{r}\vec{r}'} \hat{V}_{\vec{r}\vec{r}'} \qquad \text{------ (7.18)}$$

$$\hat{\sigma}_3^{(2)} = \frac{1}{\hbar^2} \sum_{\vec{n}\nu} \coth\frac{\beta\vec{n}}{2} \left[\hat{U}^{*}_{\vec{n}\nu}, \hat{W}\right] \hat{U}_{\vec{n}}$$

$$= \frac{1}{2\hbar M} \sum_{\vec{n}\nu} \sum_{\vec{r}\vec{r}'} b_{\vec{n}\nu}(\vec{r}) \frac{\coth\frac{\beta\vec{n}}{2}}{\omega_{\vec{n}\nu}} \left[\hat{V}_{\vec{r}\vec{r}'}, \hat{W}\right] \hat{V}_{\vec{r}\vec{r}'} \qquad \text{-- (7.19)}$$

The final expression of equations (7.18) and (7.19). have been derived by using the equations (4.15) and (4.11). The third moments consists of two parts $\hat{\sigma}_3^{(1)}$ which is independent of perturbation and $\hat{\sigma}_3^{(2)}$ which linearly depends upon the perturbation.

The third moment determines the band shape asymmetry. The asymmetric deviation of the band shape from Gaussian form can be described by the third coefficient of the Edgeworth series [17].

CHAPTER III

MOMENTS OF A→T ABSORPTION BANDS OF U-CENTRES IN KBr AND NaI

§8. MICRO-CALCULATIONS OF SECOND AND THIRD MOMENTS

In this chapter, we do the micro-calculations of second and third moments, and half width of the absorption spectra of U-centres in KBr and NaI. As it is shown by Hetrick [34] that the absorption spectrum of U-centre in KBr consists of a broad spectrum, which indicates the presence of the strong Electron-Phonon Interaction.

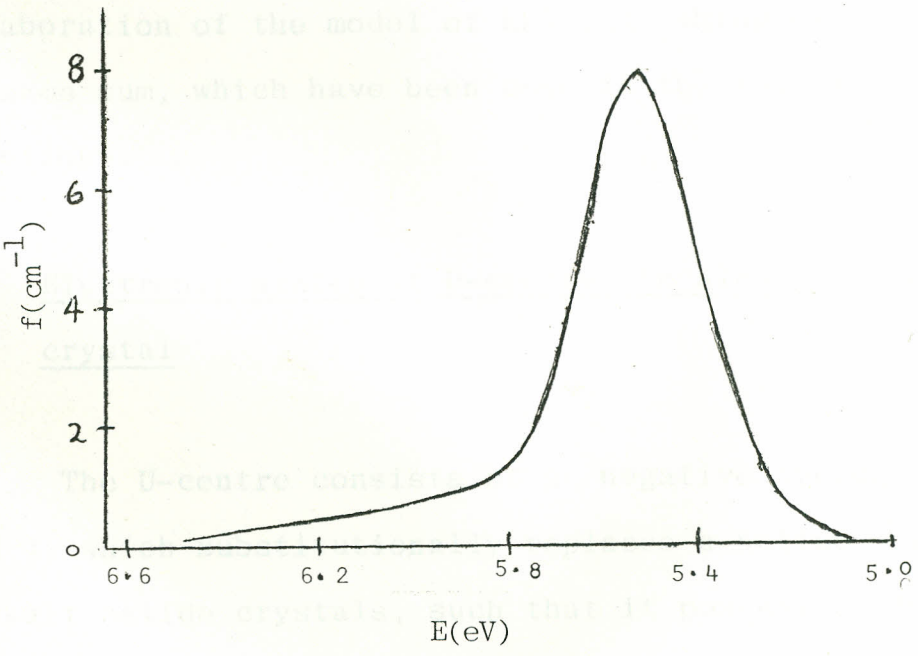


Fig. 4. Optical absorption arising from U-centres in KBr at 78^{O}K.

This situation made us interested to do such calculations. Here we are able to explain how the EPI, which is expressed in point-ion model, is applicable to the U-centre in alkali halide crystals.

The calculations of moments have been done for absorption spectra by d-electrons in CdS: Ti^{2+} and CdSe: Ti^{2+} systems by Dod [35] and for the exciton band in CsCl by Klokishner et al. [36]. Here we intend to do the calculations for the absorption spectrum by p-electrons in H^--centres/U-centres in KBr, for which the experimental values are known [34].

The analytical expression for the moments of the absorption band, which are given in §7, needs some elaboration of the model of EPI and taking of the phonon sum, which have been done in the following sections.

1. Electronic states of U-centres in alkali halide crystal

The U-centre consists of a negative hydrogen ion (H^-), which substitutionally replaces a halide ion in alkali halide crystals, such that it possesses an Octahedral (O_h) symmetry with six nearest neighbours of positive ion in the crystal lattice.

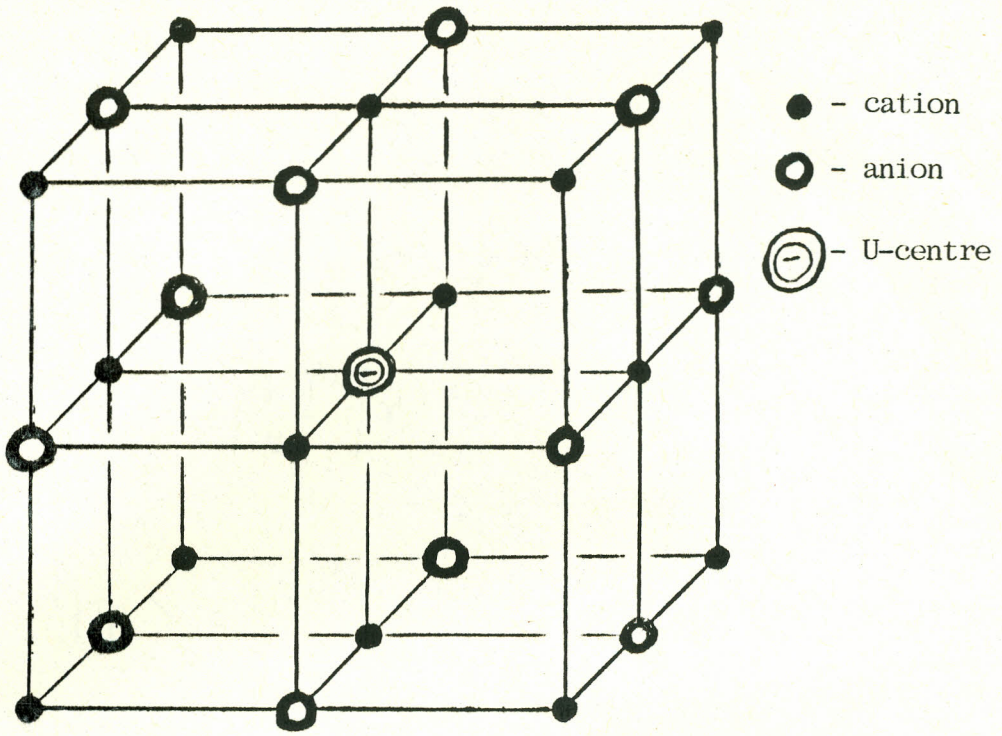


Fig. 5. U-centre in O_h-symmetry

The theoretical study of the electronic structure of U-centre in the point-ion model by Gourary [37], Spector et. al. [38] and in extended point-ion model by Wood and Öpik [39] gave us the wavefunctions and energies of ground state and excited states of U-centre, so as to compare some of the experimental data with the theoretical result, which are in good agreement. It has been established that the ground state and first excited triplet state have the configurations $1s^2$ and $1s2p$ respectively. The observed absorption spectrum of U-centre in KBr [34] is found to correspond to the transition from singlet $|A_1\rangle$ to triplet state $|T_1\rangle$ with a U-band peak absorption at 5.5eV and half width of 0.25eV at low temperature.

The two variational-parameter wavefunctions that

give a stable ground state $|A_1\rangle$ and the first triplet excited state $|T_1\rangle$ for free H^- ion are given by [38]

$$|A_1\rangle = \frac{N}{4\pi}\left[e^{-\alpha r_1}e^{-\beta r_2} + e^{-\alpha r_2}e^{-\beta r_1}\right] \quad -- (8.1)$$

$$|T_{1x}\rangle = \left[\frac{(\gamma\delta)^{3/2}}{8\pi}\right]\gamma\left[r_1 e^{-\frac{1}{2}\gamma r_1}e^{-\delta r_2}\sin\theta_1\cos\varphi_1 - r_2 e^{-\frac{1}{2}\gamma r_2}e^{-\delta r_1}\sin\theta_2\cos\varphi_2\right] \quad -- (8.2a)$$

$$|T_{1Y}\rangle = \left[\frac{(\gamma\delta)^{3/2}}{8\pi}\right]\gamma\left[r_1 e^{-\frac{1}{2}\gamma r_1}e^{-\delta r_2}\sin\theta_1\sin\varphi_1 - r_2 e^{-\frac{1}{2}\gamma r_2}e^{-\delta r_1}\sin\theta_2\sin\varphi_2\right] \quad -- (8.2b)$$

$$|T_{1z}\rangle = \left[\frac{(\gamma\delta)^{3/2}}{8\pi}\right]\gamma\left[r_1 e^{-\frac{1}{2}\gamma r_1}e^{-\delta r_2}\cos\theta_1 - r_2 e^{-\frac{1}{2}\gamma r_2}e^{-\delta r_1}\cos\theta_2\right] \quad -- (8.2c)$$

where $\alpha, \beta, \gamma, \delta$ are variational parameters. Here $|A_1\rangle$ is not normalized and $|T_1\rangle$ are normalized wavefunctions.

2. Electron-Phonon Interaction Operator

The EPI operator is expressed in point-ion lattice model of crystal field, taking into consideration only 6 nearest neighbour ions of crystal lattice, such that potential energy W of electron of U-centre in O_h-symmetry is expressed as

$$W = \sum_{k=1,2}\sum_{\alpha=1}^{6}\frac{e e^*}{4\pi\varepsilon_0|\vec{R}_\alpha - \vec{r}_k|} \quad --- (8.3)$$

where e* is the effective charge of the lattice ion and k = 1,2 are two electrons of U-centre.

If we assume that W is a small perturbation, then we can expand W in terms of Legendre polynomials [40] as follows:

$$\hat{W}(\vec{r},\vec{R}_\alpha) = \frac{ee^*}{4\pi\varepsilon_0} \sum_{\alpha=1}^{6} \sum_{l=0}^{\infty} \frac{\vec{r}_<^{\,l}}{\vec{r}_>^{\,l+1}} P_l(\cos w_\alpha) \quad \text{----- (8.4)}$$

where $\vec{r}_<$ is the lesser and $\vec{r}_>$ the greater than R(R-nearest neighbour distance and $\vec{r}$ is the position vector of electron), w_α is the angle between $\vec{R}_\alpha$ and $\vec{r}$.

When R is very large compared to r, which is true in our case of U-centre with small radius then $r_>$ and $r_<$ can be replaced by R and r respectively. The equation (8.4) can be rewritten as

$$\hat{W}(\vec{r},\vec{R}_\alpha) = \frac{ee^*}{4\pi\varepsilon_0} \sum_{\alpha=1}^{6} \sum_{l=0}^{\infty} \frac{\vec{r}^{\,l}}{\vec{R}_\alpha^{\,l+1}} P_l(\cos w_\alpha) \text{ ---- (8.5)}$$

Applying addition theorem for spherical harmonics

$$P_l(\cos w_\alpha) = \frac{4\pi}{2l+1} \sum_{m=-l} Y_{lm}(\theta\varphi)\, Y^*_{lm}(\theta_\alpha,\varphi_\alpha) \text{--- (8.6)}$$

where $Y_{lm}(\theta\varphi)$'s are the spherical harmonics

$(\vec{r}, \theta, \varphi)$ are the polar coordinates of $\vec{r}$

$(\vec{R}, \theta_\alpha, \varphi_\alpha)$ are the polar coordinates of $\vec{R}$.

$$Y^{*}_{lm}(\theta_\alpha,\varphi_\alpha) = (-1)^m Y_{l,-m}(\theta_\alpha,\varphi_\alpha) \qquad -- \quad (8.7)$$

Finally, we get

$$\hat{W}(\vec{r},\vec{R}_\alpha) = \frac{ee^*}{4\pi\varepsilon_0}\sum_{\alpha=1}^{6}\sum_{l=0}^{\infty}\sum_{m=-l}^{l}\left(\frac{4\pi}{2l+1}\right)\frac{r^l}{R_\alpha^{l+1}}Y_{lm}(\theta\varphi)\,Y^{*}_{lm}(\theta_\alpha\varphi_\alpha) \qquad (8.8)$$

For the p-state, the non-zero contribution in $\hat{W}(\vec{r},\vec{R})$ is given by the terms with $l = 0, 2$

Then

$$\hat{W}(\vec{r},\vec{R}_\alpha) = 4\pi\left(\frac{ee^*}{4\pi\varepsilon_0}\right)\left[Y_{00}(\theta\varphi)\frac{1}{R_\alpha}Y^{*}_{00}(\theta_\alpha,\varphi_\alpha) + \sum_{m=-2}^{2}\frac{r^2}{5}Y_{2m}(\theta\varphi)\frac{1}{R_\alpha^3}Y^{*}_{2m}(\theta_\alpha,\varphi_\alpha)\right] \qquad (8.9)$$

Knowing $(\theta_\alpha,\varphi_\alpha)$ for the six nearest neighbours of the U-centre, $\hat{W}(\vec{r},\vec{R})$ can be expressed in terms of spherical harmonics $Y_{lm}(\theta,\varphi)$. The symmetrized coordinates of the lattice vibrations are determined with the help of group-theory relations, equation (4.4),

$$\vec{Q}_{\Gamma\bar{\gamma}} = \frac{[\Gamma]}{g}\sum_{\hat{G}} D^{(\Gamma)}_{\bar{\gamma}\bar{\gamma}}(\hat{G})\,\hat{G}\,\vec{\Delta R}_\alpha \qquad -- \quad (4.4)$$

For O_h-symmetry, $\Gamma = A_1, E, T_2$ are the active lattice vibration modes, which are interacting with the $|T_1\rangle$ electronic state [41].

$$[T_1^2] = A_1 + E + T_2 \qquad \text{--- (8.10)}$$

Thus, the corresponding symmetrized coordinates have the following expression :

$$Q_{Ag} = \frac{1}{\sqrt{6}}(X_1 - X_4 + Y_2 - Y_5 + Z_3 - Z_6) \qquad \text{- (8.11a)}$$

$$Q_{Eu} = \frac{1}{\sqrt{12}}(2Z_3 - 2Z_6 - X_1 + X_4 - Y_2 + Y_5) \qquad \text{-- (8.11b)}$$

$$Q_{Ev} = \frac{1}{2}(X_1 - X_4 - Y_2 + Y_5) \qquad \text{--- (8.11c)}$$

$$Q_{T_2\eta} = \frac{1}{2}(X_3 - X_6 + Z_1 - Z_4) \qquad \text{--- (8.11d)}$$

$$Q_{T_2\zeta} = \frac{1}{2}(Y_1 - Y_4 + X_2 - X_5) \qquad \text{--- (8.11e)}$$

$$Q_{T_2\xi} = \frac{1}{2}(Z_2 - Z_5 + Y_3 - Y_6) \qquad \text{--- (8.11f)}$$

where (X_1, Y_1, Z_1), (X_2, Y_2, Z_2) etc. are displacements of the lattice points, as numbered in (fig 6.).

The electron-phonon interaction operator $\hat{V}_{F\bar{r}}$ (equation (4.6)) for our system of O_h symmetry becomes

$$\hat{V}_{F\bar{r}} = \sum_{\alpha=1}^{6}\left(\frac{\partial \hat{N}}{\partial R_{x\alpha}}\cdot\frac{\partial Q_{F\bar{r}}}{\partial R_{x\alpha}} + \frac{\partial \hat{N}}{\partial R_{Y\alpha}}\cdot\frac{\partial Q_{F\bar{r}}}{\partial R_{Y\alpha}} + \frac{\partial \hat{N}}{\partial R_{Z\alpha}}\cdot\frac{\partial Q_{F\bar{r}}}{\partial R_{Z\alpha}}\right) \qquad \text{--- (8.12)}$$

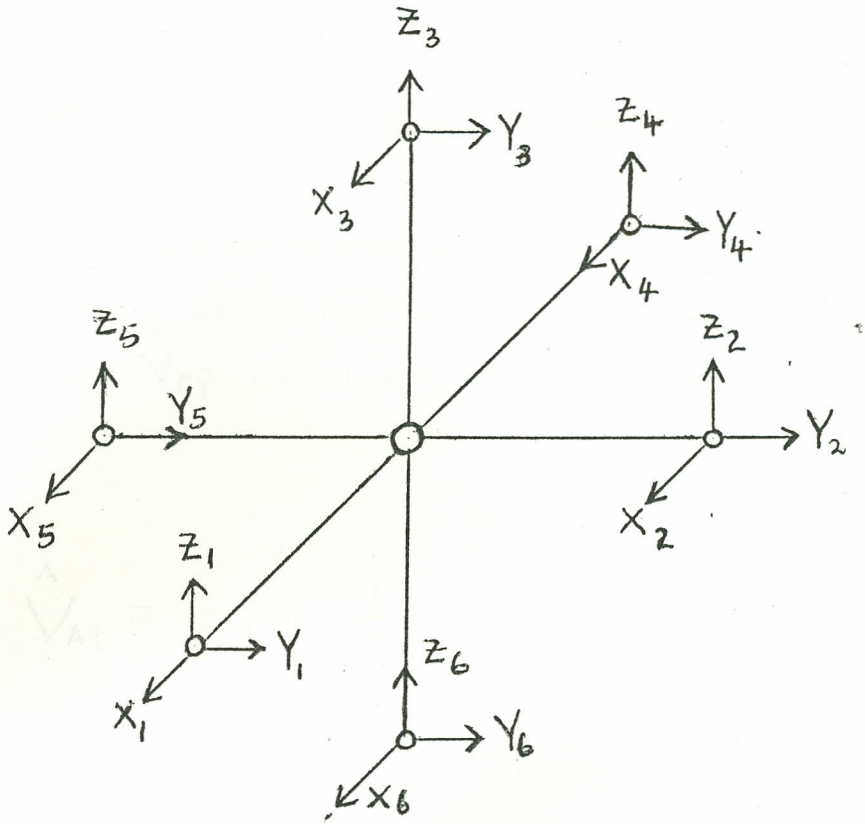


Fig. 6. General and local ligand coordinate systems for octahedral molecules (MX_6)

The differentiation of spherical Harmonics is carried out with the help of following equations [43]:-

$$\frac{\partial}{\partial R_{X\alpha}}\left[\frac{1}{R^{l+1}} Y^{*}_{lm}(\alpha)\right] = \frac{1}{2}\frac{2l+1}{R_\alpha^{l+2}} \times \left[\sqrt{\frac{(l+m+2)(l+m+1)}{(2l+3)(2l+1)}}\, Y^{*}_{(\alpha)\,l+1,m+1} - \sqrt{\frac{(l-m+2)(l-m+1)}{(2l+3)(2l+1)}}\, Y^{*}_{(\alpha)\,l+1,m-1}\right] \quad (8.13a)$$

$$\frac{\partial}{\partial R_{Y\alpha}}\left[\frac{1}{R^{l+1}} Y^{*}_{lm}(\alpha)\right] = \frac{i}{2}\frac{(2l+1)}{R_\alpha^{l+2}} \times \left[\sqrt{\frac{(l+m+2)(l+m+1)}{(2l+3)(2l+1)}}\, Y^{*}_{(\alpha)\,l+1,m+1} + \sqrt{\frac{(l-m+2)(l-m+1)}{(2l+3)(2l+1)}}\, Y^{*}_{(\alpha)\,l+1,m-1}\right] \quad (8.13b)$$

$$\frac{\partial}{\partial R_{Z\alpha}}\left[\frac{1}{R^{l+1}} Y^{*}_{lm}(\alpha)\right] = -\frac{(2l+1)}{R_\alpha^{l+2}} \sqrt{\frac{(l+m+1)(l-m+1)}{(2l+3)(2l+1)}}\, Y^{*}_{(\alpha)\,l+1,m} \quad (8.13c)$$

where (α) signifies $(\theta_\alpha, \varphi_\alpha)$ for the lattice point

Although by elementary mathematics, but quite tedious one, we get the following expression for operators $\hat{V}_{\Gamma\gamma}$ (using equations 8.8 – 8.13):

$$\hat{V}_{A1} = -\sqrt{24\pi}\,\frac{1}{R^2}\,Y_{00}(\theta,\varphi)\left(\frac{ee^*}{4\pi\varepsilon_0}\right) \quad \text{--- (8.14)}$$

$$\hat{V}_{E\theta} = -\sqrt{\frac{27\pi}{125}}\,\frac{r^2}{R^4}\,Y_{2,0}(\theta,\varphi)\left(\frac{ee^*}{4\pi\varepsilon_0}\right) \quad \text{---- (8.15)}$$

$$\hat{V}_{E\varepsilon} = -\sqrt{\frac{27\pi}{250}}\,\frac{r^2}{R^4}\left(Y_{2,-2}(\theta,\varphi)+Y_{2,2}(\theta,\varphi)\right)\left(\frac{ee^*}{4\pi\varepsilon_0}\right) \text{--- (8.16)}$$

$$\hat{V}_{T_2\xi} = 2\sqrt{\frac{6\pi}{125}}\,\frac{r^2}{R^4}\left(Y_{2,1}(\theta,\varphi)+Y_{2,-1}(\theta,\varphi)\right)\left(\frac{ee^*}{4\pi\varepsilon_0}\right) \text{--- (8.17)}$$

$$\hat{V}_{T_2\eta} = \sqrt{\frac{6\pi}{125}}\,\frac{r^2}{R^4}\left(Y_{2,-1}(\theta,\varphi)-Y_{2,1}(\theta,\varphi)\right)\left(\frac{ee^*}{4\pi\varepsilon_0}\right) \quad \text{--- (8.18)}$$

$$\hat{V}_{T_2\zeta} = i\sqrt{\frac{6\pi}{125}}\frac{r^2}{R^4}\left(Y^{(\theta,\varphi)}_{2,-2} - Y^{(\theta,\varphi)}_{2,2}\right)\left(\frac{ee^*}{4\pi\varepsilon_0}\right) \quad \text{--- (8.19)}$$

To find the reduced matrix element, we apply Wigner-Eckarts Theorem [40],

$$\langle \Gamma_1\gamma_1|\hat{V}_{\bar{\Gamma}\bar{\gamma}}|\Gamma_2\gamma_2\rangle = \frac{1}{\sqrt{g(\Gamma_1)}}\|\hat{V}_{\bar{\Gamma}}\|\langle \Gamma_1\gamma_1\Gamma_2\gamma_2|\bar{\Gamma}\bar{\gamma}\rangle$$

where $g(\Gamma_1)$ - dimension of irreducible representation of the electronic state

$\|\hat{V}_{\bar{\Gamma}}\|$ - reduced matrix element of operator $\hat{V}_{\bar{\Gamma}\bar{\gamma}}$, which does not depend upon $\bar{\gamma}$

$\langle \Gamma_1\gamma_1\Gamma_2\gamma_2|\bar{\Gamma}\bar{\gamma}\rangle$ - Clebsch-Gordon coefficient.

Now using the wavefunctions (Eqs. 8.1 and 8.2) and above written expressions for the operator $\hat{V}_{\bar{\Gamma}\bar{\gamma}}$ (Eqs. 8.14, 8.15 and 8.18) (we take only one expression for $\bar{\Gamma}$, since reduced matrix element does not depend upon $\bar{\gamma}$) and taking Clebsch-Gordon coefficients

$\langle T_{1z}T_{1z}|A_1\rangle$; $\langle T_{1z}T_{1z}|E_u\rangle$ and $\langle T_{1x}T_{1z}|T_{2\eta}\rangle$ [40],

we get the following expressions for the reduced matrix element:

$$\|\tilde{V}_{A_1}\| = -\frac{3\sqrt{6}}{R^2}\left(\frac{ee^*}{4\pi\varepsilon_0}\right) \quad \text{--- (8.20)}$$

$$\|\hat{V}_E\| = -\frac{27\sqrt{6}}{10R^4\gamma^2}\left[1-e^{-\gamma R}\sum_{m=0}^{6}\frac{(\gamma R)^m}{m!}\right]\left(\frac{ee^*}{4\pi\varepsilon_0}\right) \text{--- (8.21)}$$

$$\|\hat{V}_{T_2}\| = \frac{-9\sqrt{6}}{5R^4\gamma^2}\left[1-e^{-\gamma R}\sum_{m=0}^{6}\frac{(\gamma R)^m}{m!}\right]\left(\frac{ee^*}{4\pi\varepsilon_0}\right) \text{--- (8.23)}$$

where $\|\tilde{V}_{A_1}\|$ has been determined by renormalising the interaction operator of totally symmetrical lattice vibration [7], such that

$$\langle T_1|\tilde{V}_{A_1}|T_1\rangle = \langle T_1|\hat{V}_{A_1}|T_1\rangle - \langle A|\hat{V}_{A_1}|A\rangle \text{ --- (8.24)}$$

The different parameters $\alpha, \beta, \gamma, \delta$ have been taken from [38]. The effective charge e* of the surrounding ion has been taken equivalent to the charge of the electron for our calculation.

3. Phonon Sum:

Our next step is to calculate the Van Vleck coefficients $\vec{a}_{\vec{x}\nu}(\vec{r}\vec{r})$ equation (4.10) and the quantities $b_{\vec{x}\nu}$, equation (4.11). The exact solution of this problem is possible only if the polarization vector $\vec{e}(\vec{x}\nu)$ and dispersion relation for $\omega_{\vec{x}\nu}$ are known for all directions in Brilouin Zone and for all branches of lattice vibration. The theoretical calculation of dispersion relation for KBr, NaI has been done by Cowley et. al. [44] but there is no information about the polarization vector. Hence we can not use the results

of the above papers for our calculations of moments, so we restrict ourselves to the approximate phonon sum in the "Extended Brillouin Zone" model.

In this model, the maximum value of the wave vectors for three acoustical and three optical modes of vibrations (the alkali halide crystal has two atoms per unit primitive cell) is given by Debye cut off value

$$\kappa_D = \left(\frac{6\pi^2}{V_o}\right)^{1/3} \qquad \text{-----} \quad (8.25)$$

where V_o is the volume of unit primitive cell which is equal to $2a_o^3$ for our f.c.c. crystal lattice of KBr, NaI (a_o is the distance between nearest neighbours). And in terms of dimensionless coordinates the cut off wavevector is given as

$$\xi_D = \kappa_D R_o = \kappa_D a_o = (3\pi^2)^{1/3} \qquad \text{----} \quad (8.26)$$

since $R_o = a_o$. Further we accept Debye Dispersion relation for acoustical modes of vibrations

$$\omega_{\kappa\nu} = v_\nu \kappa$$

where v_ν is the velocity of sound and $\nu = l, t$; $l-$ for longitudinal and $t-$ for transverse modes of vibration and Einstein model for optical modes with optical phonon frequencies ω_{ol} and ω_{ot}.

The following phonon parameters have been used (Table 1) [45].

TABLE 1

	KBr	NaI
Density, ρ, ($\times 10^3$ kg m^{-3})	2.75	3.667
Nearest neighbour distance ($a_o = R_o$) ($\times 10^{-10}$ m)	3.3	3.23
Longitudinal velocity of sound, v_l (ms^{-1})	3678	3028
Transverse velocity of sound, v_t ms^{-1}	1342	1346
Longitudinal optical phonon frequency, ν_{ol} ($\times 10^{12}$ Hz)	5.0	5.1
Transverse optical phonon frequency, ν_{ot} ($\times 10^{12}$ Hz)	3.6	3.6

In our case of electronic excited state T_1 the active lattice vibrations which are interactions with T_1 state are represented by

$$[T_1^2] = A_1 + E + T_2$$

where A_1 - totally symmetrical lattice vibration,

E - two-fold degenerate lattice vibration

T_2 - three-fold degenerate lattice vibration

which are generally classified as follows:

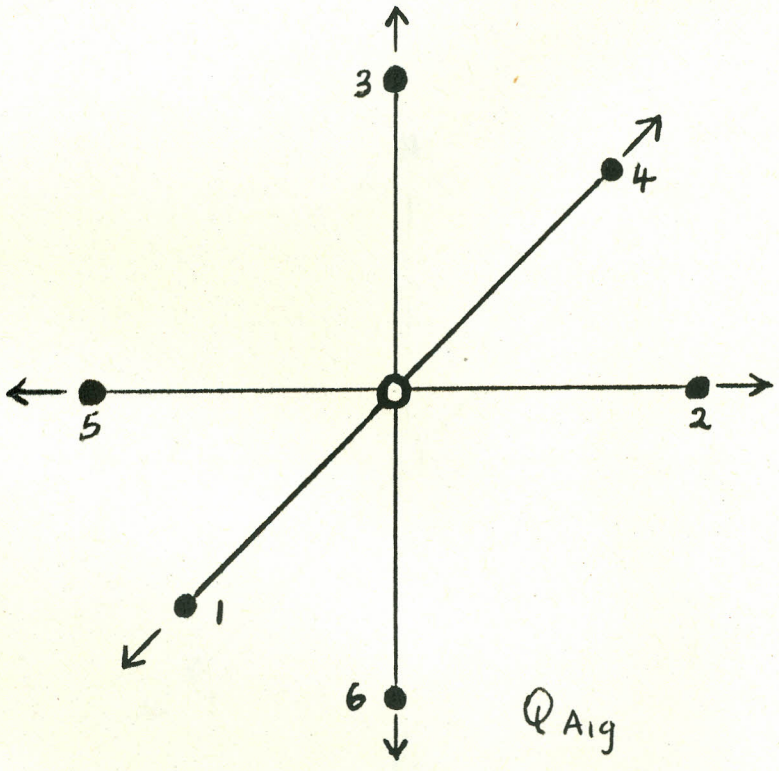
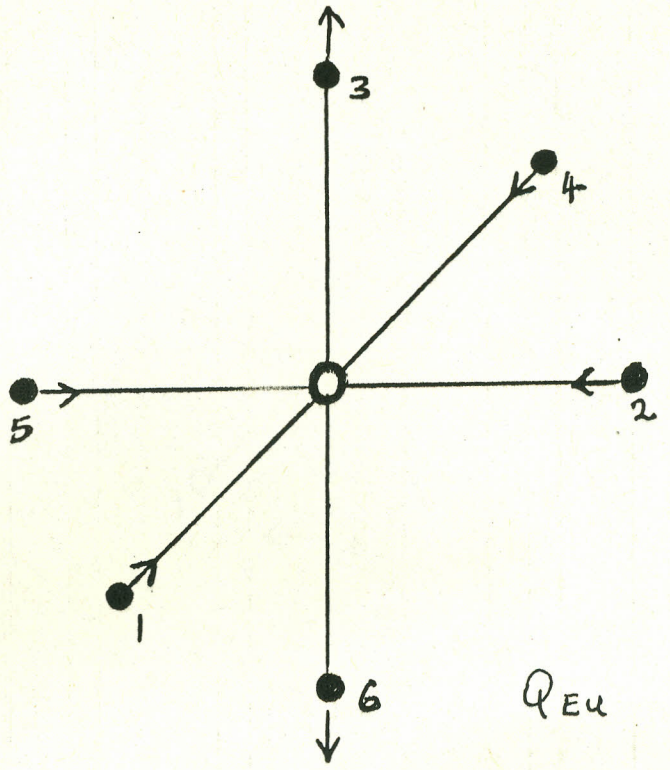
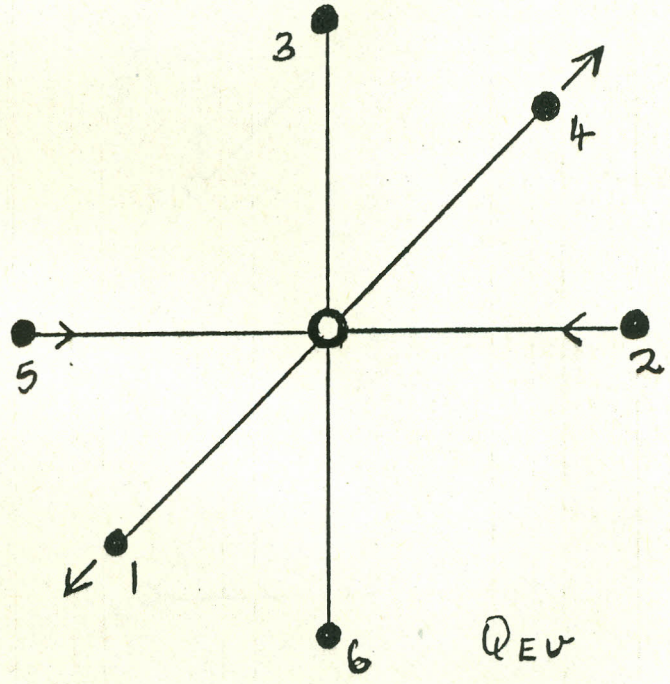
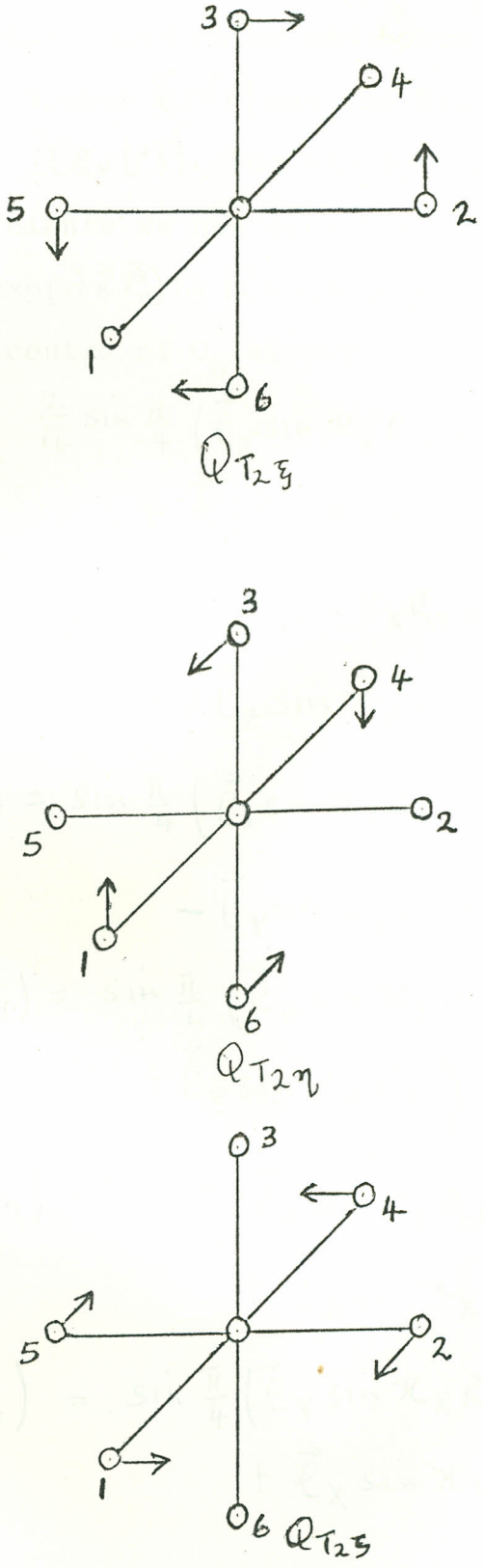


Fig. 7a: Symmetry coordinates for A_1-modes of lattice vibration of MX_6 molecule.





7b. Symmetry coordinates for E -modes of lattice vibration of MX_6 molecule.



7c. Symmetry coordinates for T_2-modes of lattice vibration of MX_6 molecule.

In the Extended Brilouin Zone model, we can use the real normal coordinates and hence the real polarization vector $\vec{e}(\vec{\kappa}\nu)$ and the Van Vleck coefficients $\vec{a}_{\vec{\kappa}\nu}(\vec{r}\gamma)$. For the determination of these coefficients we use equation (4.10) by replacing $\exp(-i\vec{\kappa}\vec{R}_a^0)$ by $\sqrt{2}\sin(\vec{\kappa}\vec{R}_a+\frac{\pi}{4})$. Thus we get (for an impurity centre of O_h symmetry) [32]

$$\vec{a}_{\vec{\kappa}\nu}(A_{1g}) = \frac{2}{\sqrt{6}}\sin\frac{\pi}{4}\left(\vec{e}_x \sin\kappa_x R_0 + \vec{e}_y \sin\kappa_y R_0 + \vec{e}_z \sin\kappa_z R_0\right) \quad \text{--- (8.27a)}$$

$$\vec{a}_{\vec{\kappa}\nu}(E_u) = \frac{1}{\sqrt{3}}\sin\frac{\pi}{4}\left(\vec{e}_x \sin\kappa_x R_0 + \vec{e}_y \sin\kappa_y R_0 - 2\vec{e}_z \sin\kappa_z R_0\right) \quad \text{--- (8.27b)}$$

$$\vec{a}_{\vec{\kappa}\nu}(E_v) = \sin\frac{\pi}{4}\left(\vec{e}_x \sin\kappa_x R_0 - \vec{e}_y \sin\kappa_y R_0\right) \quad \text{--- (8.27c)}$$

$$\vec{a}_{\kappa\nu}(T_{2\xi}) = \sin\frac{\pi}{4}\left(\vec{e}_z \sin\kappa_y R_0 + \vec{e}_y \sin\kappa_z R_0\right) \quad \text{--- (8.27d)}$$

$$\vec{a}_{\vec{\kappa}\nu}(T_{2\eta}) = \sin\frac{\pi}{4}\left(\vec{e}_x \sin\kappa_z R_0 + \vec{e}_z \sin\kappa_x R_0\right) \quad \text{--- (8.27e)}$$

$$\vec{a}_{\vec{\kappa}\nu}(T_{2\zeta}) = \sin\frac{\pi}{4}\left(\vec{e}_y \sin\kappa_x R_0 + \vec{e}_x \sin\kappa_y R_0\right) \quad \text{--- (8.27f)}$$

where, we know the orthogonality property of these coefficients is

$$\sum_{\Omega\vec{\kappa}} \vec{a}^{+}_{\kappa\nu}(\bar{r}\bar{\gamma})\vec{a}_{\kappa\nu}(\bar{r}'\bar{\gamma}') = b_{\kappa\nu}(\bar{r})\delta_{\bar{r}\bar{r}'}\delta_{\bar{\gamma}\bar{\gamma}'} \quad \text{--- (8.28)}$$

where $\sum_{\Omega\vec{\kappa}}$, means the integration along the direction of wavevector $\vec{\kappa}$ and average over the direction $\vec{e}$ for fixed $\vec{\kappa}$ direction.

Taking the angular integration and averaging over the polarization of the square of Van-Vleck coefficients we get the following expression for $b_{\xi\nu}(\bar{r}_1)$

$$b_{\xi\ell}(A_1) = \frac{1}{6} - \frac{\sin 2\xi}{4\xi} + \frac{\sin 2\xi}{8\xi^3} - \frac{\cos 2\xi}{4\xi^2} - \frac{\sin\sqrt{2}\xi}{\sqrt{2}\xi} + \frac{3\sin\sqrt{2}\xi}{2\sqrt{2}\xi^3} - \frac{3\cos\sqrt{2}\xi}{2\xi^2} \quad \text{--- (8.29a)}$$

$$b_{\xi t}(A_1) = \frac{1}{6} - \frac{\sin 2\xi}{16\xi^3} + \frac{\cos 2\xi}{8\xi^2} + \frac{\sin\sqrt{2}\xi}{2\sqrt{2}\xi} - \frac{3\sin\sqrt{2}\xi}{4\sqrt{2}\xi^3} + \frac{3\cos\sqrt{2}\xi}{4\xi^2} \quad \text{--- (8.29b)}$$

$$b_{\xi\ell}(E) = \frac{1}{6} - \frac{\sin 2\xi}{4\xi} + \frac{\sin 2\xi}{8\xi^3} - \frac{\cos 2\xi}{4\xi^2} + \frac{\sin\sqrt{2}\xi}{2\sqrt{2}\xi} - \frac{3\sin\sqrt{2}\xi}{4\sqrt{2}\xi^3} + \frac{3\cos\sqrt{2}\xi}{4\xi^2} \quad \text{--- (8.29c)}$$

$$b_{\xi t}(E) = \frac{1}{6} - \frac{\sin 2\xi}{16\xi^3} + \frac{\cos 2\xi}{8\xi^2} - \frac{\sin\sqrt{2}\xi}{4\sqrt{2}\xi} + \frac{3\sin\sqrt{2}\xi}{8\sqrt{2}\xi^3} - \frac{3\cos\sqrt{2}\xi}{8\xi^2} \quad \text{--- (8.29d)}$$

$$b_{\xi\ell}(T_2) = \frac{1}{6} - \frac{\sin 2\xi}{16\xi^3} + \frac{\cos 2\xi}{8\xi^2} - \frac{\sin\sqrt{2}\xi}{2\sqrt{2}\xi} + \frac{3\sin\sqrt{2}\xi}{4\sqrt{2}\xi^3} - \frac{3\cos\sqrt{2}\xi}{4\xi^2} \quad \text{--- (8.29e)}$$

$$b_{\xi t}(T_2) = \frac{1}{6} - \frac{\sin 2\xi}{8\xi} + \frac{\sin 2\xi}{32\xi^3} - \frac{\cos 2\xi}{16\xi^2} + \frac{\sin\sqrt{2}\xi}{4\sqrt{2}\xi} - \frac{3\sin\sqrt{2}\xi}{8\sqrt{2}\xi^3} + \frac{3\cos\sqrt{2}\xi}{8\xi^2} \quad \text{--- (8.29f)}$$

In the above expression, we have used a dimensionless coordinate $\xi = \kappa R_0$.

Using the Wigner-Eckart's Theorem for the operator $\hat{V}_{\Gamma\bar{\gamma}}$

$$\hat{V}_{\Gamma\bar{\gamma}} = \frac{1}{\sqrt{g(\Gamma)}} \| \hat{V}_{\bar{\Gamma}} \| \hat{O}_{\Gamma\bar{\gamma}} \qquad \text{--- (8.30)}$$

where

$\| \hat{V}_{\bar{\Gamma}} \|$ - is the reduced matrix element

$g(\Gamma)$ - dimension of the IR Γ of the excited state.

$\hat{O}_{\Gamma\bar{\gamma}}$ - Clebsch-Gordon coefficient matrix which satisfies the orthogonality theorem

$$\sum_{\bar{\gamma}} \hat{O}^{+}_{\Gamma\bar{\gamma}} \hat{O}_{\Gamma\bar{\gamma}} = \hat{1} \qquad \text{--- (8.31)}$$

and transferring from the summation over $\varkappa$ to integration w.r.t. $\varkappa$, equation (7.11) becomes

$$\hat{\sigma}_2 = \frac{1}{6Mk} \sum_{\bar{\Gamma},\nu} \| \hat{V}_{\bar{\Gamma}} \|^2 \frac{L^3}{(2\pi)^3} \int_0^{\varkappa_D} \frac{\varkappa^2 b_{\varkappa\nu}(\bar{\Gamma})}{\omega_{\varkappa\nu}} \coth \frac{\beta_{\varkappa\nu}}{2} d\varkappa \qquad \text{(8.32)}$$

where L^3 is the volume of the crystal.

Again in terms of dimensionless coordinate $\xi = \vec{\varkappa}\vec{R}$, and applying Debye and Einstein models for acoustical and optical modes of vibration respectively, the above expression becomes

$$\hat{\sigma}_2 = \frac{1}{48\pi^3 \rho \hbar R_0^2} \sum_{\bar{F}} \| \hat{V}_{\bar{F}} \|^2 \int_0^{\xi_D} d\xi\, \xi^2$$

$$\times \left[\frac{b_{\xi l}(\bar{F})}{\xi v_l} \coth \frac{\hbar v_l \xi}{2R_0 kT} + \frac{2 b_{\xi t}(\bar{F})}{\xi v_t} \coth \frac{\hbar v_t \xi}{2R_0 kT} \right.$$

$$+ \frac{b_{\xi l}(\bar{F})}{\omega_{0l} R_0} \coth \frac{\hbar \omega_{0l}}{2kT}$$

$$\left. + \frac{2 b_{\xi t}(\bar{F})}{\omega_{0t} R_0} \coth \frac{\hbar \omega_{0t}}{2kT} \right] \qquad \text{--- (8.33)}$$

and similarly, the formula for third moment (7.18) becomes

$$\hat{\sigma}_3^{(1)} = \frac{1}{24\pi^3 \rho \hbar R^3} \sum_{\bar{F}} \| \hat{V}_{\bar{F}} \|^2$$

$$\times \int_0^{\xi_D} d\xi\, \xi^2 \left(b_{\xi l}(\bar{F}) + 2 b_{\xi t}(\bar{F}) \right) \qquad \text{--- (8.34)}$$

The second part of third moment i.e. $\sigma_3^{(2)}$ is not of our interest, since we are not considering any perturbation $\hat{W}$.

Finally we determine the second moment and its temperature dependence by using formula (8.33) and third moment by (8.34).

4: Half-width of band shape function F(Ω)

If the moments of a function are known, then we can express the function in terms of some trial function, whose zeroth, second and third moments $\left(\langle\Omega^0\rangle, \langle\bar{\Omega}\rangle, \langle\Omega^2\rangle\right)$ coincide with each other (Gram-Charlier series [46]). Since the absorption spectrum of U-centre in KBr is not much different from Gaussian curve [34], so we take Gaussian function $F_0(\Omega)$ as the trial function, and we can express our function F(Ω) according to Edgeworth Series [46] as follows:

$$F(\Omega) = F_0(\Omega)\left[1 + \sum_{j=3}^{\infty} \frac{(-1)^j \gamma_j}{j!\, 2^{j/2}} H_j\left(\frac{\Omega-\bar{\Omega}}{\sqrt{2\sigma_2}}\right)\right] \quad \text{--- (8.35)}$$

where $H_j\left(\frac{\Omega-\bar{\Omega}}{\sqrt{2\sigma_2}}\right)$ are Hermite polynomials, and γ_j are expressed in terms of the moments, e.g.

$$\gamma_3 = -\frac{\sigma_3}{\sigma_2^{3/2}} \quad \text{--- (8.36)}$$

and

$$F_0(\Omega) = \frac{1}{\sqrt{2\pi\sigma_2}}\, e^{-\frac{(\Omega-\bar{\Omega})^2}{2\sigma_2}} \quad \text{--- (8.37)}$$

with $\bar{\Omega}$ the maxima of the band shape, which is the centre of gravity of the curve .

Taking the first term of the summation of equation (8.35), and using the Hermite polynomial $H_3\left(\frac{\Omega-\bar{\Omega}}{\sqrt{2}\sigma_2}\right)$ we get,

$$F(\Omega) = F_0(\Omega)\left[1 + \sigma_3\left\{\frac{(\Omega-\bar{\Omega})^3}{6\sigma_2^3} - \frac{(\Omega-\bar{\Omega})}{2\sigma_2}\right\}\right] \quad \text{--- (8.38)}$$

The shift of maxima, Ω_m, of band shape from the centre of gravity can be determined by taking

$$\left.\frac{\partial F}{\partial \Omega}\right|_{\Omega=\Omega_m} = 0 \quad \text{--- (8.39)}$$

and by ignoring the higher powers of $(\Omega_m - \bar{\Omega})$ in the above expression we finally get

$$\Omega_m = \bar{\Omega} - \frac{\sigma_3}{2\sigma_2} \quad \text{---- (8.40)}$$

This expression indicates that maxima has shifted to lower frequency side by :-

$$\frac{\sigma_3}{2\sigma_2}$$

The half-width $(\Delta\Omega)$ for $F(\Omega)$ is the width of the spectrum at half the maxima of the band shape function.

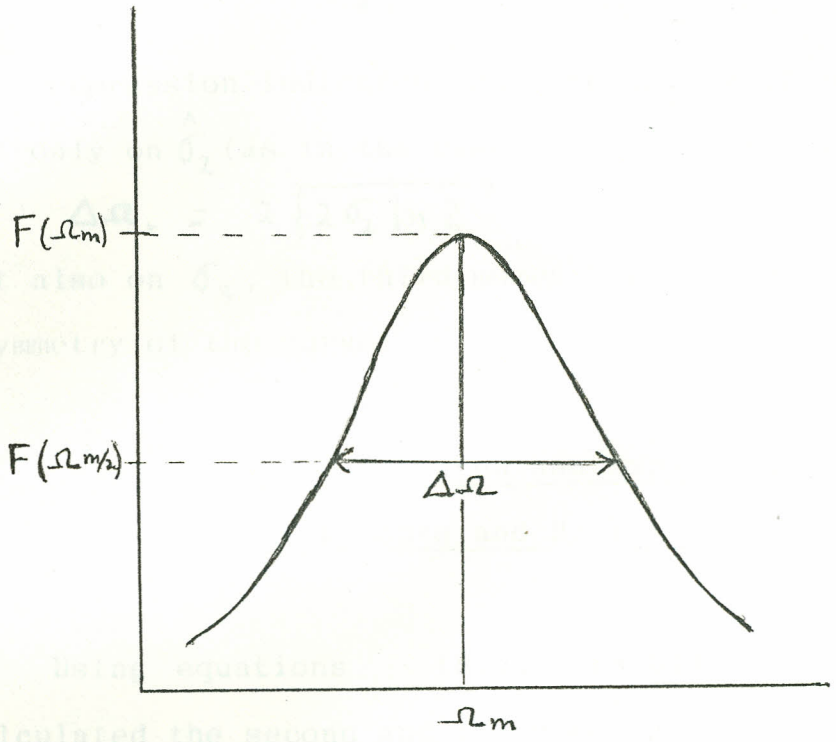


Fig. 8. Optical absorption spectra .

The expression for this half-width is derived by elementary mathematics, using equations (8.38) and (8.40), and knowing that at the half-width

$$\frac{F(\Omega_m)}{F(\Omega)} = 2 \qquad \text{--- (8.41)}$$

Finally, we get,

$$\Delta\Omega = \frac{\sigma_3}{\sigma_2}\left[1 + \frac{8\sigma_2^3}{\sigma_3^2}\ln\left(\frac{2}{1-\frac{3}{8}\frac{\sigma_3^2}{\sigma_2^3}}\right)\right]^{\frac{1}{2}} \quad \text{---} \quad (8.42)$$

This expression indicates that the half-width depends not only on $\hat{\sigma}_2$ (as in the case of Gaussian curve

$$\Delta\Omega_0 = 2\sqrt{2\sigma_2 \ln 2}$$

but also on σ_3, the third moment, which determines the asymmetry of the curve.

§9. Comparison of Calculated and Experimental Values of Moments and Half-widths

Using equations (8.33), (8.34) and (8.42), we calculated the second and third moments, and the half-widths of the broad absorption band of U-centres in KBr and NaI, which are given in table 2. (page 64.).

The temperature dependence of second moment is determined with the help of equation (8.33), which is expressed in the form of graph given in Fig.(9) (page 65.). And Fig.(10) gives the dependence of half-width on temperature (page 66.).

Table 2. Values of second and third moments and the half-widths of U bands in KBr and NaI.

	KBr		NaI
	Calculated	Experimental	Calculated
Second moment σ_2 ($\times 10^{-3}$ eV^2) 7°K	8.01	12.5±0.8	7.18
78°K	14.43	17.2±0.9	12.82
Third moment σ_3 ($\times 10^{-5}$ eV^3) 7°K	10.30	10.9±2.1	8.97
78°K		11.3±2.1	
Half-width (eV) 7°K	0.21	0.25	0.20
78°K	0.28	0.30	0.27

The experimental values have been taken from [34].

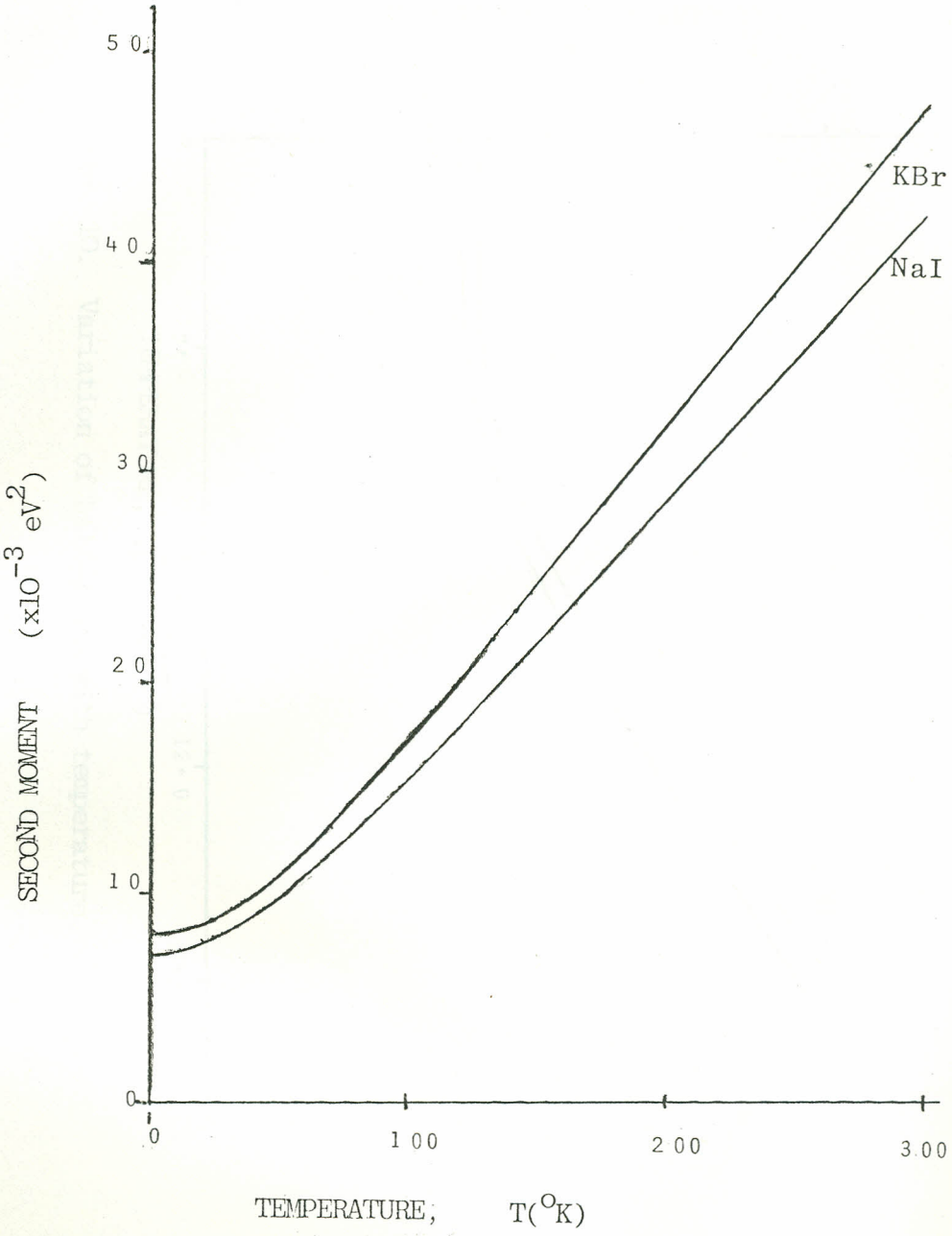


Fig. 9. Variation of second moment with temperature.

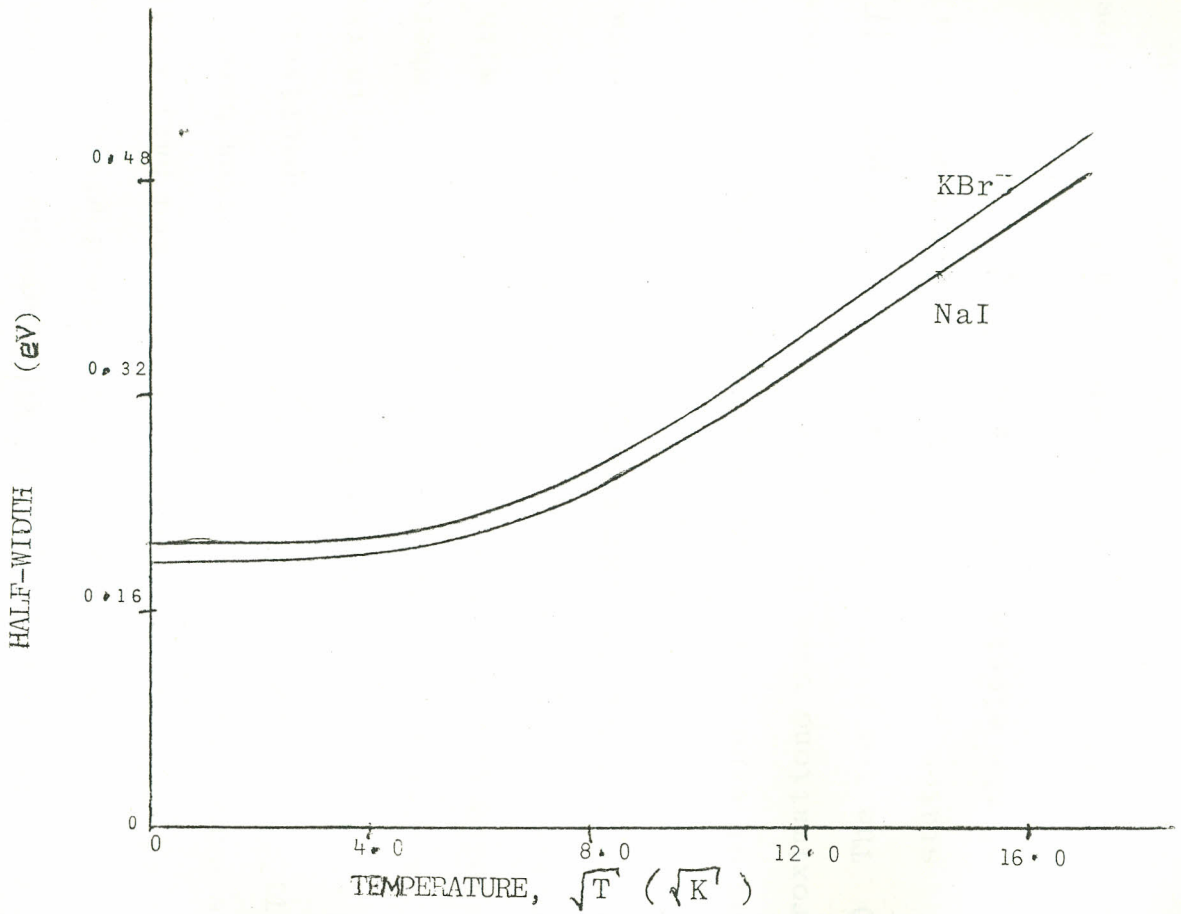


Fig. 10. Variation of half-width with temperature.

CONCLUSION

It was shown in [35] and [46] that the point-ion model of impurity centre and crystal field gives a good agreement of calculated values of moments and half-width with the experimental values for the absorption bands in $CdS:Ti^{+2}$ and $CdSe:Ti^{+2}$, and $Al_2O_3:Cr^{+3}$ respectively. We have shown that this model is also applicable to the p-electron absorption spectra of U-centre in KBr, where we have got a good agreement of calculated values with the experimental values given in table 2. We could give the comparison for KBr crystal only since no data is available for NaI. Our values are 6% to 30% less than that of experimental values, which may be due to the approximations used by us, which are the followings:

(i) The two parameter wavefunctions for $|A\rangle$ and $|T\rangle$ states used to calculate the matrix elements of the electronic operator $\hat{V}_{\Gamma\bar{\Gamma}}$

(ii) The interaction of the electron of impurities centres with the first nearest neighbours has been taken into account.

(iii) The linear electron-phonon interaction w.r.t. the normal coordinates q_α of the lattice vibrations has been taken.

(iv) The frequency effect has been ignored.

(v) The covalency of the crystal field theory has not been taken.

(vi) The phonon sum has been calculated, not based on the real phonon spectrum, but in Debye model for acoustical and Einstein model for the optical mode of vibrations.

The temperature dependences of second moment and half-width are shown in Figs. 9. and 10. respectively but comparison could not be made with the experimental values. The second moment and the half-widths are directly proportional to T and $\sqrt{T}$ respectively at high temperatures. These dependences are similar to the ones in [35] and [46]. Experimentally, temperature dependent third moment [34] is found to be temperature independent in our case where we have taken only linear electron-phonon interaction. This temperature dependence of the σ_3 can be accounted for by taking the quadratic terms w.r.t. q_κ in electron-phonon interaction operator.

Finally, we conclude that the point-ion model of the crystal field and extended Brilouin Zone scheme for the calculation of phonon sum are applicable to the absorption spectrum by p-electrons of U-centre in KBr, while the calculated values of the moments for NaI can act as prediction to the experimental values expected. The improvement of the theoretical values can be achieved if we take into account the above cited factors e.g. quadratic EPI operator, covalency

of crystal field theory, interaction with the next nearest neighbour surrounding etc.

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