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ELECTRON CAPTURE BY α CENTERS IN NaCl AT ROOM TEMPERATURE*

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ABSTRACT: Capture cross-section for electrons in an anion vacancy in NaCl at room temperature is calculated using a point-ion potential and Simpson's[5] wave function for F-center. The result is very near to those founded theoreticaly by Pekar[7] and experimentally by Alvarez Rivas[3]

I. INTRODUCTION

Capture cross-section for electrons in an anion vacancy in alkali halides have been reported by Swank and Brown[1] at temperatures below 250°K and by Crandall[2] for KBr in a range from 20 to 120°K. Recently Alvarez Rivas[3] reported a capture cross-section for NaCl at room temperature. The value that he obtained is very large compared with that which can be obtained from the formulaes of Swank and Brown or Crandall.

The purpose of this work is to look into this discrepancy using a differ-

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ent way for the calculations of the capture cross-section.

2. CALCULATION OF THE CAPTURE CROSS-SECTION

In this calculation we suppose that F-centers are formed when a crystal is heated in vapour of Na[4], and we make use of the principle of detailed balance to relate the capture cross-section to the transition due to thermal ionization.

The number of electrons captured per unit time in the centers of the solid is:

$$\nu = (N_e + N_s)\, V \int_{E_c}^{\infty} N_e(\epsilon)\, f(\epsilon)\, v\sigma(\epsilon)\, d\epsilon \qquad (1)$$

where N_s is the concentration of Na atoms on the surface of the crystal which have not yet lost their electrons, N_e the concentration of conduction electrons, $N_e(\epsilon)$ the density of electronic states (per unit volume) in the conduction band, v the velocity of an electron whose energy is ϵ, $\sigma(\epsilon)$ the capture cross-section for an electron with energy ϵ, $f(\epsilon)$ the distribution function, E_c the energy of an electron at the bottom of the conduction band, and V the volume of the crystal. Equation (1) can be rewritten in the form

$$\nu = V(N_s + N_e)\, N_e < v\sigma(\epsilon) > \, \equiv \, V(N_s + N_e < v > \sigma \qquad (2)$$

where the symbol $< v >$ indicates the average of the quantity v over the thermal distribution.

The second equality in Eq. (2) is simply the definition of the mean capture cross-section σ. Now, the number of electrons in F-centers which are excited per unit time into the conduction band is

$$\nu' = VN_F\beta \qquad (3)$$

where β is the probability per unit time for thermal ionization of an electron from the ground state of the F-center. In thermal equilibrium we must have

$$\nu = \nu' \qquad (4)$$

Taking into account that $N_e^2 \ll N_s N_e$ we can find from Eqs. (2), (3) and (4)

$$\sigma = N_F \beta / \widetilde{N}_e (N_s + \widetilde{N}_e) < v > =$$

$$= \frac{h^3 N \beta}{(2\pi)^3 m^* \sqrt{2}\, T^2 N_s} \exp\left[(E_F - \tfrac{1}{2} W)/kT\right]$$

where $\widetilde{N}_e$ is the equilibrium concentration of electrons and is equal to

$$\widetilde{N}_e = \frac{N_F}{N} \left(\frac{2\pi m^* kT}{h^2} \right)^{3/2} \exp\left[-(E_F - \tfrac{1}{2} W)/kT\right] \qquad (6)$$

This formula has been derived by Mott and Gurney[5]. It must be noticed that in obtaining Eq. (6) we have neglected the change in the vibrational frequency of the atoms next to holes, and we have assumed that Boltzmann's statistics applies to the ground state of the F-center, that is, this level is above the Fermi level. Markham has discussed this point[6] and shown its validity.

The rest of the symbols in Eq. (5) are: N the total number of lattice points, m^* the effective mass of electron in the band, k the Boltzmann's constant, h the Planck's constant, E_F the dissociation energy of an F-center, W the energy required to form a pair of separate vacant lattice points and T the temperature in degrees Kelvin.

3. CALCULATION OF β.

We take for our interaction potential the change in the potential energy experienced by the F-electron on displacement of the nearest-neighbor ions. This is

$$\Delta V = \frac{1}{4\pi\epsilon_0} \left[\frac{-e^2}{|\mathbf{a}_m - (\mathbf{r} + \mathbf{u}_m)|} + \frac{e^2}{|\mathbf{a}_n - \mathbf{r}|} \right] \qquad (7)$$

where $\mathbf{a}_m$ is the vector from the center of the vacancy to the ion at m, $\mathbf{r}$ is the vector to the electron, and $\mathbf{u}_m$ is the displacement of the ion. If we expand the right-hand side we obtain, keeping the first three terms:

$$\Delta V = -\frac{e^2}{4\pi\epsilon_0}\left[\frac{\mathbf{a}_m\cdot\mathbf{u}_m}{a_0^3}\right] - \frac{e^2}{4\pi\epsilon_0}\left[\frac{3(\mathbf{a}_m\cdot\mathbf{r})(\mathbf{a}_m\cdot\mathbf{u}_m)}{a_0^5} - \frac{\mathbf{r}\cdot\mathbf{u}_m}{a_0^3}\right] - \frac{15e^2}{8\pi\epsilon_0}\left[\frac{(\mathbf{a}_m\cdot\mathbf{r})^2(\mathbf{a}_m\cdot\mathbf{u}_m)}{a_0^7} - \frac{3(\mathbf{a}_m\cdot\mathbf{r})(\mathbf{r}\cdot\mathbf{u}_m)\mathbf{u}_m)}{a_0^5}\right] \tag{8}$$

where $a_0 = |a_m|$. We have also eliminated all terms involving second and higher powers of u_m since their contribution is negligible to those linear in u_m.

The second term in the expansion (8), linear in r, can lead to a transition between the ground state and the first excited state. In this case the interaction potential is

$$V_{\mathrm{el}} = \frac{-e^2}{4\pi\epsilon_0 a_0}\left[\frac{3(\mathbf{a}_1\cdot\mathbf{r})\,\mathbf{a}_1\cdot(\mathbf{u}_1+\mathbf{u}_{-1})}{a_0^4} - \frac{\mathbf{r}\cdot(\mathbf{u}_1+\mathbf{u}_{-1})}{a_0^2} + \frac{3(\mathbf{a}_2\cdot\mathbf{r})\,\mathbf{a}_2\cdot(\mathbf{u}_2+\mathbf{u}_{-2})}{a_0^4} - \frac{\mathbf{r}\cdot(\mathbf{u}_2+\mathbf{u}_{-2})}{a_0^2} + \frac{3(\mathbf{a}_3\cdot\mathbf{r})\,\mathbf{a}_3\cdot(\mathbf{u}_3+\mathbf{u}_{-3})}{a_0^4} - \frac{\mathbf{r}\cdot(\mathbf{u}_2+\mathbf{u}_{-2})}{a_0^2}\right] \tag{9}$$

But the displacement of an ion at $\mathbf{a}_m$ is

$$\mathbf{u}_m = \sum_{\mathbf{q},t}\left(\frac{\hbar}{2\rho V\omega_{\mathbf{q},t}}\right)^{\frac{1}{2}}\bar{\epsilon}_{\mathbf{q},t}\,(a_{\mathbf{q},t} + a^*_{\mathbf{q},t})\,e^{i\mathbf{q}\cdot\mathbf{a}_m} \tag{10}$$

where ρ is the density and V is the volume of the crystal; ω is the frequency, $\mathbf{q}$ the wave vector, and $\boldsymbol{\epsilon}$ the polarization vector of the wave; $a_{\mathbf{q}}$ and $a^*_{\mathbf{q}}$ are annihilation and creation operators, respectively. Eq. (9) together with (10) leads to

$$V_{\mathrm{el}} = - eF_x x - eF_y y - eF_z z \tag{11}$$

where

$$F_i = \frac{2e}{4\pi\epsilon_0 a_0^3} \sum_{q,t} \left(\frac{\hbar}{2\rho V \omega_{q,t}} \right)^{\frac{1}{2}} (a_{q,t} + a^*_{q,t}) \times$$

$$\times \left[2\cos q_i a_0 - \cos q_j a_0 - \cos q_k a_0 \right] \tag{12}$$

$$i \neq j \neq k$$

Specializing to a phonon traveling in the x, or $<100>$ direction,

$$V_{\mathrm{el}} = \frac{4e^2}{4\pi\epsilon_0 a_0^3} \sum_{q,t} \left(\frac{\hbar}{2\rho V \omega_{q,t}} \right)^{\frac{1}{2}} (a_{q,t} + a^*_{q,t}) \left[\cos q a_0 - 1 \right] x \tag{13}$$

Using this potential we wish to calculate a transition probability

$$W = \int \frac{2\pi}{\hbar} <\Psi_i \,|\, V_{\mathrm{el}} \,|\, \Psi_j>^2 \; \frac{4\pi V(\hbar\omega)^2 \, \delta(E_j - E_i - \hbar\omega)}{C_s^2 \hbar^3 (2\pi)^3} \, d(\hbar\omega) \tag{14}$$

where we have used a Debye approximation for the spectrum; Ψ_i and Ψ_j are the total wave functions for the initial and final states of the electron. Since $\hbar\omega_q \ll \Delta E = E_{\mathrm{exc}} - E_{gd}$, $E_j - E_i$ represents the electronic difference energy between the ground and the excited state of the F-center.

Now

$$<\Psi_i \,|\, V_{\mathrm{el}} \,|\, \Psi_j> = \frac{4e^2}{(4\pi\epsilon_0)\, a_0^3} \sum_{q,t} \left(\frac{\hbar n_{q,t}}{2\rho V \omega_{q,t}} \right)^{\frac{1}{2}} 2 \sin \frac{a_0 q}{2} <\Psi_i \,|\, x \,|\, \Psi_j> \tag{15}$$

where we use the Simpson's wave function for Ψ_i and Ψ_j; that is,

$$\Psi_i = A e^{-\alpha r} \tag{16}$$

$$\Psi_j = B r e^{-\beta r} \text{ sen } \theta \cos \varphi \tag{17}$$

$$A = 1.26 \times 10^{10}, \quad B = 1.15 \times 10^{19}, \quad \alpha = 0.52\,(\text{a.u.}), \quad \beta = 0.36\,(\text{a.u.})$$

and $< \Psi_i \mid x \mid \Psi_j > = 1.8 \times 10^{-8}$

Thence

$$W = \frac{2\pi}{\hbar} \left(\frac{4e^2}{4\pi \epsilon_0 a_0^3} \right)^2 \frac{\hbar\, 4\pi V < \Psi_i \mid x \mid \Psi_j >^2}{2\rho V C_s^3 \hbar^3 (2\pi)^3}\, 4 \int n^2 \hbar\, \frac{(\hbar\omega)^2}{\hbar\omega} \sin^4 \frac{a_0 q}{2} \times$$

$$\times\, \delta(\Delta E - \hbar\omega)\, d(\hbar\omega) \tag{18}$$

where

$$\tilde{n} = [\exp(\hbar\omega/kT) - 1]^{-1} \tag{19}$$

is the number of phonons in a mode of energy $\hbar\omega$ at temperature T.
Thence we have

$$W = \frac{256\pi^2 e^4}{\hbar^2 \rho a_0^6 C_s^3 (4\pi)^3 (4\pi\epsilon_0)^2} < \Psi_i \mid x \mid \Psi_j >^2 \tilde{n}_{\Delta E}\, \Delta E \sin^4 \frac{a_0 q}{2} = 2.82 \times 10^{-10} \text{ sec}^{-1} \tag{20}$$

with $\sin^4 \dfrac{a_0 q}{2} = 0.41$, $\Delta E = 4.16 \times 10^{-19}$ joules

$\tilde{n}_{\Delta E} = 10^{-34}$, $\dfrac{1}{4\pi\epsilon_0} = 8.98 \times 10^9$ n. m^2/coul^2

4. CONCLUSIONS

Using Eqs. (5) and (20) we obtain

$$\sigma = 5 \times 10^{-17}\,\mathrm{m}^2 = 5 \times 10^{-13}\,\mathrm{cm}^2$$

with $E_F - \frac{1}{2} W = 0.95\,\mathrm{eV}$, $N = 10^{22}$

$$N_s = 10^{16}, \quad m^* = 0.6\, m_e, \quad T = 300\,°\mathrm{K}$$

$$\rho = 2165\ \mathrm{Kg/m^3}, \quad a_0 = 2.81 \times 10^{-10}\,\mathrm{m}, \quad C_s = 3.2 \times 10^3\,\mathrm{m/sec}$$

The values for σ are given in table 1.

TABLE 1

Values for the cross-section capture reported[3] and obtained. The three first results in the table are experimental, the last two, theoretical.

Authors	σ in cm^2
Swank and Brown	9×10^{-16}
Crandall	9×10^{-17}
Alvarez Rivas	6×10^{-12}
Pekar	3.3×10^{-13}
This work	5×10^{-13}

Our result is very similar to the Pekar's[7] value for σ and very close to the Alvarez Rivas result. It must be remarket that our result is only valid at room temperature or near it. Only one excited state was used for the F-center when we know that more than one exists[8].

The expressions found by Swank and Brown or Crandall were not experimentally checked at room temperature. The value obtained for NaCl is particularly uncertain, since only one crystal was examined by the authors of reference 1, and there was considerable evidence of aggregate-center formation in the sample. The formula for σ obtained by Crandall (which in principle is valid for all alkali halides) was only verified for KBr and in a limited range of temperatures. This is the reason why we believe that the Alvarez Rivas result is the more reliable one at room temperature. As it can be seen our result agrees quite well with the one reported in Ref. 3.

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RESUMEN

Se calcula la sección de captura de un electrón por una vacancia positiva de NaCl a temperatura del cuarto usando para el Centro F un potencial que consiste de los seis primeros vecinos de la vacancia del halogeno. Para las funciones de onda del centro F se usaron las de Simpson[5]. El resultado es del mismo orden de magnitud que el encontrado teóricamente por Pekar[7] y difiere por un orden de magnitud del encontrado experimentalmente por Alvarez Rivas[3].