

# Interaction between Electronic and Vibrational States of F- and F<sub>A</sub>-Centers in KCl

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For the F and F<sub>A</sub> centers in KCl experimental data on optical absorption and fluorescence emission are evaluated to construct c.c. diagrams. From these diagrams the differences in electronic energy between ground state and excited state, the localized oscillator frequencies and ion displacements after optical excitation are derived.

The interaction between electronic and vibrational states of F-centers in alkali halides may be described in terms of a configurational coordinate (c.c.) diagram.<sup>1)</sup>

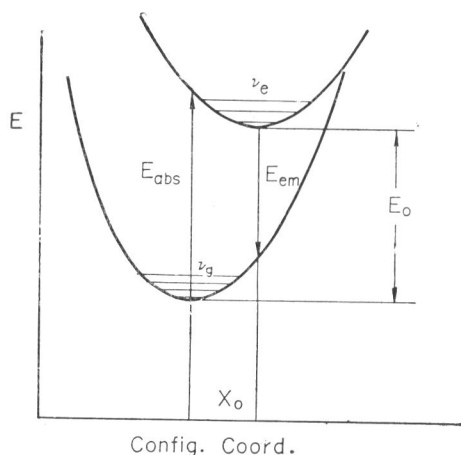


Fig. 1

It represents the potential energy of the center for a given type of configurational coordinate. (In the case of the electronic ground state of the F-center essentially this is the equal distance of the six nearest neighbours from the middle of the vacancy.) Under the assumption that a given electronic state  $i$  interacts with only one harmonic oscillator of lattice ions with the frequency  $\nu_i$  the c.c.-diagram can be constructed with a set of experimental data quantitatively. These data are:

$E_{\text{abs}}(T)$  the temperature dependence of peak position of the absorption bands and the values  $E_{\text{abs}}(0)$  for  $T \rightarrow 0$ . (1)

$E_{\text{em}}(T)$  the temperature dependence of peak position of the emission bands and the values  $E_{\text{em}}(0)$  for  $T \rightarrow 0$ . (2)

$H_{\text{abs}}(T)$  the temperature dependence of the half widths of the absorption bands. (3)

$H_{\text{em}}(T)$  the temperature dependence of the half widths of the emission bands.

For the c.c.-diagram one needs the following data for a given electronic state  $i$ :

$K_i$  the force constant of the harmonic oscillator (5)

$$M_i \text{ the oscillating mass} \quad (6)$$

$\nu_i$  the frequency of the oscillator which is

$$\nu_i = \frac{1}{2\pi} \cdot \sqrt{\frac{K_i}{M_i}} \quad (7)$$

Under favorable conditions the c.c.-diagram for different electronic states may be combined. Then one has to find:

$X_i$  the equilibrium displacement of the ions according to the electronic transitions. (8)

$E_0$  the difference in electronic energy. (9)

For the ground ( $g$ ) and excited state ( $e$ ) of the F-center the following relations can easily be derived:

$$E_{\text{abs}} = E_0 + \frac{1}{2} K_e X_0^2 - \frac{1}{2} h \nu_g \quad (10)$$

$$E_{\text{em}} = E_0 + \frac{1}{2} K_g X_0^2 + \frac{1}{2} h\nu_e \quad (11)$$

$$H_{\text{abs}} = 2 \sqrt{\ln 2 \frac{h\nu_g}{K_g}} \cdot K_e X_0 \quad (12)$$

$$H_{em} = 2\sqrt{\ln 2 \frac{h\nu_e}{K_g}} \cdot K_g X_0 \quad (13)$$

(all for  $T \rightarrow 0$ );  $1/2 h\nu$  is the zero point energy.

The justification for the assumption that for each of the two electronic states there is only one important harmonic oscillator is derived from the fact that the temperature

dependence of the half width of absorption and emission band is given by

$$\frac{H_{\text{abs}}^2(T)}{H_{\text{abs}}^2(0)} = \text{Cotg}\left(\frac{h\nu_g}{2kT}\right). \quad (14)$$

$$\frac{H_{\text{em}}^2(T)}{H_{\text{em}}^2(0)} = \text{Cotg}\left(\frac{h\nu_e}{2kT}\right). \quad (15)$$

For F-centers in KCl Markham<sup>2)</sup> found  $\nu_g = 2.96 \cdot 10^{12} \text{ sec}^{-1}$  and we may add now  $\nu_e = 4.25 \cdot 10^{12} \text{ sec}^{-1}$ .

Table I

	F-center	Na-F <sub>A</sub> -center	Li-F <sub>A</sub> -center
$E_{\text{Abs}}(0)$	2.313 —	2.356 2.116	2.256 eV 1.982 eV
$E_{\text{Em}}(0)$	1.238	1.12	0.46 eV
$H_{\text{Abs}}(0)$	0.163 —	0.195 0.119	0.195 eV 0.125 eV
$H_{\text{Em}}(0)$	0.248	0.266	— eV
$\nu_g$	2.96	3.02	$3 \cdot 10^{12}/\text{sec}$
$\nu_e$	4.25	4.72	$-10^{12}/\text{sec}$
$E_0$	1.816	1.746	1.50 eV
$X_0$	0.374	0.395	0.525 Å

Under the given conditions there is one problem left: The vibrating mass is unknown. Let us suppose as first approximation that only the six positive ions surrounding the vacancy are elastically bound to the rigid lattice. They form an octahedral system, the ground state vibration of which is a breathing mode  $\nu_1$ . In KCl the vibrating mass  $M_g$  would be six times the mass of the potassium ion. The symmetry of this type of vibration corresponds to the symmetry of the ground state wave function of the electron.

For the first excited electronic state one

derives from experimental results ( $K_e$  and  $\nu_e$ ) the value of  $M_e$ . It is found to be 2.5 times the mass of one potassium ion. This can easily be understood as the vibrating mass of the tetrahedral mode of the above mentioned octaheder.

The ratios of frequencies and vibrating masses for ground and excited electronic states derived from the octahedral model are in good agreement with experimental results. One finds

$$\frac{\nu_e}{\nu_g} = 1.4 \text{ instead of } 1.43$$

$$\text{and } \frac{M_g}{M_e} = 2.4 \text{ instead of } 2.$$

The symmetry of the tetrahedral mode corresponds to the assumed  $p$ -type function of the excited electron. As a result of these considerations the displacement of the two potassium ions, which have the highest overlap with the wave function of the excited electron can be derived from the c.c.-diagram:

$$X_0 = 0.374 \text{ Å}.$$

The other four ions move in the opposite direction, the displacement being much smaller. This change in symmetry of the oscillator has not been regarded in the previous considerations. On the basis of this model an interpretation of the absorption and emission bands of the F<sub>A</sub>-center can be given. The experimental results are in good agreement with predictions given by the c.c.-diagram.

### References

- 1 C. C. Klick: Phys. Rev. **85** (1952) 154.
- 2 J. D. Konitzer and J. J. Markham: J. Chem. Phys. **32** (1960) 843.

### DISCUSSION

**Kojima, T.:** Did you observe polarized emission from A-centers?

**Pick, H.:** 1. There is no polarization of F-center emission down to 2°K.

2. There is a mild degree of polarization in Na-F<sub>A</sub>-centers. The main part of emission is isotropic but there is a fraction of about 14% with the characteristic of a dipole with axis along K<sup>+</sup>-Na<sup>+</sup>. The explanation we give is a) either the  $p$ -function stays longer time in the K<sup>+</sup>-Na<sup>+</sup> direction, b) or the transition probability is higher for  $p$ -state along K<sup>+</sup>-Na<sup>+</sup>. This should be seen in lifetime measurements.

**Howard, R.:** As an alternative explanation of your data, is it possible, instead of assuming different effective masses for the ground and excited states, to assume cubic terms in the configuration coordinate curves? If I remember right, Charles McCombie has given a discussion along these lines.

**Pick, H.:** I agree, but you would need more parameters for a complete description of all the experimental data on F and  $F_A$  centers. So the model seems to be more adequate than one could hope.

**Knox, R. S.:** I, too, am surprised that such a simple model is successful because here we have a clear case in which different axes in configuration coordinate space should be used: one corresponding to the breathing mode in the ground state and one corresponding to the less symmetric vibrational mode in the excited state.

**Pick, H.:** The configurational coordinate of the excited state potential curve means mainly the coordinate in the direction of the  $p$ -function. This is not quite correct but it gives the right order or even more.

**Smoluchowski, R.:** Is it not surprising that such a simple model works so well? Especially the vibrating mass being the actual mass of the nearest neighbors only seems to imply a very weak coupling with second neighbors.

**Pick, H.:** We do not think that it is so much surprising because of the fact that the wave function of the electron is highly localized. The second neighbors have about a few % of the electron wave function. Furthermore the center has a high symmetry.

**Fumi, F. G.:** I wonder whether attempts have been made to observe the localized mode of vibration around the F-center, if it exists, by direct infrared absorption. The most suited alkali halides for such a study would seem to be those with a high mass ratio of the components, where the optical and acoustical bands of vibration should be more clearly separated. If the perturbation in force constants around the F-centers is sufficiently strong, one would then expect a localized mode to split off the bottom of the optical band.

**Pick, H.:** In a first attempt we had no success. But one has to realize that the transition probability will be very small, so one needs very high concentrations. There is one more difficulty. The absorption will be shadowed by the fundamental lattice vibration spectrum.

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