GROUND STATE ENERGY OF THE F' CENTER ELECTRONS

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Introduction

In this paper we shall apply a method to calculate the ground state energy of the F'center electrons. The presently accepted picture of the F'center is the lattice defect model in which two electrons trapped at a negative ion vacancy.

The ground state energy and properties of the F' center have been discussed by numerous authors and are summarized in the works of Mott and Gurney[1], Seitz[2], Pekar[3], and Gourary and Adrian[4].

The method used in this paper starts from the many body point of view in the Hartree approximation and includes the electron-phonon interaction. Furthermore, the crystal is assumed to be a dielectric medium and the negative ion vacancy for the F'center is replaced by a point charge and immersed in a dielectric medium.

Calculation

In this paper, the crystal is supposed to be a dielectric medium and the negative ion vacancy for the F'center is replaced by a positive, unity, point charge. In addition, we assume that there are interactions between phonons and electrons, and trap center.

Therefore, the total Hamiltonian for the system F'center plus phonons may be written as follows:

$$H=\frac{P_1^2}{2m}+\frac{P_2^2}{2m}+\sum_k \hbar\omega_k a^*_k a_k+\sum_k [V_k a_k(e^{i\mathbf{k}\cdot\mathbf{r}_1}+e^{i\mathbf{k}\cdot\mathbf{r}_2}-1)+C.C.]-\frac{e^2}{\epsilon_\infty r_1}-\frac{e^2}{\epsilon_\infty r_2}+\frac{e^2}{\epsilon_s r_{12}} \quad (1)$$

where V_k is

$$V_k=-i\left(\frac{2\pi e^2\hbar\omega_k}{K^2V\epsilon^*}\right)^{1/2} \quad (2)$$

Here V is the volume of crystal, $1/\epsilon^*=1/\epsilon_\infty-1/\epsilon_s$, where ϵ_∞ and ϵ_s are the optical and static dielectric constants; and ω_k is the frequency of the longitudinal optical modes for the crystal. $\mathbf{r}_1$ and $\mathbf{r}_2$ are the position vectors of the two electrons and r_{12} is the distance between them. The origin of position vectors is taken at the trap center. The first and second terms in Eq. (1) are, respectively, the kinetic energy operators for the two electrons trapped by the F'center. The third term is the phonon part of the Hamiltonian, which is written in terms of creation and annihilation operators, a_k^* and a_k. The fourth term is the sum of the interactions of the two electrons and the trap center with the phonon field. The fifth and sixth terms are the Coulomb interactions of the electrons and the trap center and the last term

is the Coulomb interaction between the two electrons. The dielectric constant in the Coulomb interaction between the two electrons is chosen as the static one since we suppose that there is an interaction between electron and phonons, i.e., the electron motion is assumed to be slow enough so that the crystal ions follow it. In the case of the Coulomb interaction of the electron with the trap center, the optical dielectricn constant is used since the effect of rigid ion displacement is included in the phonons interaction with trap center term.

The total wave function is written in the following form

$$\Psi=\psi(\mathbf{r}_1,\mathbf{r}_2)\,\Phi \tag{3}$$

Here, ψ is the electronic part wave function. Φ is the phonons wave function which is written in the Hartree form, that is

$$\Phi=\prod_{\mathbf{k}} f(\mathbf{k}) \tag{4}$$

where $f(\mathbf{k})$ is the wave function of phonons of momentum $\mathbf{k}$. It can be found by the perturbation theory using the third and fourth terms in Eq. (1) as outlined in the previous paper[5]. To first order the f (k) is

$$f(k) = [1-\frac{V_k^*}{\hbar\omega_k}(\varphi_k^*-1)\,a_k^*]\,|0> \tag{5}$$

Here $|0>$represents the phonons vacuum state and the conjugate function of φ_k^* in Eq. (5), $\varphi_k$is

$$\varphi_k=\int|\psi(\mathbf{r}_1,\mathbf{r}_2)|^2(e^{i\mathbf{k}\cdot\mathbf{r}_1}+e^{i\mathbf{k}\cdot\mathbf{r}_2})\,d^3r_1d^3r_2 \tag{6}$$

The ground state wave function for the electronic part motion is chosen as the product of the two Hydrogen like ground state wave functions, that is

$$\psi(\mathbf{r}_1,\mathbf{r}_2)=\frac{\lambda^3}{\pi}e^{-\lambda(r_1+r_2)} \tag{7}$$

where λ is a variational parameter.

Then the wave function for the phonons is given by

$$\Phi=\prod_{k}[1-\frac{V_k^*}{\hbar\omega_k}(\varphi_k^*-1)\,a_k^*]\,|0> \tag{8}$$

Making use of the phonons wave fumction given in Eq. (8), the effective Hamiltonian for the F'center is

$$H_{eff}\equiv<\Phi,H\Phi>=\frac{P_1^2}{2m}+\frac{P_2^2}{2m}+\frac{e^2}{\epsilon^*}(\frac{5}{4}\lambda-\frac{1}{a})-e^2(\frac{1}{\epsilon^*}+\frac{1}{\epsilon_\infty})(\frac{1}{r_1}+\frac{1}{r_2})$$
$$+\frac{2e^2}{\epsilon^*}[\frac{e^{-2\lambda r_1}}{r_1}(1+\lambda r_1)+\frac{e^{-2\lambda r_2}}{r_2}(1+\lambda r_2)]+\frac{e^2}{\epsilon_s r_{12}} \tag{9}$$

Here, a is twice the nearest neighbor distance.

The ground state energy for the electronic state of the F'center is given by

$$E\equiv<\psi(\mathbf{r}_1,\mathbf{r}_2),H_{eff}\psi(\mathbf{r}_1,\mathbf{r}_2)>=\frac{\lambda^2\hbar^2}{m}+\frac{5}{4}\frac{e^2}{\epsilon^*}\lambda-2e^2(\frac{1}{\epsilon^*}+\frac{1}{\epsilon_\infty})\lambda+\frac{3}{2}\frac{e^2}{\epsilon^*}\lambda+\frac{5}{8}\frac{e^2}{\epsilon_s}\lambda-\frac{e^2}{\epsilon^* a} \tag{10}$$

Minimizing E with respect to the parameter λ, we find for manimum energy

$$\lambda=\frac{me^2}{2\hbar^2}(\frac{2}{\epsilon_\infty}-\frac{5}{8\epsilon_s}-\frac{3}{4\epsilon^*}) \tag{11}$$

In the case of Kcl the value of λ given by Eq. (11) is $0.58\times10^{8}Cm^{-1}$. The corresponding ground state energy is "−3.08 ev" with respect to the zero energy. This value is high than the total energy of an F center electron and an electron rest at in the bottom of the conduction band. This is in accord with the experimental observation that the F'center can be separated into an F center plus an electron easily.

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References

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F' 中心電子的正常狀態能量

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游子結晶中，有兩個電子圍繞一負游子空位的色中心，通稱此種中心爲 F' 中心。著者在本文提出一新方法，以計算此中心電子系的正常狀態能量。