STARK EFFECT OF THE *F* CENTER IN KCl

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(Received 11 October 1966)

In this Letter we report the experimental observation of the quadratic Stark effect of the *F* center in KCl. The effect was observed in absorption at liquid-nitrogen temperature by applying to the crystal an ac electric field of frequency ν and detecting the modulation (at a frequency 2ν) of a monochromatic beam of light traversing the crystal perpendicularly to the field. The variation of the absorption coefficient $\Delta\alpha \simeq -(1/x)\Delta I/I$ of a crystal of additively colored KCl is shown, as a function of the energy of the photons, in Fig. 1. The measurements were taken with unpolarized light, though it was verified that no Stark effect was detectable with light polarized perpendicularly to the external field. Figure 2 shows the dependence of $\Delta\alpha/\alpha$ at the maximum of the *F* band upon the square of the electric field.

The results of Fig. 1 show that the main effect of the external perturbation is a broadening of the *F* band, which roughly conserves the area, on which is superimposed a small exchange of area between the *F* and the *K* bands. The fractional decrease of absorption at the peaks of the *F* and *K* band is

$$\Delta\alpha_F/\alpha_F = -2.8\times10^{-5};$$

$$\Delta\alpha_K/\alpha_K = -10.9\times10^{-5}. \tag{1}$$

The theory of the Stark effect has been given by Henry, Schnatterly, and Slichter[1] who consider the effect upon the various moments of the *F* band of an external perturbation. They assume that the electric field mixes the nearly degenerate $2S$ and $2P$ states giving rise to a second-order Stark effect. The theory shows that (i) the area of the shape function[2] is not changed by the perturbation, (ii) the change of its first moment is also zero, and (iii) the

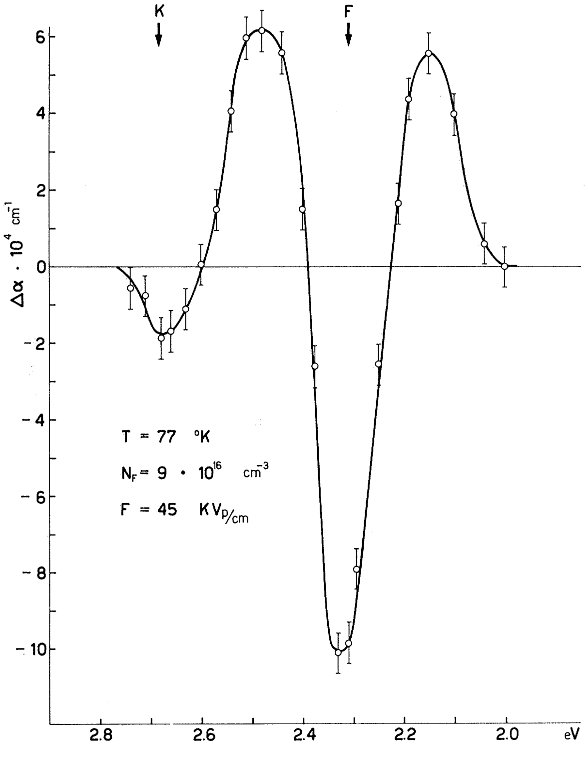

FIG. 1. Relative change of the absorption coefficient in the region of the *F* and *K* bands due to an applied electric field $F = 45$ kV (peak)/cm.

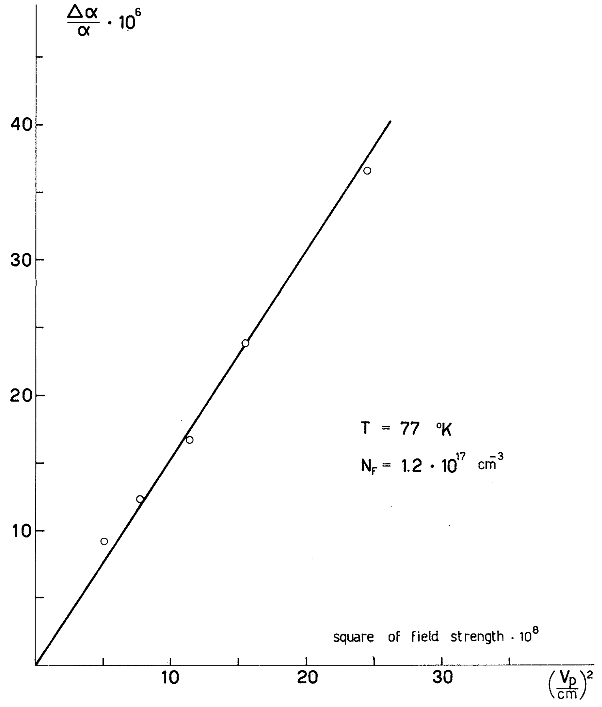

FIG. 2. Fractional decrease of the maximum of the *F* band as a function of the square of field strength.

second moment shows a positive variation that, for linearly polarized light, and for a field F in the z direction, is

$$\langle \Delta E_x^2 \rangle = \langle \Delta E_y^2 \rangle = 0; \quad \langle \Delta E_z^2 \rangle = (eF)^2 |\langle \beta | z | \gamma \rangle|^2, \tag{2}$$

$|\beta\rangle$ and $|\gamma\rangle$ being the $2P_z$ and $2S$ electronic orbitals. In case the distance between the $2S$ and $2P$ levels is much smaller than the width of the F band, the small increase of the second moment and the conservation of the area lead to a fractional decrease of the peak of the F band:

$$\Delta\alpha/\alpha \simeq -\langle \Delta E_z^2 \rangle / 2\langle E^2 \rangle. \tag{3}$$

The experimental results of Fig. 1 agree very well with the above predictions (if one neglects for the moment the exchange of area between the F and the K band) and show that the energy difference between the $2S$ and $2P$ states is smaller than the width of the F band. The matrix element in (2) is easily evaluated from the experimental results and has the approximate value $4a_0$.[3]

The exchange of oscillator strength between the F and the K band can also be explained, along the lines of the above theory (applied to the case of nonoverlapping bands), as due to the mixing of the $2S$ state with the nP-like states responsible for the K band.[4] This interpretation predicts the correct sign (negative) for $\Delta\alpha_K$. On the contrary, were the K band due to transitions to S or D states,[5] one could expect a positive $\Delta\alpha_K$ caused by the interaction with the excited $2P$ state.[6]

A straightforward application of the theory of Slichter and co-workers gives for the change of area of the K band

$$\frac{\Delta A_K}{A_K} \simeq -(eF)^2 \frac{|\langle \beta | z | \delta \rangle|^2}{(E_{3P}{}^0 - E_{2S}{}^0)^2}, \tag{4}$$

$|\delta\rangle$ being the $3P_z$ electronic orbital. Since the matrix element in (4) cannot be much larger than that in (2),[7] comparison of (4), (2), and (1) shows then that $(E_{3P}{}^0 - E_{2S}{}^0)^2$ is smaller than $\langle E^2 \rangle$; i.e., the energy of the $2S$ state is larger than that of the $2P$.

In principle, the energy of the $2S$ state could be obtained by means of an accurate analysis of the asymmetry of the variation of the shape function. However, a noticeable amount of bleaching of the F band is observed during the measurement even at liquid nitrogen temperature. More accurate measurements of the effect at liquid helium temperature are now in progress.

Experiments done with thick specimens in the regions of the L bands did not show any effect of an applied electric field to the experimental limit $\Delta\alpha/\alpha < 5\times 10^{-6}$. The L bands are due to transitions from the ground state of the F center to higher excited states.[8,9]

In case the final state were a state of the conduction band at some critical point,[10] one would expect a rather larger effect similar to the well-known Franz-Keldysh effect. The present experiments seem to indicate that the L bands are not due to transitions to the conduction band or that the effective mass involved is extremely high.

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[1] C. H. Henry, S. E. Schnatterly, and C. P. Slichter, Phys. Rev. 137, A583 (1965).

[2] The shape function $f(E)$ is defined as the absorption coefficient divided by the energy. The asymmetry of the positive peaks of the curve of Fig. 1 is greatly reduced if one plots the change of $f(E)$.

[3] The same matrix element evaluated with hydrogenic wave functions is $3a_0$ (a_0 being the Bohr radius). In evaluating the matrix element in (2) from the experimental data (1), a factor of 2 was introduced to account for the use of unpolarized light.

[4] D. Y. Smith and G. Spinolo, Phys. Rev. 140, A2121 (1965).

[5] S. E. Schnatterly, Phys. Rev. 140, A1364 (1965).

[6] The different behavior is due to the conservation of first moment which determines an increase of the weaker band.

[7] With hydrogenic functions one finds $|\langle \beta | z | \delta \rangle| / |\langle \beta | z | \gamma \rangle| = 0.83$.

[8] M. Hunger and F. Lüty, Phys. Letters 15, 114 (1965).

[9] G. Chiarotti and U. M. Grassano, Phys. Rev. Letters 16, 124 (1966).

[10] T. Kojima, in Proceedings of the International Symposium on Color Centers in Alkali Halides, University of Illinois, Urbana, October, 1965 (unpublished), p. 87.