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STARK EFFECTS IN F-CENTER EMISSION*

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The effect of an applied electric field on the polarization and lifetime of F-center emission has been measured in KCl and KF. The results are explained using a model in which emission occurs from a $2s$-like state which has some $2p$ component due to internal-field mixing.

Recent interest in the F center in alkali halides has focused on the nature of the electronic states of the excited center. Most theories[1] have assumed that the state responsible for the F-emission band is a $2p$-like state of the electron trapped at the halogen vacancy. Much effort has been directed at various effects of lattice distortion and polarization in attempts to explain the discrepancies with experiment. In this Letter, we report results on the Stark effect in F-center emission which support an alternative model for some alkali halides in which the emission occurs from a lower $2s$-like state which has some $2p$ component due to internal-field mixing.

The measurements concern the effect of an applied electric field on both the polarization and the radiative lifetime of F-center emission. These were performed on several alkali halides, but we discuss only KCl and KF as the standard cases.

For the polarization measurements, ac and dc fields of 5-50 kV/cm amplitude were applied to the sample in either the [100], [110], or [111] direction in the temperature range from 2 to 150° K. Phase-sensitive detection was used to determine the field-induced changes in the emission intensity.[2]

The dominant effect of the field at low temperatures was a quadratic increase in the intensity polarized parallel to the field with a decrease of half as much in the perpendicular intensity. This implies no net change in the total emitted intensity. The polarization $P=(I_{\parallel}-I_{\perp})/(I_{\parallel}+I_{\perp})$ was independent of field orientation. A small red shift and broadening of the emission band were also induced by the field. Values for all these quantities for KCl and KF are given in Table I. The temperature dependence of the polarization is shown in Fig. 1. Similar effects have been reported by Kühnert[3] using larger dc fields.

The effect of the field on the radiative lifetime was measured using the pulsed light source and sampling technique described previously.[4] Dc fields up to 135 kV/cm were applied to the sample in the [100] direction at 4.2°K. The field-induced changes in lifetime for KCl and KF are shown in Fig. 2. The decrease is quadratic in field strength and is the same for both polarizations in KF, the only case where both were measured. From the ac field results, we expect that the quantum efficiency for luminescence is not

Table I. Stark-effect coefficients [10^6 (kV/cm)^2].

	KCl	KF
Polarization, $P(0)$	10 ± 3 (13)[a]	8 ± 3
Red shift, $\Delta E/E_{em}$	-0.3 ± 0.1	-0.3 ± 0.1
Broadening, $(\Delta H/H)_{\parallel}$	~1	~0
Lifetime change, $\Delta\tau/\tau_0$	-5.8 ± 1.0	-4.0 ± 1.0

[a]Ref. 3

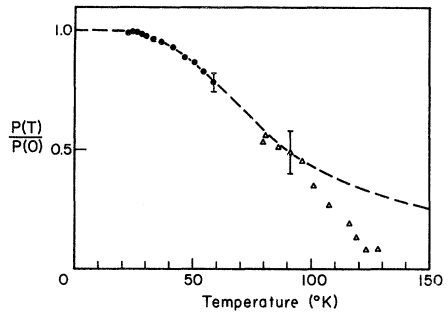

FIG. 1. Temperature dependence of the electric-field–induced polarization of F-center emission in KCl, for a [100] field of 27 kV/cm. Circles represent ac field data, triangles dc field data. Measurements at other field values established that P is temperature independent below 30°K. The dashed line represents Eq. (5) with $\delta E = 0.017$ eV and $3R = 8$.

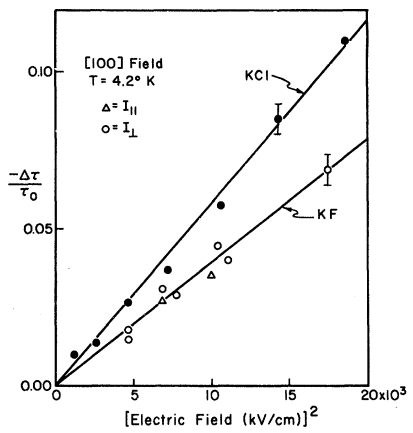

FIG. 2. The electric-field–induced decrease in lifetime for F-center emission in KCl and KF. The zero-field lifetimes were 715 ± 15 nsec and 380 ± 20 nsec, respectively.

appreciably affected by the field in this range. Thus the lifetime changes measured are presumably just the changes in radiative lifetime. These are listed in Table I. Earlier measurements by Spinolo and Fowler[5] and Kühnert[6] showed that there was some decrease in lifetime with electric field, but did not establish the field dependence. These authors also made very different assumptions in estimating the change in radiative lifetime.

Our polarization and lifetime results for the Stark effect, and the temperature dependence of the lifetime reported earlier,[4] suggest certain qualitative conclusions about the emitting state of the F center. First, the temperature independence of P at low temperatures implies that the lowest emitting state is not split by the applied electric field, and that thermal population of higher lying states is negligible below about 30°K. Second, the decrease in lifetime indicates that the polarization is due not to some reorientation effect, but rather to a mixing effect which enhances the transition probability for parallel emission. Finally, the decrease in radiative lifetime with increasing temperature reported previously shows that the higher lying states have a stronger transition probability, and presumably these are the states mixed in by the field.

All these conclusions support a new model for the relaxed excited states of the F center which has been developed in detail by one of us (L.D.B.).[2] In this model, the relaxed states are taken to be quasihydrogenic, but with the $2s$ state lying slightly below the $2p$ states. These states are mixed by odd-parity internal fields, such as those from optical phonons[2,7,8] or from a pseudo Jahn-Teller effect.[9] Since this coupled vibronic problem has not yet been solved, we use a simple model for the F-center states based on a quasistatic Stark mixing. For an F center distorted by an internal field in the x direction, for instance, we take the mixed states to be as follows. The lowest state, $|2s'\rangle$, is now $(|2s\rangle + \alpha \times |2p_x\rangle)/(1+\alpha^2)^{1/2}$. At an energy δE above this state is the degenerate pair of states $|2p_y\rangle$ and $|2p_z\rangle$, and above these is the mixed state $(|2p_x\rangle - \alpha|2s\rangle)/(1+\alpha^2)^{1/2}$.

The radiative lifetime of the distorted lowest state, $|2s'\rangle$, will depend on the mixing coefficient α as

$$1/\tau_s' \propto \textstyle\sum_j |\langle 1s|x_j|2s'\rangle|^2 = [\alpha^2/(1+\alpha^2)]M^2, \quad (1)$$

where $M^2 = |\langle 1s|x|2p_x\rangle|^2$.

If an external electric field is applied, say in the z direction, this will cause mixing of $2p_z$ state into the lowest state. When summed over all distortion orientations, this mixing will increase the emission polarized parallel to the field at the expense of the perpendicular emission, and will decrease the radiative lifetime for this state.

The change in lifetime can be written as

$$\frac{\Delta\tau_s'}{\tau_s'} = \frac{-\Delta(1/\tau_s')}{1/\tau_s'} = \frac{-(\Delta\alpha)^2}{\alpha^2(1+\alpha^2)}, \quad (2)$$

where $\Delta\alpha$ is proportional to the applied electric field F. The polarization induced by this mixing will be

$$P = \frac{M_\parallel^2 - M_\perp^2}{M_\parallel^2 + M_\perp^2} = \frac{3}{2}\frac{(\Delta\alpha)^2}{\alpha^2}, \quad (3)$$

where

$$M_{\parallel}^2 = |\langle 1s|z|2s'\rangle|^2$$

and

$$M_{\perp}^2 = |\langle 1s|x|2s'\rangle|^2 = |\langle 1s|y|2s'\rangle|^2.$$

Thus, the change in radiative lifetime at low temperatures is related to the polarization as

$$\Delta\tau/\tau = -\tfrac{2}{3}[1/(1+\alpha^2)]P. \quad (4)$$

Models which invoke tunneling or p-state orientation do not predict the change in lifetime.

At higher temperatures, emission from the higher lying $2p'$ states becomes important. In the simplest model,

$$P(T) \approx P(0)\frac{1-e^{-\delta E/kT}}{1+3Re^{-\delta E/kT}}, \quad (5)$$

where $R = (1+\frac{2}{3}\alpha^2)/\alpha^2$ is the ratio of $2s'$ and $2p'$ lifetimes.

Using Eq. (4) to determine the mixing parameter, and $P(T)$ to determine δE, we find for KCl, $\alpha \simeq 0.7$, $\delta E \simeq 0.017$ eV and for KF, $\alpha \simeq 0.7$, $\delta E \simeq 0.016$ eV. These parameters are consistent with the temperature dependence of the lifetime reported earlier.[4]

The energy separation δE is consistent with recent theoretical estimates[10,11] for the $2s$-$2p$ separation in the relaxed states when mixing is ignored.

The large value of the mixing parameter implies that the states of the undistorted center would be nearly degenerate. This complicates the problem considerably, and suggests that a treatment following the approach of Öpik and Pryce[9] may be necessary.

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MAGNETIC CIRCULAR POLARIZATION OF F-CENTER EMISSION*

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Magnetic-field–induced circular polarization of F-center emission has been observed in KF. The effect is small and temperature independent in the range 1.3 to 4.2°K, and is interpreted as orbital Zeeman mixing with $g_{\mathrm{orb}} \sim 0.04$.

A new model for the states of the excited F center in alkali halides was presented in the preceding Letter.[1] Numerous attempts to observe electron spin resonance or magneto-optic effects in the "relaxed" excited states have been unsuccessful. In this Letter, we report the successful observation of such an effect, a small magnetic-field–induced circular polarization of the F-center emission in potassium fluoride. The small size and temperature independence of this effect support the new model.

KF was chosen for this study because its F-center absorption and emission bands lie at wavelengths which are technically favorable for high sensitivity. From earlier emission studies[1,2] we know that the relaxed excited states of the F center in KF are very similar to those in KCl and other "standard" alkali halides.

Samples of Harshaw KF were cleaved to dimensions of a few mm and colored by x irradiation at 78°K until the F-center concentration was about $10^{16}/\mathrm{cm}^3$. The sample then was placed in