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A Model for the Interaction Between F centers and H Atoms in Ionic Crystals*

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The interaction between an F center and neutral hydrogen atoms, the most simple paramagnetic defects in ionic crystals, is described in terms of a perturbation theory of two square potential wells. The good agreement with experimental data indicates that lattice distortion due to the presence of the hydrogen atoms is negligible.

Descreve-se a interação entre um centro F e átomos neutros de hidrogênio, os defeitos paramagnéticos mais simples em cristais iônicos, em termos de uma teoria de perturbações de dois poços quadrados. O bom acordo com os dados experimentais indica que a distorção da rede, devida à presença dos átomos de hidrogênio é desprezível.

1. Introduetion

Radiation damage studies of alkali halide crystals have contributed to the basic understanding of the interaction between the ionizing radiation and matter. For a review of earlier work see Ref. (1). Recently, we have studied the radiation damage by *u.v.* and X-rays of *KCl*, *KBr* and *RbCl* doped with H^- or D^- substitutional ions[2]. The addition of hydrogen (*U* Centers) in alkali halides increases the F center production efficiency of the crystal. Since it is possible to follow the hydrogen in the several forms that it can occur in the lattice – as a negative substitutional ion, negative interstitial ion and neutral interstitial atom – much useful information can be obtained about the mechanisms of defect production and its aggregation mechanisms.

In the experimental work[2], new optical transitions were reported (named FU_2 and F*)and attributed to the interaction between F centers

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and interstitial hydrogen atoms (U_2 Centers). Although greater knowledge results when new experiments involving other techniques are performed, such as EPR and ENDOR, even so, with the available results it is useful to establish a theoretical model for the interaction between F centers and hydrogen atoms.

The several models proposed for the F center, from that presented by DeBoer until the most recent ones, almost all have a common characteristic. In the neighborhood of the negative ion vacancy, the potential energy comes near to a square well. The essential physical fact is that both, the ground and excited states, have compact wave functions considering that the real potential in the region of the vacancy is approximately that of a square well. Wood[3] investigated the details of the justification for this model.

It seems reasonable to admit that the perturbation between F centers and hydrogen atoms can be described by the perturbation between two square well potentials. It is expected that this model will work better for the confígurations that correspond to the F*, where the F and the hydrogen atoms are not at the closest approach.

2. Fitting the Square Well Potential

For a finite square well potential with depth V_0 and width a, containing a particle with energy $E > -V_0$, the non normalized wave function that describes this particle is well known to be of the form

$$\Psi = \begin{cases} e^{Kx}, & (x < 0), \\ Ae^{ikx} + Be^{-ikx}, & (0 < x < a), \\ Ce^{-Kx}, & (x > a), \end{cases}$$

where $K = (-2mE)^{1/2}$; $k = [2m(E + V_0)]^{1/2}$ with m as the mass of the particle.

From the application of the boundary conditions it follows that

$$2 \text{ cotg } ka = \frac{k}{K} - \frac{K}{k}.$$

By introduction of the following defínitions

$$\gamma = (2mV_0a^2/\hbar^2)^{1/2} \quad \text{and} \quad \alpha = \frac{ka}{\gamma} = \left(1 + \frac{E}{V_0}\right)^{1/2},$$

the above equation is written as

$$\gamma\alpha = (n-1)\pi + 2\cos^{-1}\alpha \quad (n = 1, 2 \ldots)$$

Figure 1 shows the graphical solution of this equation for the following values $\gamma = 1$; $\gamma = 4$; $\gamma = 12$. From the formula $E = V_0(1 - a^2)$, the abscissa of the intersection points permit to obtain the corresponding energy states.

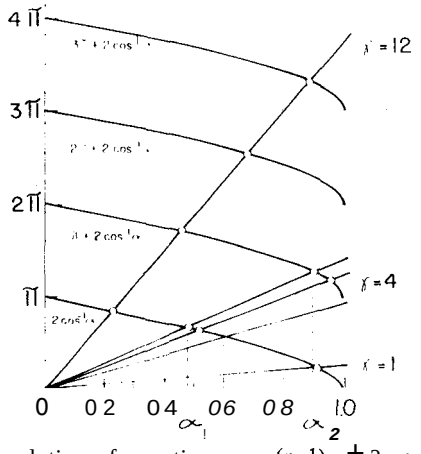


Figure 1 - Graphical solution of equation $\gamma\alpha = (n-1)\pi + 2\cos^{-1}\alpha$ for three values.

The fitting of the potential well that represents the F center potential is now made using the energy differences between the conduction band and the 1*s* and 2p levels, $E_1 = -3.1$ eV for the ground state and $E_2 = .80$ eV for the excited state[4]. As the relation $E_1/E_2 = (1-\alpha_1^2)/(1-\alpha_2^2)$ has the value 3.87 for these levels, an adjusted line (Fig. 1) for two intersections (two levels), must satisfy this relation. Selecting a, $= .48$ and $\alpha_2 = .89$, the relation approaches to 3.87 and γ assume the value 4.5. For the depth of the F center potential well, V_1, assume the value $V_1 = V_0 = E_1/(1-\alpha_1^2) = -4.0$ eV. From Eq. 3, it follows that $ma^2 = 1.7 \times 10^{-49}$ (MKS). Admitting an effective mass $m_e = 0.7\, m_0$ (Ref. 5), it turns out that $a = 5.2$ Å, a reasonable value for the F center well width, since the present model is unidimensional.

For the hydrogen atom (U_2 center), the potential well parameters were obtained fitting one single level. It is assumed that the first excited state is very close to the conduction band. From the peak of the optical *u.v.* absorption at 5.4 eV, the following values for the U_2 potential well parameters are obtained:

$V_2 = V_0 = -8.42$ eV; $\alpha = 0.60$ and $mb^2 = 3.62 \times 10^{-50}$ (M.K.S.).

Considering again the same effective mass $m_e = 0.7\, m_0$, the well width for the U_2 center turns out to be b = 2.4 Å. This value is of the magnitude of the interstitial diameter as also has been pointed out by Mimura and Uemura[6]. The hydrogen atom would remain compact and so is located without perturbation in the interstitial space.

Figure 2 shows the potential wells for the F and U_2 centers, without perturbation taken in account, for their closest configuration. The perturbation, AE, on the energy levels of the F center is given by

$$\Delta E = \int_{d_1}^{d_2} \Psi_{x>a}\, V_2\, \Psi_{x>a}\, dx,$$

whose solution is

$$\Delta E = -\frac{V_2 N^2}{2K} \left[e^{-2K(x-a)} \right]_{d_1}^{d_2}$$

The values of N are $N_2 = 3.9 \times 10^4$ and $N_1 = 2.4 \times 10^4$ (M.K.S.). These will correspond to ΔE_2 and ΔE_1 perturbations on the levels E_2 and E_1. It turns out that ΔE_1 values are very small. In Table I the calculated perturbations of the F center absorption due to the presence of the H_0 atom is shown. Figure 3 shows the possible positions for the H^0 atom relative to the F center.

POSITION	Dist. d (A°)	ΔE (eV)	λ(mμ)
1	5.1	0.52	670
2	7.0	0.12	570
3	8.3	0.05	550
4	9.3	0.03	545
5	11.5	0.00	540

Table I

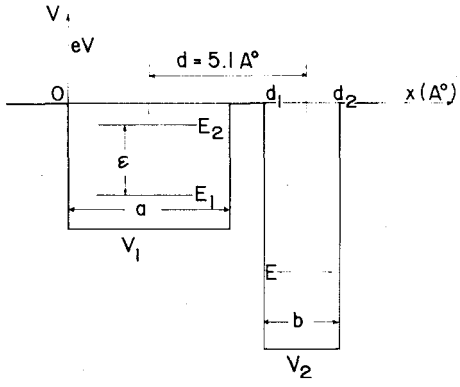
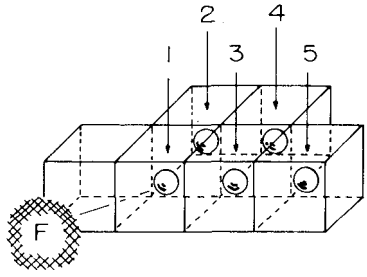


Figure 2 – **F** center and U_2 center potential wells for the nearest position of these two centers.



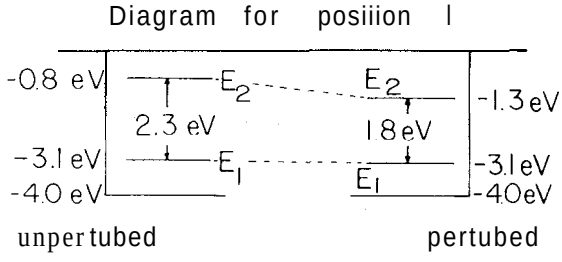


Figure 3 – Possible interstitial positions of the hydrogen atom. Position 1 corresponds to FU_2 center and positions 2, or more distant ones, correspond to the F^* center. The perturbed and unperturbed energy level diagram for position 1 is also shown.

3. Discussion

From Table I, it can be concluded that closest distance between the F and the U_2 centers gives rise to the FU_2 absorption band. The other configurations are responsible by the F^* absorption bands. The AE calculated values show a strong dependence on the interaction distance of the two centers. The perturbation for the nearest distance is much higher than for the next nearest distance, which is in accordance with the experimental data. Due to the F center band-width, positions 2, 3, 4 and 5 can not be distinguished experimentally by their optical absorption peaks.

The experimental AE value found for the FU_2 is smaller than the calculation shown in Table I. This deviation is attributed to the fact that perturbation theory is not strictly valid, mainly for the closest distance.

As the population of positions 2, 3 and 4 by the hydrogen atoms can not be established, a comparison between calculated and experimental data is difficult. However, by selective optical bleaching of F^*, it was found that Table I does not contradict the experimental data.

The interaction between H_0 atoms and M centers was also experimentally detected[2]. However, calculations similar to that developed for the F center would be much more difficult to be performed.

The optical bands Y and Y' recently discovered by Matsura and Kuczymsky[7], although with nearly the same absorption peaks as the FU_2 and F^* centers, are not of the same origin. The high mobility of H_0 atoms at the high temperatures where the Y and Y' bands are formed, make it more probable that H_0 atoms associate into H_2 molecules than with F centers.

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