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Position of a d-like State of the F Center in KCl

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The Stark effect on the F center measured with light polarized perpendicular to the electric field has allowed the determination of an excited state of the F center 0.21 eV above the $2p$ level. Polarization dependence of the selection rules for electronic transitions allowed by the electric field assigns to this level a Γ_5^+ character. This state is related to a d-like state of the F-center hydrogenic model.

I. INTRODUCTION

The knowledge of the F center in alkali halides, despite more than 40 years of study, is still far from being complete. Questions such as the nature of the relaxed excited state or the states responsible for the L bands absorption are still open, but also simpler properties such as the energy position of the lower excited states of the F center in the unrelaxed configuration, are insufficiently known.

In the hydrogenic model of the F center, the F band is due to a transition from the s-like ground state to the first excited state, of p-like symmetry.[1] Transitions from the same ground state to all higher np-like states ($n \geq 3$) are responsible for the K band, whose shape is a convolution of individual $1s \rightarrow np$ transitions, which are too close to be resolved in the optical spectrum.[2]

No other optical transition is dipole allowed in this model and the positions of other levels, s like and d like, must be sought by means of perturbations which modify symmetry and selection rules and make transitions, forbidden to first order, partially allowed. In this way the position of the $2s$-like states in various alkali halides was determined.[3]

From the theoretical point of view, while many authors have calculated the position of the $1s \rightarrow 2p$ transition,[4,5] only a few have extended the calculations to the higher states.[2,6] To our knowledge only Kübler and Friauf[7] and Fowler, Calabrese and Smith[8] have given results on $3d$ states, but no check could be done on these calculations because there were no experimental measurements on the position of the $3d$-like level.

In this paper we report on the evaluation of the position of a d-like state measured by means of the Stark effect. The effect was detected with the measuring light polarized perpendicular to the applied field. This "perpendicular" Stark effect is not predicted by the theory of Henry, Schnatterly, and Slichter[9] (HSS), which takes into account only the electric field mixing of $2s$ and $2p$ levels, and it can be explained by the presence of a d-like state.

II. EXPERIMENTAL RESULTS

The experimental apparatus is substantially identical to the one described previously[10] and the only difference is the geometry of the applied field with respect to the measuring light. In order to detect the "perpendicular" Stark effect, the ac electric field was applied along the direction of light propagation, and thus perpendicular to the light polarization. The crystals, about 0.5 mm thick were sandwiched between two semitransparent electrodes consisting of a fine mesh of copper wire. The maximum applied field was about 80 kV cm^{-1} (peak). Although the field in this configuration was almost twice as large as in the "parallel" Stark effect, in order to obtain good signal-to-noise ratio, the output of the lock-in amplifier, tuned at twice the field frequency, had to be integrated for times up to 1000 sec. In this way, it was possible to measure transmission changes $\Delta\alpha$ of the order of 5×10^{-6}. All measurements were performed at a temperature of approximately 77 °K.

The change $\Delta\alpha(E)$ of the absorption coefficient in the region of the F band is shown in Fig. 1 for light polarized parallel and perpendicular to the electric field. The applied electric field was 43 kV cm^{-1} (peak); the F-center concentration $N_F = 7\times10^{16}$ cm^{-3}.

The "perpendicular" Stark effect is about seven times smaller than the parallel and has the same general shape. However, the peaks of the curve are clearly displaced toward the high-energy region. The "perpendicular" Stark effect is shown again in Fig. 2 in different experimental conditions: applied electric field 78 kV cm^{-1} (peak) and $N_F = 2.9\times10^{17}$ cm^{-3}.

Figure 3 shows the quadratic behavior of the "perpendicular" Stark effect as a function of the external electric field.

The samples which were quenched before the run and mounted in red safety light did not show any appreciable M band. However, in order to exclude any effect in our measurement from the M centers (the M_F band is in the F band spectral re-

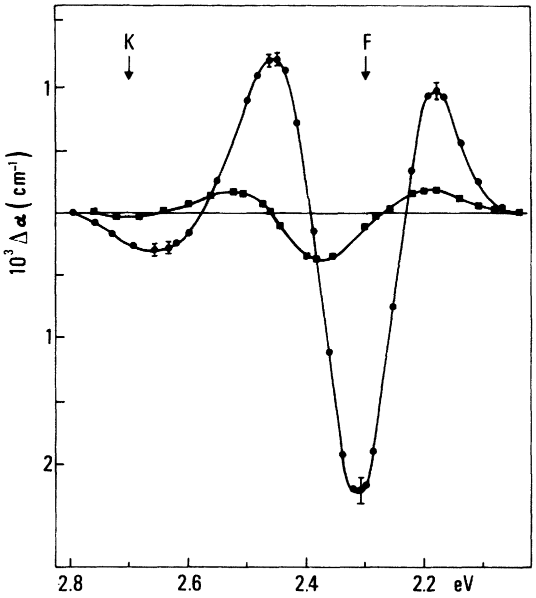

FIG. 1. Change of absorption coefficient due to the parallel (–●–●–) and perpendicular (– ■ – ■ –) Stark effect measured at 77 °K in a KCl crystal containing $N_F = 7\times10^{16}$ F center cm^{-3} with an applied electric field of 43 kV cm^{-1} (peak).

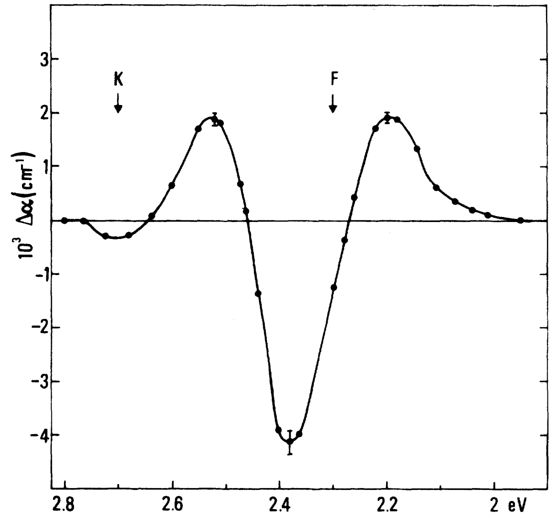

FIG. 2. Change of absorption coefficient produced by an electric field of 78 kV cm^{-1} (peak) applied perpendicular to the polarization of the light. $N_F = 2.9\times10^{17}$ F center cm^{-3}; $T = 77$ °K.

gion), we repeated the measurements with a high concentration of M centers. (Ratio of the absorption coefficient of the two bands was $\alpha_M/\alpha_F = 0.4$.) The measured Stark effect was equal in both cases within the experimental errors (10%) and dependent only upon the F-center concentration.

Measurements were also taken rotating the cryostat about 15° in both directions in order to change the angle between the electric field and the direction of polarization. Both rotations introduce in the signal a "parallel" component and the position of the minimum was taken as the true perpendicular position. Beside this care, the difference in the peaks positions assures that the measured effect is not a component of the "parallel" Stark effect, arising from an imperfect geometry of the experimental setup.[11]

The data of Fig. 2 can be analyzed with the method of moments introducing the shape function $f(E) = \alpha(E)/E$. One observes that the change of the area of the shape function is zero and that the center of mass is constant. The change of the second moment, $\langle \Delta E^2\rangle_\perp$, is

$$\langle \Delta E^2\rangle_\perp = 0.35\times10^{-6}\ \mathrm{eV}^2 . \tag{1}$$

III. DISCUSSION

A. Energy Position of the New Level

The change in the absorption coefficient $\Delta\alpha(E)$ in the "perpendicular" Stark effect has been interpreted in analogy to the "parallel" one.[10] In this case, however, the effect of the electric field on the K band has been included into the model considering the $1s$-$3p$ transition. The electric field shifts the $2p$ and $3p$ levels and mixes them with a new level of different parity. The optical absorption in the presence of the field consists of three Gaussian absorption bands corresponding to transitions from the $1s$ ground state to the levels $2p$, $3p$, and to the new level shifted by the field from their original position of the amounts δ_{2p}, δ_{3p}, and δ_x, respectively. The δ_i are defined positive.

The absorption without the electric field consists of the usual F and K bands approximated for simplicity to simple Gaussians of width $W_{0F} = 0.12$ eV

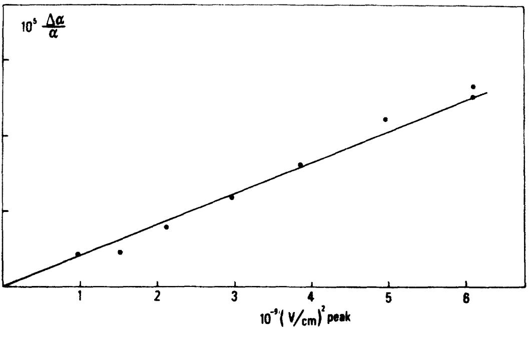

FIG. 3. Fractional decrease of the absorption coefficient at the peak of the F band as a function of the square of the electric field. $N_F = 2.9\times10^{17}$ F center cm^{-3}; $T = 77$ °K.

and $W_{0K} = 0.266$ eV, and peak amplitude α_{0F} and α_{0K}, respectively.

The formula used for fitting the experimental $\Delta\alpha(\epsilon)$ is thus:

$$\Delta\alpha(\epsilon) = \{\alpha_{0F}(1-x)\exp[-(\epsilon+\delta_{2p})^2/W_{0F}^2] + \alpha_{0K}(1-y)\exp[-(\epsilon-0.4-\delta_{3p})^2/W_{0K}^2] + \alpha_{0F}\,z\,\exp[-(\epsilon-\Delta+\delta_x)^2/W^2]\} - \{\alpha_{0F}\exp(-\epsilon^2/W_{0F}^2) + \alpha_{0K}\exp[-(\epsilon-0.4)^2/W_{0K}^2]\}. \quad (2)$$

The energies are measured from the peak of the F band, and the K band is located 0.4 eV higher; x, y, and z give the exchange of area among the transitions, Δ and W define the position of the new level and the width of the transition, respectively.

The conservation of the area and of the first moment impose two conditions among the parameters, and thus x and z are no longer independent variables. The parameters used in the fitting are

$$\delta_{2p} = 0.24\times10^{-5}\ \text{eV}, \quad \delta_{3p} = 1\times10^{-5}\ \text{eV},$$
$$\delta_x = 0.72\times10^{-5}\ \text{eV}, \quad W = 0.09\ \text{eV}, \quad (3)$$
$$y = 3.3\times10^{-5}, \quad \Delta = 0.21\ \text{eV}.$$

The result is plotted in Fig. 4 (full line). The new energy level is found 0.21 eV above the $2p$ level. The agreement is good and all experimental details appear in the fitted curve.

As shown in a preliminary report of this work,[12] the contribution of the F band alone is unable to explain the signal in the high-energy region, and an effect due to the K band is certainly present.[10] The oscillator strength of the K-band transition is fairly small, but the new level is almost equidistant from the $2p$ and $3p$ levels. For this reason, the approximation of neglecting the $3p$ state is too crude in the region of the K band. The contributions to the signal due to the Stark effect of the F and K bands can be separated by neglecting in Eq. (2) the terms referring to the K band or to the F band, respectively. The results are shown in Fig. 4 (dashed lines). The change of the second moment of the shape function due to the F band alone can now be evaluated:

$$\langle\Delta E^2\rangle_{\perp F} = 0.38\times10^{-6}\ (\text{eV})^2. \quad (4)$$

B. Symmetry of the New Level

The symmetry of the new excited state is obtained by group-theory considerations. The true symmetry of the hydrogenlike orbitals in a cubic lattice is not described by the angular momentum component s, p, etc., but by the representations Γ_i of the O_h group. Moreover, since the crystal symmetry is lowered by the electric field applied in the ⟨001⟩ direction, from O_h to C_{4v}, the Γ_i representations are decomposed in the representations of the subgroup C_{4v}, as is shown schematically in Fig. 5.

Selection rules for the dipole transitions between the lower A_1 level and the higher states depend upon the direction of light polarization with respect to the symmetry axis, i.e., the direction of the electric field. The transition $A_1 \to A_1$ is the only one allowed with parallel polarization and $A_1 \to E$ with the perpendicular polarization.

The transitions allowed also in the cubic symmetry are shown with full lines in Fig. 5 and corresponds to the usual F and K absorption bands. The new transitions, present only with the applied field, are indicated by dotted lines. The final state for the perpendicular polarization corresponds to a Γ_5^+ state of the cubic symmetry and henceforth to a d-like hydrogenic state. Assuming that the $3p$ level coincides with the peak of the K band at 2.70 eV, the position of the $3d$ level is 0.19 eV below it.

This result is not in agreement with the theoretical calculation of a d-like state of the F center in RbCl,[8] where the $3p$ and $3d$ levels are almost coincident, with the latter slightly above. The inversion between the $3p$ and $3d$ levels with respect to the normal order of hydrogenlike atoms is, however, analogous to the inversion between the $2s$ and $2p$ levels found with the parallel Stark effect.[3]

Another state of the correct E symmetry respon-

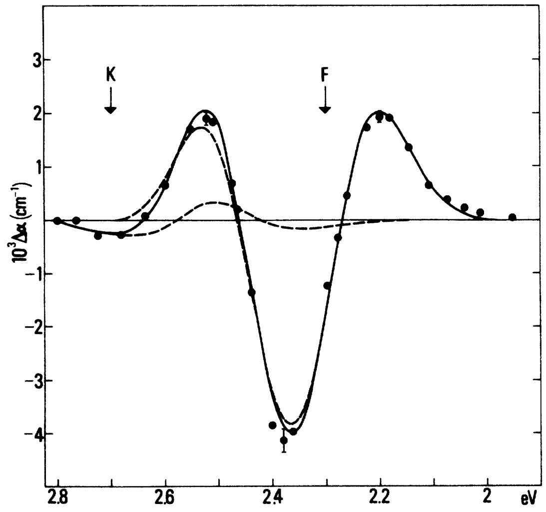

FIG. 4. Best fitting of the change of the absorption coefficient obtained with the model described in the text: (solid line) compared with the experimental results (dots). The contributions of the F and K bands are shown separately in the dashed curves.

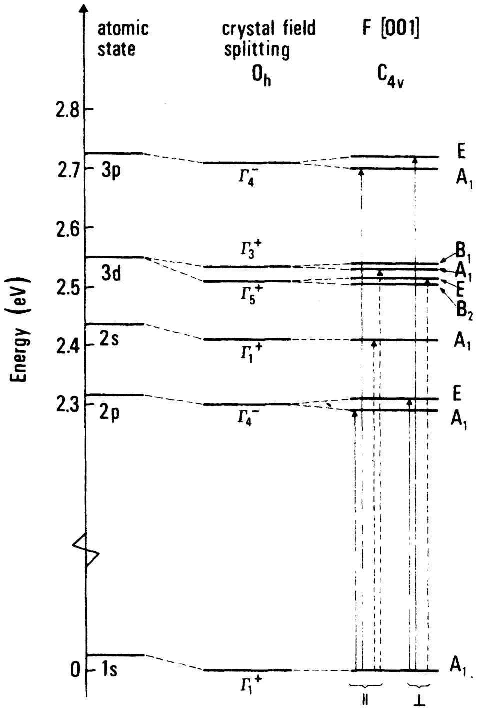

FIG. 5. Energy-level diagram of the F center in KCl and selection rules for transitions, with light polarized parallel or perpendicular to the external electric field applied in the [001] direction. Full lines represent transitions allowed also without field (F and K bands); dashed lines represent field-induced transitions. The position of the atomic states and the amount of the electric field splitting are only approximate.

sible for the perpendicular effect may originate also from a higher $4f$ state or from a mixing of s and p states of the F center below the six equivalent minima of the conduction band at the point X of the Brillouin zone giving rise to levels of Γ_4^- and Γ_5^- symmetry.[13] However, the energy positions of these levels lie above the K band in the region of the L bands, too high to account for the observations.

The theory of the Stark effect of the F band, given in the classical paper of HSS,[9] discusses only the case of two excited states of the F-center, of s-like and of p-like symmetry. Their parity is altered by the field mixing and the two transitions from the s-like ground state are both allowed, but only for light polarized parallel to the field. With this theory the "parallel" Stark effect was interpreted and the position of the $2s$ level was found in various alkali halides.[3]

An extension of the HSS theory was made, including the excited level of s-, p-, and d-like symmetry. Because the distance between the $2p$ and $3d$ states is larger than between the $2p$ and $2s$, the field mixing and henceforth the "perpendicular" Stark effect is smaller than the "parallel".

With the applied field F in the z direction, the changes of the second moment of the shape function are[12]

$$\langle \Delta E_z^2 \rangle = (eF)^2 (|\langle 2p_z | z | 2s \rangle|^2 + |\langle 2p_z | z | 3d_{3z^2-1} \rangle|^2), \tag{5}$$

$$\langle \Delta E_x^2 \rangle = (eF)^2 |\langle 2p_x | z | 3d_{xz} \rangle|^2, \tag{6}$$

$$\langle \Delta E_y^2 \rangle = (eF)^2 |\langle 2p_y | z | 3d_{yz} \rangle|^2 . \tag{7}$$

The subscripts of the $|2p\rangle$ and $|3d\rangle$ indicate which of the base functions of the p and d states are involved. Two terms contribute to the "parallel" Stark effect $\langle \Delta E_z^2 \rangle$ and the first, coincident with the HSS theory, is predominant. The "perpendicular" Stark effect is present for the two directions perpendicular to the field.

From the experimental value of $\langle \Delta E^2 \rangle_{\perp F} = \langle \Delta E_x^2 \rangle = \langle \Delta E_y^2 \rangle = 0.38 \times 10^{-6}$ (eV)^2, and using the Lorentz correction for the local field

$$F_l = 178 \text{ kV cm}^{-1} \text{ (peak)}, \tag{8}$$

one obtains

$$\langle 2p_x | z | 3d_{xz} \rangle = 0.65 a_0 , \tag{9}$$

where a_0 is the Bohr radius. The overlapping between p and d states is fairly small, confirming the diffuse character of the wave functions of the excited levels of the F center.

The dipole matrix elements between p and d states can also be evaluated from the perturbation theory. The displacements of the levels upon application of the electric field is given approximately by

$$\delta_{2p} = (eF)^2 \frac{|\langle 2p_x | z | 3d_{xz} \rangle|^2}{|E_{3d} - E_{2p}|}, \tag{10}$$

$$\delta_{3p} = (eF)^2 \frac{|\langle 3p_x | z | 3d_{xz} \rangle|^2}{|E_{3d} - E_{3p}|}. \tag{11}$$

From the values given in (3) and (8) one obtains

$$\langle 2p_x | z | 3d_{xz} \rangle = 0.75 a_0 , \tag{12}$$

In good agreement with (9), confirming the appropriate choice of the parameter used in the fitting. From Eq. (11) one has

$$\langle 3p_x | z | 3d_{xz} \rangle = 1.46 a_0 . \tag{13}$$

As for the hydrogenic wave functions, the latter matrix element is larger than the former.

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