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Unrelaxed 2S State of the F Center in Alkali Halides Studied by the Stark Effect

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The Stark effect in the F-center absorption has been observed in KCl, KBr, KI, RbCl, and NaCl. Changes of the absorption coefficient due to the electric field have been measured as a function of photon energy. From these data the energy difference between the $2S$ and $2P$ levels, and the dipole matrix element $\langle 2S \mid z \mid 2P \rangle$, have been evaluated.

I. INTRODUCTION

Experimental results on the electronic excited states of the F center have been obtained in recent years by studying the effects of external perturbations on the optical properties.

The application of electric, magnetic, and stress fields produces shifts or splittings of energy levels that are, in general, smaller than the bandwidth. However, the small changes of the optical absorption and emission bands can be measured by using modulation techniques and phase sensitive detection.

In particular, the observation of the change of the F band induced by an electric field (Stark effect) allows an experimental determination of the position of the $2S$ level, otherwise impossible because the optical transition $1S(\Gamma_1) \rightarrow 2S(\Gamma_1)$ is parity forbidden.

Measurements of the Stark effect in the F-center absorption band in alkali halides were reported by the authors[1,2] and by Rhyner and Cameron.[3] In Ref. 2 it was pointed out that the effect depends on the energy difference between the $2S$ and $2P$ levels, and that in KCl the $2S$ level lies above the $2P$ in the unrelaxed configuration.

On the other hand, Bogan, Stiles, and Fitchen[4] have observed the Stark effect in F-center emission band and have found that in the relaxed configuration the $2S$ state lies below the $2P$, so that a crossing of the two levels must occur during relaxation.

A theoretical interpretation of the Stark effect in the F center has been given by Henry, Schnatterly, and Slichter[5] by applying the method of moments. In particular they show that the change of second moment of the absorption band is related to the dipole matrix element $\langle 2S \mid z \mid 2P \rangle$.

Calculations of the position of the $2S$ level and of the value of the matrix element $\langle 2S \mid z \mid 2P \rangle$ were made by Fowler, Calabrese, and Smith[6] for RbCl using a semicontinuum approximation, and by Wood and Öpik[7] for KCl, KBr, KI, and NaCl using a Hartree-Fock type of approximation.

The present paper is an extension of the authors' previous work.[2] Complete measurements of the Stark effect of the F-center absorption are reported for KCl, KBr, KI, RbCl, and NaCl from which the $2S-2P$ energy splitting and the $\langle 2S \mid z \mid 2P \rangle$ dipole matrix element are evaluated.

II. EXPERIMENTAL RESULTS

The change $\Delta\alpha$ of the absorption coefficient of the F center induced by an ac electric field was measured using phase sensitive amplifiers. The experimental apparatus was described previously.[2]

The F centers were produced in Harshaw Chemical Co. single crystals by additive coloration, using K atmosphere for KCl, KBr, KI, and RbCl, and Na atmosphere for NaCl. Subsequently the cleaved samples were quenched from high temperatures to room temperature on a copper block. The F-center concentrations, N_F, ranged from 10^{16} to 10^{17} cm^{-3}.

Figures 1–5 show the change of the absorption coefficient $\Delta\alpha$ as a function of photon energy for the crystals of KCl, KBr, KI, RbCl, and NaCl, respectively. The measuring light was linearly polarized, with the electric vector parallel to the external field. The measurements were taken at the fixed temperature of 55 °K. The values of the electric field in the figures refer to the zero-to-peak value of the applied field, corrected for the local field by the Lorentz factor.[8]

From the experimental data one observes that, in agreement with the theory, the area and the center of gravity of the band are not changed by the electric field.

III. INTERPRETATION OF DATA AND DISCUSSION

A. Evaluation of $2S-2P$ Energy Splitting

The experimental curves can be interpreted by using the following model already discussed[2]: The electric field causes a repulsion between the $2S$ and $2P$ levels, changing their splitting from Δ to $\Delta + 2\delta$ (see Fig. 6), while the forbidden $1S \rightarrow 2S$ tran-

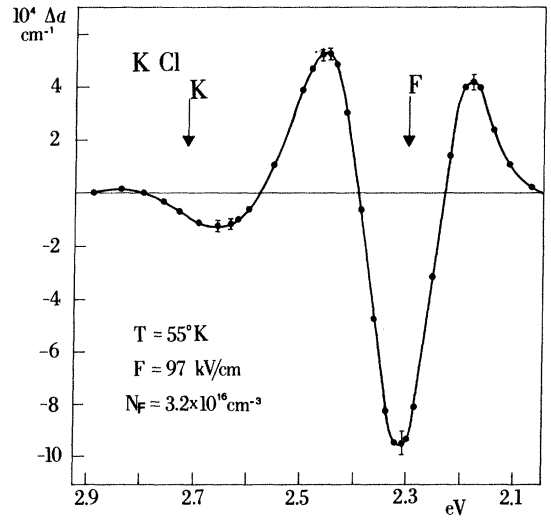

FIG. 1. Change of the absorption coefficient of a crystal of KCl containing $N_F = 3.2\times10^{16}$ (F centers)/cm^3 due to a local electric field $F = 97$ kV/cm at $T = 55$ °K.

sition becomes partially allowed.

The unperturbed $1S \rightarrow 2P$ transition, whose shape can be approximated by a Gaussian of width W_0, is replaced, when the field is applied, by two transi-

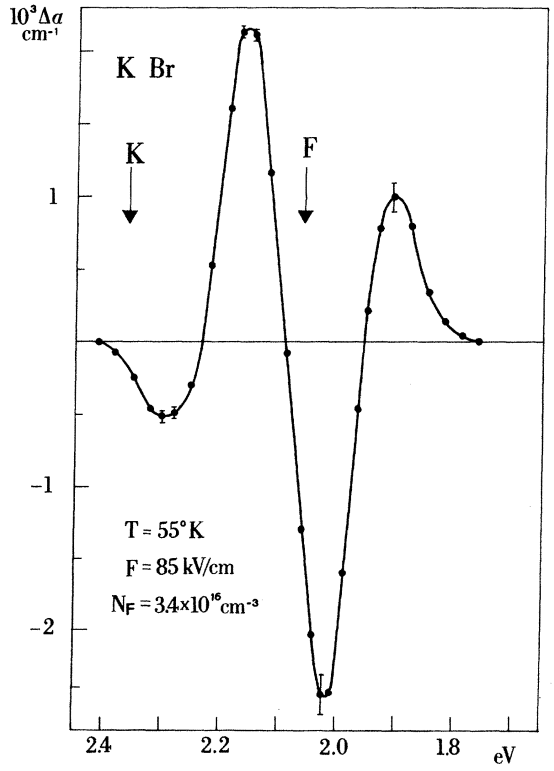

FIG. 2. Change of the absorption coefficient of a crystal of KBr containing $N_F = 3.4\times10^{16}$ (F centers)/cm^3 due to a local electric field $F = 85$ kV/cm at $T = 55$ °K.

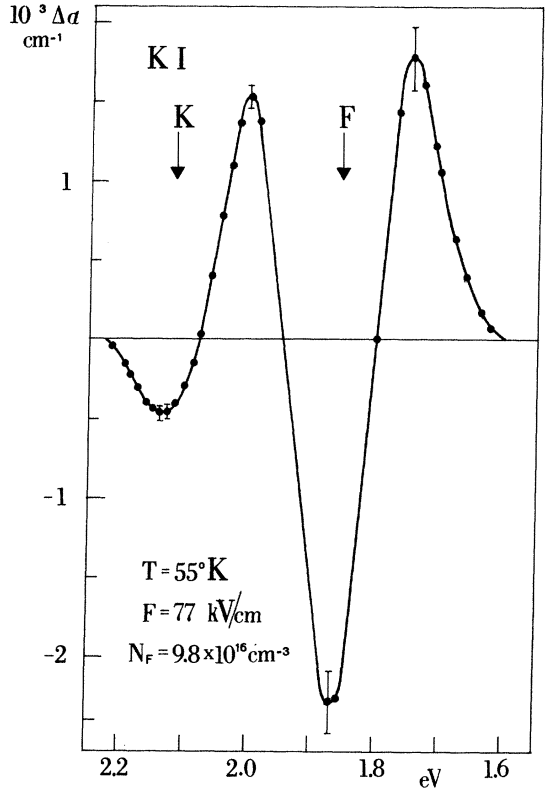

FIG. 3. Change of the absorption coefficient of a crystal of KI containing $N_F = 9.3\times10^{16}$ (F centers)/cm^3 due to a local electric field $F = 77$ kV/cm at $T = 55$ °K.

tions $1S \rightarrow 2P$ and $1S \rightarrow 2S$, differing in energy by $\Delta + 2\delta$. The new transitions also have an approximately Gaussian shape with different widths: W_{0F} and W, respectively.

These transitions must satisfy the conditions of the theory of Henry, Schnatterly, and Slichter,[5] and of the more recent theory of Perlin and Perlin[9] on the optical transitions involving nearly degenerate energy levels; namely, (a) the area and the center of gravity of $\alpha(E)$ (absorption coefficient as a function of photon energy) are not changed by the field[10]; (b) the perturbed width of the $1S \rightarrow 2P$ transition W_{0F} is related to the unperturbed width W_0 by the following equation:

$$W_{0F}^2 = W_0^2 + \delta\,(W^2 - W_0^2)/\Delta\,. \tag{1}$$

Under these conditions, the variation of the absorption coefficient $\Delta\alpha$ based on our model is given by the following expression:

$$\Delta\alpha(\epsilon;\,\Delta,\,\delta,\,W) = \alpha_0\{[(1-x)W_0/W_{0F}]$$

$$\times\exp[-(\epsilon+\delta)^2/W_{0F}^2] + (x\,W_0/W)$$

$$\times\exp[-(\epsilon-\delta-\Delta)^2/W^2] - \exp(-\epsilon^2/W_0^2)\}\,, \tag{2}$$

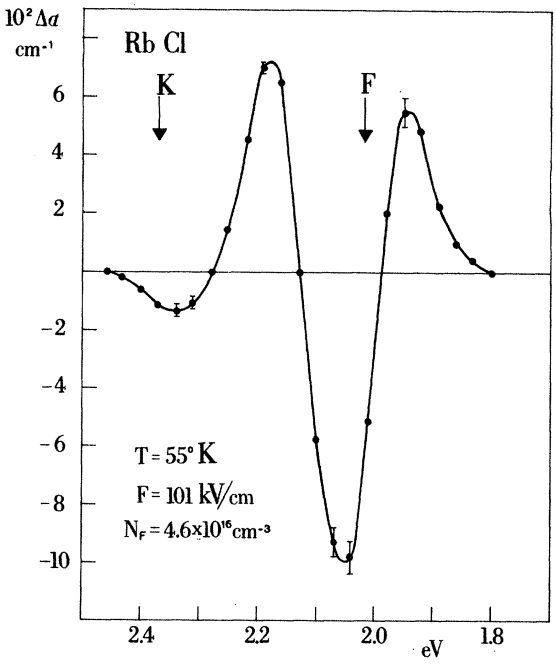

FIG. 4. Change of the absorption coefficient of a crystal of RbCl containing $N_F = 4.6\times10^{16}$ (F centers)/cm^3 due to a local electric field $F = 101$ kV/cm at $T = 55$ °K.

where α_0 is the maximum of the unperturbed F band, ϵ is the photon energy measured from the peak of the F band, and x determines the relative weight of the $1S \rightarrow 2P$ and the $1S \rightarrow 2S$ transitions.

The change of the area of the absorption coefficient is zero for $\Delta\alpha$ given by (2), while the condition on the center of gravity yields the following relation:

$$x = \delta/(\Delta + 2\delta) \simeq \delta/\Delta \ . \tag{3}$$

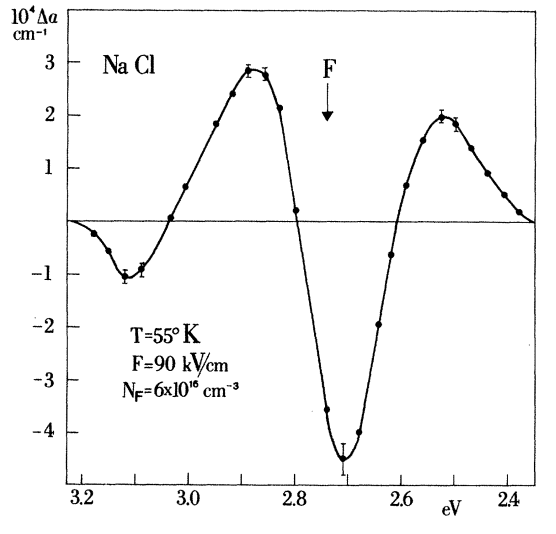

FIG. 5. Change of the absorption coefficient of a crystal of NaCl containing $N_F = 6.0\times10^{16}$ F centers/cm^3 due to a local electric field $F = 90$ kV/cm at $T = 55$ °K.

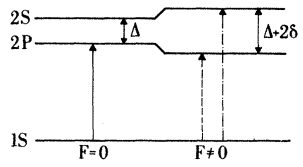

FIG. 6. Energy-level diagram of the Stark effect in the F center (the energy distance Δ and its variation 2 δ are not drawn to scale).

The F bandwidths have been measured from the experimental absorption coefficients. Their values agree, within the experimental errors, with those recently reported by Dawson and Pooley.[11]

The experimental data have been fitted to Eq. (2), varying the parameters W, δ, and Δ.[12]

Table I shows the values obtained for the $1S \rightarrow 2S$ transition widths, W, and the values of the $2S - 2P$ energy splittings. Theoretical calculations of Δ are also reported in the last column.

The positive values of Δ confirm that in all the five crystals the $2S$ energy level lies above the $2P$.

The agreement of the theory with our results is particularly good especially for the calculations of Wood and Öpik. One must note, however, that the discrepancies between experiment and theory are of of the same order of magnitude as Δ.

B. Evaluation of Dipole Matrix Element $\langle 2S|z|2P\rangle$

The second moment $\langle \Delta E_z^2 \rangle$ of $\Delta\alpha$ for light polarized parallel to the electric field in the direction z is related to the dipole matrix element $\langle 2S|z|2P\rangle$ by[13]

$$\langle \Delta E_z^2 \rangle = (eF)^2 |\langle 2S|z|2P\rangle|^2 [1 + (W^2 - W_0^2)/\Delta^2] \ . \tag{4}$$

TABLE I. Observed bandwidths W of the $1S \rightarrow 2S$ transition induced by the electric field, and experimental and theoretical values of the energy differences Δ between the $2S$ and $2P$ states.

	W (eV)	Δ Experiment (eV)	Δ Theory (eV)
KCl	0.077	0.11	0.06 (Ref. 7)
KBr	0.099	0.07	0.06 (Ref. 7)
KI	0.068	0.09	0.07 (Ref. 7)
RbCl	0.038	0.14	0.07 (Ref. 6)
NaCl	0.103	0.17	0.17 (Ref. 7)

$\langle \Delta E_z^2 \rangle$ can be evaluated from the experimental data assuming that $\Delta\alpha$ is due only to changes in the F band. However, the negative signal in the K-band region could be partly due to the K band itself and it is difficult to make an exact evaluation of this contribution.[14]

$\langle \Delta E_z^2 \rangle$ can also be calculated using the approximate relation[5]

$$\langle \Delta E_z^2 \rangle \simeq -2(\Delta\alpha_0/\alpha_0)\langle E^2 \rangle \quad , \tag{5}$$

which is deduced for a symmetrical absorption band ($\Delta\alpha_0/\alpha_0$ is the relative change of the absorption coefficient α at the peak of the F band and $\langle E^2 \rangle$ is the second moment of the F band). Table II shows the values of $\langle 2S \mid z \mid 2P \rangle$ obtained from (4) and (5), and their theoretical estimates.

TABLE II. Experimental and theoretical evaluations of the dipole matrix element $\langle 2S \mid z \mid 2P \rangle$ in different crystals. The first two columns show the absolute values in a.u., while the last two report the values normalized to KCl.

	$\langle 2S \mid z \mid 2P \rangle$		$\frac{\langle 2S \mid z \mid 2P \rangle}{\langle 2S \mid z \mid 2P \rangle_{KCl}}$	
	Experiment (a.u.)	Theory (a.u.)	Experiment (a.u.)	Theory (a.u.)
KCl	2.4	5.91 (Ref. 7)		
KBr	3.6	8.00 (Ref. 7)	1.5	1.35 (Ref. 7)
KI	2.7	7.28 (Ref. 7)	1.1	1.23 (Ref. 7)
RbCl	2.4	6.5 (Ref. 6)	1.0	...
NaCl	2.3	4.18 (Ref. 7)	0.96	0.71 (Ref. 7)

The theoretical values of the dipole matrix elements are consistently larger than the experimental values. However, the behavior of the different crystals is the same in both sets of data, as shown in the last two columns of Table II where the values of $\langle 2S \mid z \mid 2P \rangle$ for the various crystals are reported normalized to the value of KCl.

This indicates that, despite the poor agreement between measured and calculated matrix elements, nevertheless the theoretical approach reflects the essential differences between the crystals.

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[10]This holds exactly for the shape function $\alpha(E)/E$, but is approximately valid also for $\alpha(E)$.

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[12]However the experimental shape of the F band, (approximated by a double Gaussian) was used in this calculation instead of a simple Gaussian for the $1S \rightarrow 2P$ transition.

[13]See Ref. 2, formula (20).

[14]Upper and lower limits of $\langle \Delta E_z^2 \rangle$ have been calculated from the experimental $\Delta\alpha$ in the previous paper (Ref. 2). The corresponding interval for the matrix element evaluated from (4) is, for KCl, 1.9–2.7 a.u.