

## Transition Energies of the $F_2$ Color Center

CHIA-HSIUNG YANG (楊佳雄)

*Tsing Hua University, Hsinchu, Taiwan*

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Several quantum states of the  $F_2$  center in KCl crystal have been calculated by a new assumption. The relation between the  $F_2$  center and the  $M$  absorption bands in KCl crystal is discussed. The results of the present work give the preference of attributing the  $M$  absorption bands to the  $F_2$  center.

### 1. INTRODUCTION

IN the present paper, the interaction between electrons and phonon field is taken into account under the assumption that the vacant centers are regarded as point charges immersed in a continuum dielectric medium with an effective dielectric constant. Therefore, the interactions of the phonons with the electrons and the trap centers exist regardless of electron position. This idea can be explained as following:

There is no electron-phonon interaction when the electron is in the region of the vacancy, since ion cannot follow the motion of electron. The electron-phonon interaction occurs only when the electron is moving outside of the vacancies. So far as we know, the ratio of the electron moving inside of the vacancy to outside of the vacancy is inversely proportional to the state of the electron, *i. e.* the higher the electron state, the smaller the ratio. In addition, the dielectric constant  $1/\epsilon^*$  appears only when the electron-phonon interaction is introduced. Therefore, the dielectric  $1/\epsilon^*$  can be used as an effective constant which is different from state to state and can be calculated from the known energy values below the bottom of the conduction band of each state of the  $F$  center.

In the calculation of the energy states of the  $F_2^+$  and  $F_2$  centers, the electron part wave functions are taken to be a linear combination of hydrogen like wave function which are also used in  $F$  center. Owing to this fact,  $1/\epsilon^*$  can be considered as a characteristic of a given state wave function.

### 2. THE DETERMINATION OF EFFECTIVE DIELECTRIC CONSTANT BY $F$ CENTER

The presently accepted picture of the  $F$  center is the lattice defect model in which an electron is trapped by a negative ion vacancy. Both theoretical calculations and experimental facts tend to conclude that the  $F$  absorption band arises from the  $1s-2p$  transition of the trapped electron. The experimental values of

energy below the bottom of the conduction band of the  $1s$  and  $2p$  states of the  $F$  center are  $-2.5$  ev. and  $-0.2$  ev., respectively. ( ) We can use these two values to calculate the effective dielectric constants for the  $1s$  and  $2p$ 's wave functions under our present assumption.

Following the work of S. F. Wang<sup>(2,3)</sup>, the Hamiltonian of the  $F$  center under our present assumption is

$$H = \frac{p^2}{2m} + \sum_k \hbar w_k a_k^* a_k + \sum_k (V_k a_k e^{i\mathbf{k}\cdot\mathbf{r}} + V_k^* a_k^* e^{-i\mathbf{k}\cdot\mathbf{r}}) - \sum_k (V_k a_k + V_k^* a_k^*) - \frac{e^2}{\epsilon_\infty r}. \quad (1)$$

Here we neglect the zero point energy  $\sum_k (1/2\hbar w_k)$ , since we shall use the energy below the bottom of the conduction band of  $F$  center to calculate the effective dielectric constant  $1/\epsilon^*$ . And after an integration, the zero point energy becomes a constant, containing no variational parameter which can be regarded as the conduction band energy. The physical meaning of all the symbols are the same as interpreted in references 2 and 3.

Using the canonical transformation  $A_k = a_k - \frac{V_k^*}{\hbar w_k}$ , Eq. (1) is simplified as

$$H = \frac{p^2}{2m} + \sum_k \hbar w_k A_k^* A_k + \sum_k (A_k V_k e^{i\mathbf{k}\cdot\mathbf{r}} + C. C.) - \frac{e^2}{\epsilon_s r} \quad (2)$$

Then following the methods introduced in references 2 and 3, but with

$$f(\mathbf{K}) = [1 - \frac{V_k^* \varphi_k^*}{\hbar w_k} A_k^*] |0\rangle \text{ and } \varphi_k = \int |\varphi(\mathbf{r})|^2 e^{i\mathbf{k}\cdot\mathbf{r}} d^3r$$

and taking the  $1s$  hydrogen-like wave function

$$\psi_{1s}(\mathbf{r}) = \left(\frac{a^3}{\pi}\right)^{1/2} e^{-a r}$$

as the ground state trial function of the  $F$  center, we get the effective Hamiltonian

$$H_{eff} = \frac{p^2}{2m} + \frac{e^2}{\epsilon^*} \frac{1}{7} (e^{-2ar} - a r e^{-2ar}) + \frac{5}{16} \frac{e^2}{\epsilon^*} + \frac{e^2}{\epsilon_\infty r}. \quad (3)$$

The  $1s$  state energy of the  $F$  center is

$$E_{1s} = \langle \psi_{1s}, H_{eff} \psi_{1s} \rangle = \frac{\hbar^2 a^2}{2m} + \frac{11}{16} \frac{e^2}{\epsilon^*} a - \frac{e^2}{\epsilon_\infty} a. \quad (4)$$

Eq. (4) gives  $E_{1s}$  as a function of parameter  $a$ , and as  $a \rightarrow 0$ ,  $E_{1s} \rightarrow 0$ . It shows that the zero energy is at the bottom of the conduction band.

Next we use

$$\psi_{2p} = \left(\frac{\beta^5}{2\pi}\right)^{1/2} r e^{-\beta r} \cos \theta$$

(1) R. K Swank and F. C. Brown, Phys. Rev. Letters **8**,10 (1962)

(2) S. F. Wang, Phys. Rev. **132**, 573 (1963)

(3) S. F. Wang, Chin. J. Phys. **2**, 6 (1964)

as the trial wave function for the  $2p$  state of the  $F$  center, and use Eq. (3) as the effective Hamiltonian for this state because we consider the optical transition.

We get

$$E_{2p} = \frac{\hbar^2 \alpha^2}{2m} + \frac{5}{16} \frac{e^2}{\epsilon^*} \alpha - \frac{e^2}{2\epsilon_\infty} \beta + \frac{e^2}{\epsilon^*} \left( \frac{\beta^5}{2(a+\beta)^4} + \frac{\beta^5}{(a+\beta)^5} \right) \quad (5)$$

Using the variational method to minimize the energies of Eqs. (4) and (5) and then substituting all known values into them, we get

$$(1/\epsilon^*)_{1s} = 0.059, \quad (6)$$

$$\text{and } (1/\epsilon^*)_{2p} = 0.149. \quad (7)$$

We have applied the present assumption to calculate two most low lying states of  $F_2^+$  center. The results are listed in table 1. We find that the values obtained by this new assumption agree with other methods very well.

### 3. THE TRANSITION ENERGIES OF THE $F_2$ CENTER

Under the same assumption the Hamiltonian of the  $F_2$  center is written as:

$$\begin{aligned} H = & \frac{p_1^2}{2m} + \frac{p_2^2}{2m} + \frac{e^2}{\epsilon_\infty b} + \frac{e^2}{\epsilon_\infty r_{12}} + \frac{-e^2}{\epsilon_\infty r_{1a}} + \frac{-e^2}{\epsilon_\infty r_{1b}} - \sum_k (V_k a_k e^{ik \cdot r_{1a}} + c. c.) \\ & + \sum_k (V_k a_k e^{ik \cdot r_{1b}} + c. c.) + \frac{-e^2}{\epsilon_\infty r_{2a}} + \frac{-e^2}{\epsilon_\infty r_{2b}} + \sum_k (V_k a_k e^{ik \cdot r_{2a}} + c. c.) \\ & + \sum_k (V_k a_k e^{ik \cdot r_{2b}} + c. c.) + \sum_k \hbar \omega_k a_k^\dagger a_k - \sum_k (V_k a_k e^{ik \cdot R_a} + c. c.) \\ & - \sum_k (V_k a_k e^{ik \cdot R_b} + c. c.), \end{aligned} \quad (8)$$

where  $r_{12}, r_{1a}, r_{1b}, r_{2a}, r_{2b}, R_a, R_b$  are respectively the distances between the electrons, 1st electron and a-center, 1st electron and b-center, 2nd electron and a-center, 2nd electron and b-center and the position vectors of a-center and b-center.

With the help of the canonical transformation  $A_k = a_k - \frac{V_k^*}{\hbar \omega_k} (e^{-ik \cdot R_a} - e^{-ik \cdot R_b})$ ,

Eq. (8) can be simplified to the form

$$\begin{aligned} H = & \frac{p_1^2}{2m} + \frac{p_2^2}{2m} + \frac{e^2}{\epsilon_\infty b} + \frac{e^2}{\epsilon_\infty r_{12}} + \sum_k \hbar \omega_k A_k^\dagger A_k \\ & - \frac{e^2}{\epsilon_s r_{1a}} - \frac{e^2}{\epsilon_s r_{1b}} + \sum_k (V_k A_k e^{ik \cdot r_1} + C. C.) \\ & - \frac{e^2}{\epsilon_s r_{2a}} - \frac{e^2}{\epsilon_s r_{2b}} + \sum_k (V_k A_k e^{ik \cdot r_2} + C. C.). \end{aligned} \quad (10)$$

To the first order perturbation, the one phonon wave function was obtained as follows:

$$f(k) = [1 - \frac{2V_k^* \phi_k^*}{\hbar \omega_k} A_k^\dagger] |0\rangle.$$

The ground state trial wave function of the  $F_2$  center is chosen to be

$$\psi_g(r_1, r_2) = \phi_g(r_1) \phi_g(r_2), \quad (11)$$

where  $\phi_g(\mathbf{r}) = \frac{1}{\sqrt{2(1+D_g)}}(u_a(\mathbf{r}) + u_b(\mathbf{r}))$  and  $u(\mathbf{r}) = \left(\frac{\alpha^3}{\pi}\right)^{1/2} e^{-\alpha r}$ .

$D_g$  is the interlapped integral.

Using the total phonon wave function  $\Phi = \Pi_k f(k)$ , the effective Hamiltonian for the system of  $F_2$  center is

$$\begin{aligned} H_{eff} &\equiv \langle \Phi, H \Phi \rangle \\ &= \frac{p_1^2}{2m} + \frac{p_2^2}{2m} + \frac{e^2}{\epsilon_\infty b} + \frac{e^2}{\epsilon_\infty r_{12}} - \frac{e^2}{\epsilon_s} \left( \frac{1}{r_{1a}} + \frac{1}{r_{2a}} + \frac{1}{r_{1b}} + \frac{1}{r_{2b}} \right) \\ &+ \frac{e^2}{\epsilon^*} \frac{4}{(1+D_g)^2} \left( \frac{5}{16} \alpha + \alpha D_g \right) + \frac{-2e^2}{\epsilon^* r_{1a}} + \frac{-2e^2}{\epsilon^* r_{2b}} \\ &+ \frac{2}{1+D_g} \frac{e^2}{\epsilon^* r_{1a}} (e^{-2\alpha r_{1a}} + \alpha r_{1a} e^{-2\alpha r_{1a}}) + \frac{2}{1+D_g} \frac{e^2}{\epsilon^* r_{2b}} (e^{-2\alpha r_{2b}} + \alpha r_{2b} e^{-2\alpha r_{2b}}). \end{aligned} \quad (12)$$

Using Eq. (11) as the ground state trial wave function, we get the ground state energy

$$\begin{aligned} E_g &= \langle \psi_g, H_{eff} \psi_g \rangle \\ &= \frac{2}{1+D_g} \frac{\hbar^2 \alpha^2}{2m} \left[ 1 + (1+ab - \frac{1}{3} \alpha^2 b^2) e^{-\alpha b} \right] + \frac{e^2}{\epsilon^*} \frac{4}{(1+D_g)^2} \left( \frac{5}{16} \alpha + \alpha D_g \right) \\ &+ \frac{1}{[2(1+D_g)]^2} \frac{e^2}{\epsilon_\infty} (2I_{11} + 8I_{12} + 4I_{13} + 2I_{14}) \\ &- 4 \frac{e^2}{\epsilon_\infty} \frac{1}{2(1+D_g)} \left\{ \alpha + \frac{2}{b} (ab + \alpha^2 b^2) e^{-\alpha b} + \frac{1}{b} [1 - (1+ab) e^{-2\alpha b}] \right\} + \frac{e^2}{\epsilon_\infty b}, \end{aligned} \quad (13)$$

where  $I_{11} = \int u_a^2(1) \frac{1}{r_{12}} u_a^2(2) d^3 r_1 d^3 r_2$

$$I_{12} = \int u_a^2(1) \frac{1}{r_{12}} u_a(2) u_b(2) d^3 r_1 d^3 r_2$$

$$I_{13} = \int u_a(1) u_b(1) \frac{1}{r_{12}} u_a(2) u_b(2) d^3 r_1 d^3 r_2,$$

$$I_{14} = \int u_a^2(1) \frac{1}{r_{12}} u_b^2(2) d^3 r_1 d^3 r_2.$$

The trial wave functions of the other three lowest excited states, say, A, B, C, are chosen as follow:

State, A (or  $1s\sigma 2p\sigma$ )

$$\psi_A(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} [\phi_g(\mathbf{r}_1) \phi_A(\mathbf{r}_2) + \phi_g(\mathbf{r}_2) \phi_A(\mathbf{r}_1)], \quad (14)$$

where  $\phi_g(\mathbf{r}) = \frac{1}{\sqrt{2(1+D_g)}} [u_a(\mathbf{r}) + u_b(\mathbf{r})]$ ;  $u(\mathbf{r}) = \left(\frac{\alpha^3}{\pi}\right)^{1/2} e^{-\alpha r}$ .

$$\phi_A(\mathbf{r}) = \frac{1}{\sqrt{2(1-D_A)}} [x_a(\mathbf{r}) - x_b(\mathbf{r})]; \quad x(\mathbf{r}) = \left(\frac{\beta^3}{\pi}\right)^{1/2} e^{-\beta r}.$$

State B (or  $1s\sigma 2p\pi$ )

$$\psi_B(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} [\phi_g(\mathbf{r}_1) \phi_B(\mathbf{r}_2) + \phi_g(\mathbf{r}_2) \phi_B(\mathbf{r}_1)], \quad (15)$$

where  $\phi_B(\mathbf{r}) = \frac{1}{\sqrt{2(1+A_B)}}[y_a(\mathbf{r}) + y_b(\mathbf{r})]$ ;  $y(\mathbf{r}) = \left(\frac{\lambda^5}{\pi}\right)^{1/2} r e^{-\lambda r} \sin \theta \cos \varphi$ .

State C (or  $1s\sigma 4f\sigma$ )

$$\psi_C(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}}[\phi_z(\mathbf{r}_1)\phi_C(\mathbf{r}_2) + \phi_z(\mathbf{r}_2)\phi_C(\mathbf{r}_1)], \quad (16)$$

where

$$\phi_C(\mathbf{r}) = \frac{1}{\sqrt{2(1+A_C)}}[Z_a(\mathbf{r}) + Z_b(\mathbf{r})]; \quad Z(\mathbf{r}) = \left(\frac{\delta^5}{\pi}\right)^{1/2} r e^{-\delta r} \cos \theta.$$

All of the above three excited state wave functions are symmetry. They are all orthogonal to the ground state, trial wave function. Since we consider the optical transition, Eq. (12) has been used as the effective Hamiltonian of the above three states. In a similar way, we can evaluate the energy of each state. Each energy state contains two variational parameters. But in real calculation both parameters are changed in a similar way, i. e. we regard as if every state has only one parameter. There are several integrals which: cannot be evaluated explicitly. Those integrals can be found from the tables of references 4 and 5. One more concept which we have used in the calculation should be emphasized here, that is, we consider the optical transition. The transition is so quick that at the moment of transition the phonon field is unchanged. Therefore, we use the same dielectric constant as used in its ground state for the terms which become constant after treating by phonon function.

The energy for the states described above are computed by variation principle for KCl crystal with  $b=4.44 \text{ \AA}$ . The calculated transition energies for various transitions of the  $F_2^+$  and  $F_2$  centers, and experimental values of the  $M_1, M_2, M_3$  and  $M_4$  bands in KCl are listed in the following table.

Table 1

Centers	Transitions	$\Delta E$ (ev.) (present method)	$\Delta E$ (ev.) <sup>(6)</sup> (H. W. W. method)	$\Delta E$ (ev.) <sup>(7)</sup> (S. F. Wang Method)	Experiment <sup>(8)</sup> Band $\Delta E$ (ev.)
$F_2$	$(1s\sigma)^2 - (1s\sigma)(2p\sigma)$	1.49	1.62	1.62	$M_1$ 1.55
$F_2$	$(1s\sigma)^2 - (1s\sigma)(2p\pi)$	2.21	2.01	—	$M_2$ 2.27
$F_2$	$(1s\sigma)^2 - (1s\sigma)(4f\sigma)$	2.32	—	—	$M_3$ 2.52
					$M_4$ 1.96
$F_2^+$	$1s\sigma - 2p\sigma$	0.73	0.66	0.93	
$F_2^+$	$1s\sigma - 2p\pi$	2.64	—	—	

(4) J. O. Hirschfelder, C. F. Curtiss and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954)

(5) M. Kotani, A. Amemiya, E. Ishiguro, T. Kimura, *Tables of Molecular Integrals* (Maruzen Co. Ltd. Tokyo)

(6) R.C. Hermann, M. C. Wallis, and R. F. Wallis, *Phys. Rev.* **103**, 87 (1956)

(7) S. F. Wang, *Prog. Theor. Phys.* **33**, No. 6 (1965) and **34**, No. 2 (1965)

(8) F. Okamoto, *Phys. Rev.* **124**, 1090 (1961)

### DISCUSSION

As shown in table 1, the  $M_1$ ,  $M_2$  and  $M_3$  bands can be attributed to the transitions of  $(1s\sigma)^2-(1s\sigma)(2p\sigma)$ ,  $(1s\sigma)^2-(1s\sigma)(2p\pi)$  and  $(1s\sigma)^2-(1s\sigma)(4f\sigma)$  of  $F_2$  center, respectively. But from the results of the present work, it seems to be difficult to attribute the  $M_4$  band to a proper allowable transition of the  $F_2$  center, since the  $(1s\sigma)^2-(1s\sigma)(2p\pi)$  is the second lowest allowable transition. Experiments show that the  $M_3$  and  $M_4$  bands are closely connected with the  $M$  center, though their origin are still unknown. Recently, S. F. Wang<sup>(7)</sup> pointed out a possibility to attribute the  $M_3$  and  $M_4$  bands to the  $F_2$  center itself, provided that a transition between the singlet group and the triplet group is allowed. However, we may also consider the possibility to attribute the  $M_4$  band to the impure  $F_2$  center, i. e. the center which is consisted of an impure atom associated with an  $F_2$  center. Of course, this suggestion still requires a more detailed investigation.

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