

$F^+$  center in ZnO

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The energy levels of the ground state and the first excited state of a single electron, trapped at an oxygen-ion vacancy in a ZnO crystal, have been calculated in this paper by using a semicontinuum model. The electrostatic polarization potential of the vacancy is calculated by direct summations over the electronic and atomic dipoles of the neighboring ions. The data of Tessman, Kahn, and Shockley on electronic polarizabilities of the zinc ion and the oxygen ion in ZnO are used. Absorption and emission occurs according to the Franck-Condon principle. The energy difference between the computed ground state and the excited state agrees well with the experimental absorption wavelength. The evaluated value of the wavelength for the emission in the transition of the electron from the relaxed excited state to the relaxed ground state is also in agreement with observation.

## I. INTRODUCTION

Energy levels of an electron trapped at a negative-ion vacancy in alkali halides have been calculated by the semicontinuum model. In this treatment, the vacancy is represented by a potential well of depth  $V_0$  and radius  $R$ . The principle contribution to  $V_0$  is the Madelung potential  $V_M$ , and the electrostatic polarization potential  $V_p$  of the surrounding medium of the vacant ion. Krumhansl and Schwartz<sup>1</sup> suggested that polarization can follow the motion of the electron adiabatically. The average polarization potential  $(1 - 1/\epsilon_\infty)/2R$  should be used in determining  $V_0$ . Here  $\epsilon_\infty$  is the optical dielectric constant. Such a correction has been recognized correct in the calculation of the  $F$  center in alkali halides. The polarization potential may be calculated with the proper choice of the value of  $R$ .

In this paper we actually calculate the electrostatic polarization potential at the center of an oxygen-ion vacancy by adding the potentials at the center contributed by the surrounding polarized electronic dipoles and ionic displacements; a basic method made by Mott and Littleton.<sup>2</sup> Such a calculation is possible by using the results of the electronic polarizabilities of ions in ZnO obtained by Tessman, Kahn, and Shockley<sup>3</sup> (TKS), and the effective ionic charges of ions in ZnO obtained by Coulson, Redei, and Stocker.<sup>4</sup> The energy-level calculations are based upon Fowler's treatment in alkali halides.<sup>5</sup> Trial hydrogenlike wave functions are assumed for the ground and the excited states. The energies are found by using the variational method. The optical absorption in a transition from the ground state of the  $F^+$  center to its  $2p$ -like excited state occurs according to the Franck-Condon principle. We take into account the distortion of the lattice in

the relaxed ground state and the relaxed excited state for the emission by assuming that the potential remains spherically symmetric.

## II. ELECTROSTATIC POLARIZATION POTENTIAL

The electronic polarizabilities of ions in ZnO have been determined by TKS<sup>3</sup> in a reverse process. Starting by taking the measured index of refraction, using simple additivity, and assuming the correctness of the Lorentz formula, they worked backward to find the electronic polarizability. By using these data of the electronic polarizabilities of ions in ZnO, the Lorentz equation holds. Here we assume that an oxygen-ion vacancy exists in ZnO. The vacancy will give an electric field which will produce electronic and atomic polarizations. We follow the treatment of Dekker<sup>6</sup> for such a problem by assuming an ionic displacement  $x$  of the zinc-ion lattice related to the oxygen-ion lattice in a molecule. Let the effective ionic charge be  $Z$ . The atomic polarization is represented by a point dipole of moment  $Zx$  at the location of each positive ion, and the ionic displacement is related to the force by the equation  $ZE_i = fx$ . Here  $E_i$  is the internal field at the molecule and  $f$  is the restoring force constant. Writing  $\alpha_a$  for  $Z^2/f$ , we obtain

$$\mu_+ = \alpha_+ E_i, \quad \mu_- = \alpha_- E_i, \quad \text{and} \quad Zx = \alpha_a E_i, \quad (1)$$

where  $\mu_+$  and  $\mu_-$  are the dipole moments of the zinc ion and oxygen ion, respectively,  $\alpha_+$  and  $\alpha_-$  represent the electronic polarizabilities of the zinc ion and the oxygen ion, respectively, and  $\alpha_a$  is the atomic polarizability. The value of  $\alpha_a$  may be calculated from the equation<sup>6</sup>

$$(\epsilon_s - 1)/(\epsilon_s + 2) = \frac{4}{3} \pi N(\alpha_+ + \alpha_- + \alpha_a), \quad (2)$$

where  $N$  represents the number of molecules

(ion pairs) per unit volume, and  $\epsilon_s$  is the static dielectric constant. The internal electric field may be calculated from TKS's data in  $\alpha_+$  and  $\alpha_-$  for zinc and oxygen ions by the equation<sup>3</sup>

$$P_e = N(\alpha_+ + \alpha_-)E_i = [(\epsilon_\infty - 1)/4\pi]E, \quad (3)$$

where  $E$  is the electric field in the crystal arising from the vacancy.

The electric field  $E$  at a large distance  $r$  from the center of the vacancy arising from the vacancy is  $Z/(\epsilon_s r^2)$ , and a dipole  $\mu$  at a lattice point gives a potential  $\mu/r^2$  at the center of the vacancy. Let  $r_i$  and  $r_j$  be the distances of the zinc ion and the oxygen ion of a molecule (ion pair) to the center of the vacancy. The potential at the center of the vacancy due to an ion pair is given by

$$\begin{aligned} \mathcal{V}_p = & [Z(\epsilon_\infty - 1)/4\pi N\epsilon_s (\alpha_+ + \alpha_-)] \\ & \times [(\alpha_+ + \alpha_-)r_i^{-4} + \alpha_- r_j^{-4}]. \end{aligned} \quad (4)$$

The total potential  $V_p$  at the center of the vacancy arising from polarization is obtained by adding the contributions of all its neighboring ion pairs of the lattice. The summations are carried out according to the structure of the hexagonal lattice, and we obtain

$$\begin{aligned} a^4 \sum_i r_i^{-4} = & \sum_l \sum_m \sum_n [(l - \frac{1}{2}m)^2 + \frac{3}{4}m^2 + \frac{8}{3}(\frac{3}{8} + n)^2]^{-2} \\ & + \sum_l \sum_m \sum_n [(l - \frac{1}{2}m)^2 + \frac{3}{4}(\frac{2}{3} + m)^2 \\ & + \frac{8}{3}(-\frac{1}{8} + n)^2]^{-2} \end{aligned} \quad (5)$$

for zinc ions, and

$$\begin{aligned} a^4 \sum_j r_j^{-4} = & \sum_l \sum_m \sum_n [(l - \frac{1}{2}m)^2 + \frac{3}{4}m^2 + \frac{8}{3}n^2]^{-2} \\ & + \sum_l \sum_m \sum_n [(l - \frac{1}{2}m)^2 + \frac{3}{4}(\frac{2}{3} + m)^2 \\ & + \frac{8}{3}(\frac{1}{2} + n)^2]^{-2} \end{aligned} \quad (6)$$

for oxygen ions. The summations include the potentials of all lattice points, except the vacancy, within a sphere of 80 rings of like ions. Calculations with a computer give the values of the first equation, 47.30, and the second, 26.14. The primes on the summations indicate that the lattice point with  $l = m = n = 0$  simultaneously is excluded. The lattice constant  $a$  is the distance of the nearest like ions. There are two molecules per unit cell in ZnO;  $N$  in terms of  $a$  is  $\sqrt{2}/a^3$ .

For the numerical calculation of  $V_p$ , we use  $Z = 1.20$ ,<sup>4</sup>  $a = 6.12$  a.u.,<sup>7</sup>  $\epsilon_s = (\epsilon_{||} \epsilon_{\perp})^{1/2}$ , with  $\epsilon_{||} = 8.6$  and  $\epsilon_{\perp} = 7.6$ ,<sup>8</sup>  $\epsilon_\infty = 4.04$ ,  $\alpha_+ = 0.79 \times 10^{-24}$  cm<sup>3</sup>, and  $\alpha_- = 2.1 \times 10^{-24}$  cm<sup>3</sup>. The last three quantities are data of TKS.<sup>3</sup> The value of  $V_p$  is found to be 0.211

a.u. By using the equation  $V_p = Z(1 - 1/\epsilon_\infty)/R$ , we found  $R = 4.28$  a.u. This value is comparable to the nearest-neighbor distance 3.69 a.u.<sup>7</sup> Similar results have been obtained for the  $F$  center in alkali halides<sup>9</sup> and the  $F^+$  center in the magnesium oxide.<sup>10</sup>

### III. ENERGY STATES

The present calculations in electronic energy states are based on the semicontinuum model developed by Fowler.<sup>5</sup> The Hamiltonian for the electron trapped at a negative-ion vacancy is

$$H = \frac{p^2}{2m} + \sum_v' V_{\text{perf}}(\vec{r} - \vec{R}_v) + V_{\text{pol}}(\vec{r}), \quad (7)$$

where the sum is over all lattice points  $\vec{R}_v$ , except the vacancy  $V_{\text{perf}}(\vec{r} - \vec{R}_v)$  is the perfect-crystal potential centered at  $\vec{R}_v$ , and  $V_{\text{pol}}(\vec{r})$  takes into account all the polarization effect. Inside the vacancy,

$$H \approx p^2/2m + V_0. \quad (8)$$

Following Simpson<sup>11</sup> and Fowler,<sup>5</sup> we write

$$V_0 = -\frac{ZM}{a} + \frac{1}{2}V_p - \chi + \frac{1}{\epsilon^*} \int_R^\infty q(r)r^{-2} dr, \quad (9)$$

where  $M$  is the Madelung constant (1.641),  $d$  is the nearest-neighbor distance,  $\chi$  is the electron affinity,  $1/\epsilon^* = 1/\epsilon_\infty - 1/\epsilon_s$ , and  $q(r)$  is the fraction of the electronic charge outside a sphere of radius  $r$  in the low-frequency part of polarization and is given by

$$q(\vec{r}) = \int_V^\infty |\Psi(\vec{s})|^2 d^3s. \quad (10)$$

Here  $\Psi$  is the wave function of the state from which absorption or emission takes place.  $V_0$  is measured from the bottom of the conduction band. Outside the vacancy the Hamiltonian is written

$$H \approx p^2/2m^* - Z/\epsilon_{\text{eff}}r, \quad (11)$$

where the effect of the electrostatic potential is approximated by using an effective mass  $m^*$  in the conduction-band mass approximation, i.e.,

$$\frac{p^2}{2m} + \sum V_{\text{perf}}(\vec{r} - \vec{R}_v) \approx \frac{p^2}{2m^*}$$

and  $V_{\text{pol}}(\vec{r}) - V_{\text{perf}}(\vec{r})$  are written in terms of an effective dielectric constant  $\epsilon_{\text{eff}}(\vec{r})$ . Here the prime in the summation over  $v$  is removed by adding  $V_{\text{perf}}(\vec{r})$ . According to Simpson<sup>11</sup> and Fowler,<sup>5</sup> we get

$$-\frac{Z}{\epsilon_{\text{eff}}r} = -\left(\frac{1}{\epsilon_\infty} + \frac{Z-1}{\epsilon_s}\right)\frac{1}{r} + \frac{1}{\epsilon^*} \int_r^\infty q(s)s^{-2} ds. \quad (12)$$

As in the calculations of energy levels of the  $F^+$  center for alkali halides, we choose the wave functions

$$\Psi_{1s} = (\alpha^3/7\pi)^{1/2}(1 + \alpha r)e^{-\alpha r}, \quad (13)$$

$$\Psi_{2p} = (\beta^5/\pi)^{1/2} r e^{-\beta r} \cos\theta \quad (14)$$

for the  $F^+$ -center calculations in ZnO. Here  $\alpha$  and  $\beta$  are variational parameters. The energies for the ground state and the excited state are then

$$W_k = \langle \Psi_k | \frac{p^2}{2m} | \Psi_k \rangle_i + \langle \Psi_k | \frac{p^2}{2m^*} | \Psi_k \rangle_o \quad (15)$$

$$+ V_0 \langle \Psi_k | \Psi_k \rangle_i - \frac{Z}{\epsilon_{\text{eff}}} \langle \Psi_k | \frac{1}{r} | \Psi_k \rangle_o,$$

where  $i$  means the integration to be taken over the inside of the potential well of radius  $r < R$ , and  $o$  means the outside of the same region. The energies are found to be

$$W_{1s} = (1/56R^2)[3t^2 - \frac{1}{8}(1 - 1/m^*)(24t^2 + 24t^3 + 12t^4 - t^6)e^{-t}]$$

$$+ V_0[1 - \frac{1}{56}(56 + 56t + 28t^2 + 8t^3 + t^4)e^{-t}] - (Z/56\epsilon_{\text{eff}}R)(18t + 18t^2 + 7t^3 + t^4)e^{-t}, \quad (16)$$

where  $t = 2\alpha R$ , and

$$W_{2p} = (1/8R^2)[u^2 - \frac{1}{24}(1 - 1/m^*)(24u^2 + 24u^3 + 12u^4 + 4u^5 - u^6)e^{-u}]$$

$$+ V_0[1 - \frac{1}{24}(24 + 24u + 12u^2 + 4u^3 + u^4)e^{-u}] - \frac{Z}{24\epsilon_{\text{eff}}R}(6u + 6u^2 + 3u^3 + u^4)e^{-u}, \quad (17)$$

where  $u = 2\beta R$ .

In order to get the energy of absorption for the  $F^+$  center we minimize the  $W_{1s}$  and  $W_{2p}$  with respect to the variational parameters to get the energies of the states. The Madelung energy is  $-0.534$  a.u. The energy obtained from uv-induced electron emission from the top of the valence band is  $-8.5$  eV.<sup>12</sup> Since the band gap of ZnO at room temperature is 3.34 eV, the electron affinity is about  $-5.16$  eV ( $-0.190$  a.u.). The value of  $V_0$  for the absorption is evaluated from  $\Psi_{1s}$ . We found  $V_0 = -0.238 + (56 + 76t + 10t^2 + t^3)e^{-t}/56R\epsilon^*$  a.u. As explained by Fowler,<sup>5</sup> the Eq. (12) is not adequate for evaluating  $\epsilon_{\text{eff}}$ . Since the electron in the ground state is moving with optical frequency in a very small orbit, the electronic wave function is very compact and the electron-phonon interaction may be negligible. We choose  $\epsilon_{\text{eff}} = \epsilon_\infty$  as done by Fowler in his calculation for NaCl. We use the conduction-band effective mass of the electron,  $m^* = 0.27m$ ,<sup>13</sup> where  $m$  is the mass of a free electron. We found  $W_{1s} = -3.18$  eV,  $W_{2p} = -0.05$  eV,  $\alpha = 0.65$  a.u., and  $\beta = 0.04$  a.u. The energy difference for the absorption is 3.13 eV, which corresponds to a band of  $\lambda = 4000 \text{ \AA}$ . An energy level at 3.2 eV below the conduction band associated with oxygen-ion vacancies in ZnO has been obtained by Harrison,<sup>14</sup> and the 4000- $\text{\AA}$  absorption band associated with the same vacancies in ZnO has been recorded by Smith and Vehse<sup>15</sup> and Meese and Locker.<sup>16</sup> The result obtained here is in agreement with observations.

After absorption the lattice relaxes. The positions of the neighboring ions change, the electrostatic polarization potential changes, and the Madelung energy is less negative. A change of the order of 10% in the nearest-neighbor distance has been assumed by Fowler<sup>5</sup> and Wood and Joy<sup>17</sup> for the case of alkali halides. The expansion of the relaxed  $F^+$  center in ZnO should be similar. By assuming an expansion of 6%; the vacancy in ZnO obtained is  $R = 4.54$  a.u. for the emission calculation. The related change gives  $V_p = 0.199$  a.u., the same order of change in Madelung energy gives  $V_M = -0.502$  a.u. The value of  $V_0$  is evaluated from  $\Psi_{2p}$ , the result is  $V_0 = -0.212 + (24 + 18u + 6u^2 + u^3)e^{-u}/24R\epsilon^*$  a.u. The electron in the relaxed excited state has a very large orbit, its velocity is much slower as compared to its ground state, and the electronic charge is essentially outside the vacancy. The value of  $\epsilon_{\text{eff}}$  becomes  $\epsilon_s$  so that we choose  $\epsilon_{\text{eff}} = \epsilon_s$  for the emission calculation. The energy level of the relaxed excited state is higher than the ground state and the electron conduction-band effective mass is larger. The Langreth's formula<sup>18</sup> gives  $m^* = 0.483m$ . The energies  $W_{1s}$  and  $W_{2p}$  in Eqs. (16) and (17) for the emission are again minimized and we found  $W_{1s} = -2.47$  eV,  $W_{2p} = -0.04$  eV,  $\alpha = 0.56$  a.u., and  $\beta = 0.04$  a.u. The emission energy is found to be 2.43 eV which corresponds to a band of wavelength 5100  $\text{\AA}$ . Harrison<sup>14</sup> has also found an energy level associated with the oxygen-ion vacancies in ZnO at the donor level which is

about  $-0.05$  eV.<sup>13</sup> Evidence of luminescence emission associated with the oxygen-ion vacancies in ZnO at a maximum wavelength of  $5100 \text{ \AA}$  has been obtained by Van Craeynest *et al.*<sup>19</sup>

#### IV. DISCUSSION

The degree of accuracy in the calculations of the electronic energies in the ground state and the excited state for the F<sup>+</sup> center in ZnO depends upon the selection of the wave functions for the electrons and the constants of the crystals. We select the hydrogenic wave functions for the electrons in ZnO since the use of a model of a hydrogenlike electron orbit in ZnO has been proven satisfactory by Hutson.<sup>13</sup> The electronic polarizabilities of ions in ZnO, determined by TKS<sup>3</sup> using least-squares fit of experimental data, appear very accurate. The values of the effective charges of ions in ZnO evaluated by Coulson *et al.*<sup>4</sup> should be good since Suchet<sup>20</sup> has obtained the same values for ZnO with a different method. In the evaluation of the polarization potential at the center of the vacancy arising from the polarized dipoles, the summations in Eqs. (5) and (6) have been carried out over  $5 \times 10^6$  neighboring-ion pairs.

The results should be very good approximations. For the emission calculation, the initial state is the relaxed excited state. The conduction-band effective mass is calculated by the formula<sup>18</sup>  $m^* = (1 - 0.0008\delta^2)(0.27m)/(1 - \delta/6 + 0.0034\delta^2)$ . Here  $\delta$  is the coupling constant, equal to  $e^2(m/2\hbar w)^{1/2}/\hbar\epsilon^*$ . The larger electron effective mass gives correct values in the energies of the relaxed states.

The value of  $\beta$  is found very small so that the mean radius of the electron orbit  $\langle \Psi_{2p} | r | \Psi_{2p} \rangle$  is very large. The choice of  $\epsilon_{\text{eff}} = \epsilon_s$  in the emission calculation should be appropriate. The value of the term involving  $\epsilon_{\text{eff}}$  in Eqs. (16) and (17) is very small as compared with the values of the other terms. Such an approximation has very little effect in the values of  $W_{1s}$  and  $W_{2p}$  even if this approximation may not be accurate. Thus the 6% distortion of the relaxed F<sup>+</sup> center in ZnO may be a close approximation.

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