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OPTICAL ABSORPTION OF COPPER IONS IN SODIUM CHLORIDE CRYSTALS

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ABSTRACT

The Born-Oppenheimer approximation is used to obtain the oscillator strength of copper ions in sodium chloride crystals. We obtain the wave functions for the copper free ion corresponding to the states $3d^{10}$ *and* $3d^9\,4s'$ *using the Slater-Zener rules. Thenceforth, by a second order perturbation method we obtain the wave functions for the copper ion perturbed by a simplified lattice potential. Finally, the matrix elements corresponding to the dipole moment are calculated, and these are related to the oscillator strength at low temperatures.*

RESUMEN

Se hace un cálculo del tipo Born-Oppenheimer para determinar la intensidad del oscilador para iones de Cobre en cristales de NaCl. Se obtienen las funciones *de onda para el ión libre de Cu a partir de las relas de Slater-Zener correspondientes a los estados* $3d^{10}$ *y* $3d^9\,4s'$*. A continuación por un cálculo perturbativo a segundo orden se obtienen las funciones para el ion de Cu perturbadas por el potencial de la red simplificado. Finalmente se calculan los elementos de matriz correspondientes al momento dipolar para relacionarlas con la intensidad del oscilador a bajas temperaturas.*

INTRODUCTION

There exists already in the literature some calculations of the type we give in this paper. Williams, Knox[1] and Dexter[2] have treated the optical absorption of Tl^+ ions in KCl in detail, Conway et al[3] have considered the optical absorption of Ag ions in NaCl using a simplified model. Unfortunatelly there are many printing errors in this paper, which makes it very difficult to follow. Using a similar method to the ones cited above, we have studied the absorption of Cu^+ ions in NaCl. The ground state of the Cu^+ free ion is assumed to be a $3d^{10}$ state, and the excited state $3d^9\,4s'$ state. We assume with Krumhamsel that the introduction of a Cu^+ ion in NaCl lattice causes a mixing of the above mentioned states with the states of the next level, i.e., the 4p states. To calculate the wave functions of the Cu^+ free ion we used the Slater-Zenes rules[4] and for the lattice potential we considered only the first six nearest neighbors. Using this potential we calculate the wave functions perturbed by the lattice potential and with these wave functions the dipolar matrix elements can be calculated. These are directly related to the oscillator strength in the low temperature limit.

A. DETERMINATION OF THE WAVE FUNCTIONS OF THE FREE CU^+ ION

The perturbation theory is based on the use of the hydrogen-like orbitals in the zero-order wave functions.

These functions have the form

$$\Psi_{nlm} = R_{nl}(r)\, e^{-\frac{zr}{n}}\, Y_{lm}(\theta, \varphi)$$

For the present purpose they can be simplified into the form;

$$\Psi_{n^* lm} = r^{n^*-1} e^{-\frac{(z-s)r}{n^*}} Y_{lm}(\theta, \varphi)$$

Where n^* and s are obtained by the Slater-Zener rules. For the 4s and 4p orbitals the value obtained for S is $S_4 = 24.45$ and for the 3d orbital $S_3 = 21.15$.

The values obtained for n^* is $n^*_4 = 3.7$, $n^*_3 = 3$. So that, for Cu with $Z - 29$ we obtain:

$$\underset{4s \text{ or } 4p}{\Psi} (\text{radial}) = r^{2\cdot 7} e^{-1\cdot 23 r}$$

and

$$\Psi_{3d} (\text{radial}) = r^2 e^{-2\cdot 62 r}$$

In normalizing these functions we use the definition of $\Gamma(z)$;

$$\Gamma(z) = \int^{\infty} e^{-t} t^{z-1} dt$$

Thus, with the normalization condition:

$$c^2 \int \Psi^2 r^2 dr = 1$$

We obtain for the normalized wave-functions:

$$X_{4s}(r) = \frac{r^{2\cdot 7} e^{-1\cdot 23 r}}{\left[\frac{\Gamma(8.4)}{(2.46)^{8\cdot 4}}\right]^{\frac{1}{2}}}$$

and

$$X_{3d}(r) = \frac{r^2 e^{-2.62r}}{\left[\frac{\Gamma(7)}{(5.24)^7}\right]^{\frac{1}{2}}}$$

In the same way we obtain the wave functions corresponding to the normalized angular parts[5]

$$s = \left(\frac{1}{4\Pi}\right)^{\frac{1}{2}}, \; p_1 = p_x = \left(\frac{3}{4\Pi}\right)^{\frac{1}{2}} \sin\theta \cos\varphi$$

$$p_2 = p_y = \left(\frac{3}{4\Pi}\right)^{\frac{1}{2}} \sin\theta \sin\varphi, \; p_3 = p_z = \left(\frac{3}{4\Pi}\right)^{\frac{1}{2}} \cos\theta$$

$$d_{zx} = \left(\frac{15}{4\Pi}\right)^{\frac{1}{2}} \sin\theta \cos\theta \cos\varphi$$

$$d_{x^2-z^2} = \left(\frac{15}{16\Pi}\right)^{\frac{1}{2}} \sin^2\theta \cos\varphi \sin\varphi$$

$$d_{x4} = \left(\frac{15}{4\Pi}\right)^{\frac{1}{2}} \sin^2\theta \cos\varphi \sin\varphi$$

$$d_{z^2} = \left(\frac{5}{16\Pi}\right)^{\frac{1}{2}} (3\cos^2\theta - 1)$$

$$d_{4z} = \left(\frac{15}{4\Pi}\right)^{\frac{1}{2}} \sin\theta \cos\theta \,\mathrm{sih}\,\varphi$$

B. THE LATTICE POTENTIAL

We consider now the potential experienced by a 3d electron of the Cu^+ ion due to the six nearest neighbor (Cl ions) which are assumed to act as point charges.

We take the reference frame in such a way that the Cu^+ ion is at the origin and its displacement from this equilibrium position is denoted by $\overline{w}$ - the Cl^- ions are in the positions $\overline{a}_1, -\overline{a}_1, \overline{a}_2, -\overline{a}_2, \overline{a}_3, -\overline{a}_3$ where $\overline{a}_1, \overline{a}_2, \overline{a}_3$ are the basic lattice vectors and the displacements of these ions are denoted respectively by $\overline{u}_1, \overline{u}_{-1}, \overline{u}_2, \overline{u}_{-2}, \overline{u}_3$ and $\overline{u}_{-3}$. If the position of the electron is denoted by $\overline{r}$, then the change in potential (ΔV_1) due to the displacement from equilibrium of the Cl^- ion at $\overline{a}_1$ and the Cu^+ ion is given by,

$$\Delta V_1 = \frac{-e}{|\overline{a}_1 + \overline{u}_1 - (r + \overline{w})|} + \frac{e}{|\overline{a}_1 - \overline{r}|}$$

Denoting $\overline{w} - \overline{u}_1$ by d and expanding the first term, we have

$$\frac{1}{|\overline{a}_1 - (\overline{r} + \overline{d})|} = a_1^{-1}\Bigg[1 + \frac{\overline{a}_1 \cdot \overline{r}}{a_1^2} + \frac{\overline{a}_1 \cdot \overline{d}}{a_1^2} - \frac{\overline{a} \cdot \overline{d}}{a_1^2} -$$

$$- \frac{1}{2}\left(\frac{r^2}{a_1^2} + \frac{d^2}{a_1^2}\right) + 3\,\frac{(\overline{a}_1 \cdot \overline{r})(\overline{a}_1 \cdot \overline{d})}{a_1^4} +$$

$$+ 3\,\frac{\overline{a}_1 \cdot \overline{r}}{2a_1^4} + 3\,\frac{\overline{r} \cdot \overline{d}}{2a_1^4} + \frac{3}{2}\,\frac{(\overline{a}_1 \cdot \overline{d})^2}{a_1^4} -$$

$$- 3\,\frac{(\overline{a}_1 \cdot \overline{r})(\overline{r} \cdot \overline{d})}{a_1^4} - 3\,\frac{(\overline{a}_1 \cdot \overline{d})(\overline{r} \cdot \overline{d})}{a_1^4} + \frac{3}{16}\left(\frac{r^2}{a_1^2} + \frac{d^2}{a_1^2}\right) + \dots\Bigg]$$

The expansion of the second term gives:

$$\frac{1}{|\overline{a}_1 - \overline{r}|} = a_1^{-1}\left[1 + \frac{\overline{r} \cdot \overline{a}_1}{a_1^2} - \frac{1}{2}\,\frac{r^2}{a_1^2} + \frac{3}{8}\left(\frac{r^2}{a_1^2} - 2\,\frac{\overline{r} \cdot \overline{d}_1}{a_1^2}\right)^2 + \dots\right]$$

Since $|\bar{d}| << 1$ all terms but the first may be neglected, thus

$$\Delta V_1 = - e\Big[\frac{\bar{a}_1 \cdot \bar{d}}{a_1^3} + \frac{3}{2}\,\frac{\bar{a}_1 \cdot \bar{d}}{a_1^5} - \frac{1}{2}\,\frac{\bar{d}^2}{a_1^3} + 3\,\frac{(\bar{a}_1 \cdot \bar{r})(\bar{a}_1 \cdot \bar{d})}{a_1^5} -$$

$$- \frac{(\bar{d} \cdot \bar{r})}{a_1^3} + O^+ \ldots \Big]$$

We note that the first three terms do not involve electron-phonon interaction since they contain $\bar{d}$ but not $\bar{r}$. So if we multiply this result by the charge of the Cu^+ ion and add to it the contribution of the six nearest neighbors (Cl^- ions) we have,

$$\Delta V = e^2 \Big[3\,\frac{(\bar{a}_1 \cdot \bar{r})(\bar{a}_1 - (\bar{u}_1 + \bar{u}_{-1})}{a^5} - \frac{\bar{r} \cdot (\bar{u}_1 + \bar{u}_{-1})}{a_1^3} +$$

$$+ 3\,\frac{(\bar{a}_2 \cdot \bar{r})\,\bar{a}_2 \cdot (\bar{u}_2 + \bar{u}_{-2})}{a^5} - \frac{\bar{r} \cdot (\bar{u}_2 \cdot \bar{u}_{-2})}{a^3} +$$

$$+ 3\,\frac{(\bar{a}_3 \cdot \bar{r})\,\bar{a}_3 \cdot (\bar{u}_3 + \bar{u}_{-3})}{a^5} - \frac{\bar{r} \cdot (\bar{u}_3 + \bar{u}_{-3})}{a^3} \Big]$$

Since $|\bar{a}_1| = |\bar{a}_2| = |\bar{a}_3| = a$

Now following Peierls[6] notation for the lattice displacement we use

$$U_n = \sum_{f,s} q(f,s) \exp(i\bar{f} \cdot \bar{a}'_n)\, \bar{V}(f,s)$$

Where $\bar{f}$ is a vector within the basic cell of the reciprocal lattice.

For each given $\overline{f}$ there are 3 different modes, corresponding to different solutions of the equation;

$$w^2 \overline{V}_j = \sum_{j'} \overline{G}_{j',\, j}(\overline{f})\, \overline{V}_{j'}$$

In general there are a number of solutions $V_{j'}(f, s)$ corresponding to fre frequencies $w(f, s)$ with $S = 1, 2, 3, \ldots, 3r$ and with the values of q satisfying the equation

$$\ddot{q}_{f,s} + \{w(f, s)\}^2 q_{f,s} = 0$$

Now let us take the first two terms of ΔV_1,

$$3\,\frac{(\overline{a}_1 \cdot \overline{r})\,\overline{a}_1 \cdot (\overline{u}_1 + \overline{u}_{-1})}{a^5} - \frac{\overline{r} \cdot (\overline{u}_1 + \overline{u}_{-1})}{a^3} =$$

$$= \sum_{f,s} 3\,\frac{q(f, s)\, V_x(f, s)}{a^3} \left\{ \exp(i\overline{f} \cdot \overline{a}_0)\,[\exp(if_1 a) + \exp(-if_1 a)] \right\}$$

$$- \Sigma_{f,s} \frac{(xV_x + yV_x + zV_z)\exp(i\overline{f} \cdot \overline{a}_2\{\exp(if_1 a) + \exp(-if_1 a)\}}{a^3}$$

Here we have taken into account that, $\overline{a}'_n = \overline{a}_0 + \overline{a}_n$, where $\overline{a}_0$ is a vector from the crystal origin of the unit cell in consideration, and $\overline{a}_n$ are vectors with origin at the end of $\overline{a}_0$ and describes the equilibrium positions of the Cl$^-$ ions, and also, that $\overline{f} = f_1\overline{b}_1 + f_2\overline{b}_2 + f_3\overline{b}_3$ where $\overline{b}_1$, $\overline{b}_2$ and $\overline{b}_3$ define the reciprocal lattice.

The addition of the exponentials gives a term $2\cos(f_1 a)$ and the other four terms of ΔV gives a similar contribution. So we finally hav

$$\Delta V = -\frac{2e^2}{a^3} \sum_{f,s} q_{f,s} \exp(i\overline{f} \cdot \overline{a}_0) \sum_i x_i V_i(f, s)$$

$$[2\cos f_i a - \cos f_j a - \cos f_k a]$$

with $i \neq j \neq k = 1, 2, 3$

To simplify the latter expression we define;

$$\Delta_i = -\frac{2e^2}{a^3} \sum_{f,s} q_{f,s} \exp(i\overline{f} \cdot \overline{a}_0) V_i(f, s)$$

$$[2\cos f_i a - \cos f_j a - \cos f_k a]$$

Thus

$$\Delta V = \sum_i x_i A_i$$

C. WAVE FUNCTIONS PERTURBED BY THE LATTICE POTENTIAL

The ground state of the Cu^+ ion is the configuration $3d^{10}$, and when excited the configuration is $3d^9 4s$' we suppose that the lattice potential can mix the s and d orbitals with the 4p states, so that the perturbed functions φ_{3d} and φ_{4s} will be of the form:

$$\varphi_{3d} = \left[\chi_{3d} + \sum_{i,j} \frac{A_i \langle p_i | x_j | d \rangle \chi_{4p_i}}{E_{3d} - E_{4p}} \right]$$

$$\varphi_{4s} = \left[\chi_{4s} + \sum_{i,j} \frac{A_i \langle p_i | x_j | s \rangle \chi_{4p_i}}{E_{4s} - E_{4p}} \right]$$

where the letter d represents any of the five d functions given previously.

The Born-Oppenheimer approximation is used when we suppose that the wave function of the electron in the initial lattice configuration, as described by X, can be expressed as the following product;

$$\Psi_i(r, X) = \varphi_{3d}\,\Theta_\alpha(X)$$

Where $\Theta_\alpha(X)$ represents the lattice configuration before the transition. In the same manner, the final state of the electron is described by the function:

$$\Psi_f(r, X) = \varphi_{4s}\,\Theta_\beta(X)$$

Where $\Theta_\beta(X)$ represents the final configuration of the lattice.

D. EXPRESSION FOR THE OSCILLATOR STRENGTH IN THE LOW TEMPERATURE LIMIT.

The oscillator strength $f_{ab\alpha\beta}$ is obtained from the following expression:

$$f_{ab\alpha\beta} = \frac{2m^*}{\hbar^2} \int E \left| r_{ab\alpha\beta} \right|^2 S^{(a)}_{ab\alpha\beta}(E)\, dE$$

Where m^* refers to the effective mass of the electron; a, α are referred to the initial states of the electron and the lattice respectivelly, and b, β the final states of the electron and lattice respectively. $S^{a}_{ab\alpha\beta}(E)$ refers to the absorption line shape which can be approximated by:

$$\delta(E_{b\beta} - E_{a\alpha} - E)$$

and $$r_{ab\alpha\beta} = \int dr \int \langle \varphi_{4s}\,\Theta_p(X) \left| r \right| \varphi_{3d}\,\Theta_\alpha(X) \rangle\, dX$$

Averaging over the initial states, and taking a summation over the final states β, the final expression for $f_{ab\alpha\beta}$ takes the form:

$$f_{ab} = \sum_{\beta} Av_{\alpha} f_{ab\alpha\beta}$$

That is

$$f_{ab} = \frac{2m^{\star}}{3b^{2}} Av_{\alpha} \sum_{\beta} (E_{b\beta} - E_{a\alpha}) \left| r_{ab\alpha\beta} \right|^{2}$$

Taking into account that the energy due to the change in the lattice, configuration is small with respect to the electronic transition energy, f_{ab} can be written as

$$f_{ab} = \frac{2m^{\star}}{3b^{2}} (E_{b'} - E_{a}) A \quad \sum_{\beta} \left| r_{ab\alpha\beta} \right|^{2}$$

then the problem reduces to the solving of:

$$\sum_{\beta} \left| r_{ab\alpha\beta} \right|^{2} = \sum_{\beta} \Big| \iint dX dr \left[\chi_{3d} + \sum_{i,f} A_{i} \frac{\langle p_{i} | x_{i} | d \rangle \chi_{4p_{i}}}{E_{3d} - E_{4p}} \right]^{\star} \Theta_{\alpha}^{\star}(X)\, \bar{r} \left[\chi_{4s} + \sum_{i,j} \frac{A_{i} \langle p_{i} | x_{i} | s \rangle \chi_{4p_{i}}}{E_{4s} - E_{4p}} \right] \Theta_{\beta}(X) \Big|^{2}$$

Here *d* again represent any of the five possible *d* states.

Taking into account that[3]

$$\langle \chi_{3d} | \bar{r} | \chi_{4s} \rangle = \langle \chi_{4p_i} | \bar{r} | \chi_{4p_j} \rangle = 0$$

We obtain

$$\sum_{\beta} \left| \Gamma_{ab\alpha\beta} \right|^2 = \sum_{\beta} \left| \int dX \sum_{i,j} \frac{A_j \langle p_i | x_j | d \rangle \langle \chi_{4p_i} | r | \chi_{4s} \rangle}{E_{3d} - E_{4p}} \right.$$

$$\left. \Theta^{*}_{\alpha}(X)\, \Theta_{\beta}(X) + \sum_{i,j} \frac{A_j \langle p_i | x_i | s \rangle \langle \chi_{3d} | r | \chi_{4p_i} \rangle}{E_{4s} - E_{4p}} \Theta^{*}_{\alpha}(X)\, \Theta_{\beta}(X) \right|^2$$

To simplify the calculations let us define γ_j and η_j in the following form:

$$\gamma_j = \sum_i \frac{\langle p_i | x_j | d \rangle \langle \chi_{4p_i} | r | \chi_{4s} \rangle}{E_{3d} - E_{4p}}$$

$$\eta_j = \sum_i \frac{\langle p_i | x_j | s \rangle \langle \chi_{3d} | r | \chi_{4p_i} \rangle}{E_{4s} - E_{4p}}$$

in this case we have

$$\sum_{\beta} \left| \Gamma_{ab\alpha\beta} \right|^2 = \sum_{\beta, j} \left| \langle \Theta_{\alpha} | A_j \gamma_j | \Theta_{\beta} \rangle + \langle \Theta_{\alpha} | A_j \eta_j | \Theta_{\beta} \rangle \right|^2$$

Now B_i can be defined in the following way

$$B_i \equiv - \frac{2e^2}{a^3} \exp(i\bar{f} \cdot \bar{a}_0)\, V_i(f, s) \left[2\cos f_i a - \cos f_j a - \cos f_k a \right]$$

Also it is known[6] that $q_{f,s}$ can be stated in the following form,

$$q_{f,s} = Q(f,s) + Q^{\star}(f,-s)$$

Where the Q's represent the elastic waves travelling in ppposite direction.

Now if the $|\Theta_{\beta}\rangle$ state is expanded in terms of the $|\Theta_{\alpha}\rangle$ set of normal co-ordinates, i.e.,

$$|\Theta_{\beta}\rangle = \sum_{\alpha'} (\langle \Theta_{\alpha'} | \Theta_{\beta}\rangle) | \Theta_{\alpha'} \rangle$$

We have:

$$\sum_{\beta} |\Gamma_{ab\alpha\beta}|^{2} = \sum_{\beta, j, f, s, \alpha'} | \langle \Theta_{\alpha'} | \Theta_{\beta} \rangle \gamma_j B_j \langle \Theta_{\alpha} | Q_{f,s} + Q^{\star}_{-f,s} | \Theta_{\alpha'} \rangle$$

$$+ \langle \Theta_{\alpha'} | \Theta_{\beta} \rangle \eta_j B_j \langle \Theta_{\alpha} | Q_{f,s} + Q^{\star}_{-f,s} | \Theta_{\alpha'} \rangle |^{2}$$

Now, $Q(f,s)$ and $Q^{\star}(f,-s)$ in the quantum representation are the annihilation and creation operators respectively, and obey the following relations

$$\langle \Theta_{\alpha} | Q_{f,s} | \Theta_{\alpha} + 1 \rangle = \left(\frac{\hbar}{2M^{N}\omega_{f,s}} \right)^{\frac{1}{2}} \sqrt{N_{\alpha} + 1}$$

$$\langle \Theta_{\alpha} | Q^{\star}_{-f,s} | \Theta_{\alpha} - 1 \rangle = \left(\frac{\hbar}{2M^{N}\omega_{f,s}} \right)^{\frac{1}{2}} \sqrt{N_{\alpha}}$$

the other matrix elements being zero.[6]

Thus,

$$\sum_{\alpha', \beta} [\langle \Theta_\alpha | Q_{f,s} + Q^{\star}_{-f,s} | \Theta_{\alpha'} \rangle \langle \Theta_\beta \rangle]^2 =$$

$$= \sum_\beta \frac{b(N_\alpha + 1)}{2M^N \omega_{f,s}} \langle \Theta_{\alpha+1} | \Theta_\beta \rangle^2 + \frac{\hbar}{2M^N \omega_{f,s}} N_\alpha \langle \Theta_{\alpha-1} | \Theta_\beta \rangle^2$$

$$= \frac{b}{2M^N \omega_{f,s}} (2N_\alpha + 1)$$

Where we have made use of the fact that

$$\sum_\beta \langle \Theta_{\alpha+1} | \Theta_\beta \rangle^2 = \sum_\beta \langle \Theta_{\alpha-1} | \Theta_\beta \rangle^2 = 1$$

and also, $N_\alpha (f, s) = N_\alpha (f, -s)$ in thermal equilibrium. It can be shown[6] that at $T = O^0 k$, $N_\alpha = 0$.

So we have finally:

$$\sum_\beta | \Gamma_{ab\alpha\beta} |^2 = \sum_{f,s,j} | \gamma_j B_j (f,s) + \eta_j B_j (f,s) |^2 \frac{b}{2M^N \omega_{f,s}}$$

E. CALCULATION OF MATRIX ELEMENTS

For the radial part of the matrix elements, we have

$$\langle \chi_d | r | \chi_p \rangle = \int_0^\infty \frac{r^2 e^{-2.6 r^2}}{\left(\frac{\Gamma(7)}{5.24^7}\right)^{1/2}} r \frac{r^{2.7} e^{-1.23 r}}{(\Gamma(8.4) / 2.46^{8.4})^{1/2}} = 0.87$$

and

$$\langle \chi_p | r | \chi_s \rangle = \int_0^\infty \frac{r^{5.4} e^{-2.46 r} r^3 \, dr}{[\Gamma(8.4) / 2.46^{8.4}]} = 3.41$$

For the angular part, let us take the function d_{xy} i.e.,

$$\langle d_{xy} | r_i | p_1 \rangle = \left(\frac{15}{16\Pi}\right)^{\frac{1}{2}} \iint \sin^2\theta \cos\varphi \sin\varphi \left\{ \begin{matrix} \sin\theta \cos\varphi \\ \sin\theta \sin\varphi \\ \cos\theta \end{matrix} \right\} \times$$

$$\left(\frac{3}{4\Pi}\right)^{\frac{1}{2}} \sin\theta \cos\varphi \sin\theta \, d\theta \, d\varphi =$$

$$= \left(\frac{45}{64\Pi^2}\right)^{\frac{1}{2}} \left\{ \begin{matrix} 0 \\ 16\Pi/60 \\ 0 \end{matrix} \right\}$$

Where we have calculated simultaneously the three components. Also we have

$$\langle d_{xy} | r_i | p_y \rangle = \left(\frac{45}{64\Pi^2}\right)^{\frac{1}{2}} \left\{ \begin{matrix} 16\Pi/60 \\ 0 \\ 0 \end{matrix} \right\}$$

$$\langle d_{xy} | r_i | p_z \rangle = \left(\frac{45}{64\Pi^2}\right)^{\frac{1}{2}} \left\{ \begin{matrix} 0 \\ 0 \\ 0 \end{matrix} \right\}$$

$$\langle p_x | r_i | s \rangle = \left(\frac{3}{16\Pi^2}\right)^{\frac{1}{2}} \left\{ \begin{matrix} 4\Pi/3 \\ 0 \\ 0 \end{matrix} \right\}$$

$$\langle p_y | r_i | s \rangle = \left(\frac{3}{16\Pi^2}\right)^{\frac{1}{2}} \left\{ \begin{matrix} 0 \\ \Pi \\ 0 \end{matrix} \right\}$$

$$\langle p_z | r_i | s \rangle = \left(\frac{3}{16\Pi^2}\right)^{\frac{1}{2}} \left\{ \begin{matrix} 0 \\ 0 \\ 0 \end{matrix} \right\}$$

F. FINAL EXPRESSION FOR THE OSCILLATOR STRENGTH

In expanding the expression

$$|\gamma_j B_j + \eta_j B_j|^2$$

There are many terms that cancel out due to the fact that the matrix elements are zero.

Also we have considered only one atom for unit cell, we have only one displacement vector $\overline{v}(f,s)$, thus, by the symmetry of the crystal with respect to the three axis chosen, we have,

$$|B_i|^2 = |B_j|^2$$

where the sub-indexes refers to the components of B along the different axis.

Also from the normalization condition for the $\overline{v}_i$ we have[6] $|\overline{v}|^2 = 1$ in the case of one a form per unit cell.

Thus, we obtain

$$\sum_{\beta} |r_{aba\beta}|^2 = \sum_{f,s,j} |\gamma_j B_j + \eta_j B_j|^2 \frac{\hbar}{2M^N\omega_{f,s}}$$

$$= \sum_{f,s} \frac{2\hbar}{2M^N\omega_{f,s}} \left(\frac{1}{E_{3d} - E_{4p}} + \frac{1}{E_{4s} - E_{4p}} \right)^2 \langle p_x |x| s\rangle^2 \langle d_{xy} |y| p_x\rangle^2 \times$$

$$\langle \chi_{4p} |r| \chi_{4s}\rangle^2 \langle \chi_{3d} |r| \chi_{4p}\rangle^2 |B_1|^2$$

Now, form the symmetry $|v_x|^2 = \frac{1}{3} |\overline{v}|^2$

and

$$|B_1|^2 = \frac{4e^4}{a^6}\frac{1}{3}|\overline{v}|^2 [2\cos f_1 a - \cos f_2 a - \cos f_3 a]^2$$

If now we use the Debye approximation[6] the summation over s is the change to a factor 3, $\omega_{f,s} = cf$ and the summation over f is changed into an integral, so that taking into account the symmetry; we have

$$\iiint \frac{\cos r_i}{|\overline{r}|} d^3r = \iiint \frac{\cos^2 r_j}{|\overline{r}|}$$

and

$$\iiint \frac{\cos r_i \cos r_j}{|\overline{r}|} d^3r = \iiint \frac{\cos r_i \cos r_k}{|\overline{r}|} d^3r$$

thence

$$\sum_\beta |r_{ab\alpha\beta}|^2 = \frac{\hbar}{M^N}\left(\frac{1}{E_{3d} - E_{5p}} + \frac{1}{E_{4s} - E_{4p}}\right)^2 \langle p_x | x | s\rangle^2 \langle d_{xy} | y | p_x\rangle^2$$

$$\langle x_{4p} | r | x_{4s}\rangle^2 \langle x_{3d} | r | x_{4p}\rangle^2 \frac{4e^2}{a^6} \frac{V}{(2\Pi)^3}\, 6 \iiint_{-\Pi}^{\Pi} \frac{d^3r\,(2\cos x - \cos y - \cos z)}{a^2 c |\overline{r}|}$$

where $a^2 = v_c^{2/3}$ with v_c the volume of unity cell.

The terms $V/(2\Pi)^3$ appear because of the Debye approximation, and c is the propagation velocity and is given by the equation[6] $c = \frac{h}{K\theta_D} 3\sqrt{\frac{9}{4\Pi V_c}}$

Finally, for a trapped electron, the effective mass is $m^* = m$ where m is the mass of the free electron, so we have

$$f_{ab} = \frac{2m}{3h^2} (E_b - E_a) A v_3 \sum_\beta |r_{ab\alpha\beta}|^2$$

This value fiven for f_{ab} is only for the function d_{xy}, the other four d functions are missing; but in evaluating the matrix elements corresponding to these missing functions, it is found that the result is the same . Thus the final expression for F_{ab} is given by

$$F_{ab} = 5f_{ab}$$

The numerical values obtained from these final expressions are:

$E_b - E_a \simeq 5\text{ev}$ $\qquad Av_a = 2$

$\langle p_x | x | s \rangle \langle x_{4p} | r | x_{4s} \rangle = 1.96$

$\langle p_x | y | d_{xy} \rangle \langle x_{3d} | r | x_{4p} \rangle = 0.19$

$$\mathrm{I} = \iiint_{-\Pi}^{\Pi} \frac{(2\cos x - \cos y - \cos z)}{|\bar{r}|} d^3 r = 41.10$$

$E_{3d} - E_{4p} \simeq 10\text{ev}$ $\qquad E_{4s} - E_{4p} \simeq 5\text{ev}$

$a = 2.81\ \text{Å}$

$M = 17$

The propagation velocity is given in terms of Debye temperature θ_D, which is taking to be 300°K. All the values are given in atomic units[4] giving a value for $F_{ab} = 10^{-4}$ which is typical of this type of calculation[7] the only matter left is to compare this value with that obtained experimentally.

CONCLUSIONS

Complete calculations on realistic models of a lattice with an imperfection are extremely involved, and so far they have not been carried out except in a formal manner. During the last 50 years Physicists have made calculations on unrealistic models hoping to gain some insight into the properties of phonons and phonon-electron interactions. In calculations of the oscillator strength for absorption it is necessary to obtain an expression for the local field, that is, the actual field at the imperfection. At present no reliable theory exists. With respect to the applicability of the Born-Oppenheimer approximation, Lax[8] has sufficiently justified it. It must be noted that even if several works have been published[9], where the local lattice modes are taken into account, these have been carried out in one dimensional lattices only[10]. Finally, about the validity of the multipole expansion of the electromagnetic field, which has been used implicitly in the calculation of f, we can say that it is always valid for wave functions whose extension is small compared to the wave length of the radiation that can be absorbed[11]. This is the case for an electron trapped in a crystal.

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