Luminescence and F' Formation Involving Spin-Polarized F Centers in KCl†

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The electronic processes following optical excitation of F centers in KCl are drastically changed if the F electrons are spin polarized by magnetic fields at low temperatures (1.7°K). As the spin-aligned configuration of the F' center is forbidden, two effects appear: (1) The $F \rightarrow F'$ conversion by conduction electrons becomes suppressed, and (2) the radiationless de-excitation of excited F centers (caused by electron tunneling into neighboring F' center states) becomes suppressed, producing increases of the F luminescence up to a factor 4.

Optical excitation of F centers in KCl produces a weakly bound, relaxed excited state $\tilde{F}^*$, about 0.15 eV below the conduction band. The subsequent electronic processes originating from this $\tilde{F}^*$ state (radiative and radiationless de-excitation, and electron ionization, conduction, and trapping) have been studied extensively, so that their kinetics and interrelations are well understood.[1] In pure and dilute F-center systems at low temperatures, only one process exists: the radiative transition to the ground state $\tilde{F}_0$, giving rise, with full quantum efficiency $\eta_{rad} = 1$, to the infrared F emission (process I in Fig. 1).

Two perturbations can change this simple low-temperature behavior:

(a) Application of high electric fields E produces a competing field-ionization process[2] with an efficiency $\eta_{ion}(E)$, reducing the liminescence efficiency to $\eta_{rad} = 1 - \eta_{ion}(E)$. The field-emitted conduction electrons can be trapped by other F centers (with probability β) forming the two-electron F' center (processes II_A and II_B in Fig. 1). As a result of recapture of conduction electrons by the ionized F centers (with probability α) and of partial overlap of the F and F' bands, a steady-state ratio F'/F given by[3]

$$\left[\frac{F'}{F}(E)\right]^2 \propto \frac{\beta}{\alpha}\eta_{ion}(E) \qquad (1)$$

is achieved under F-light illumination.

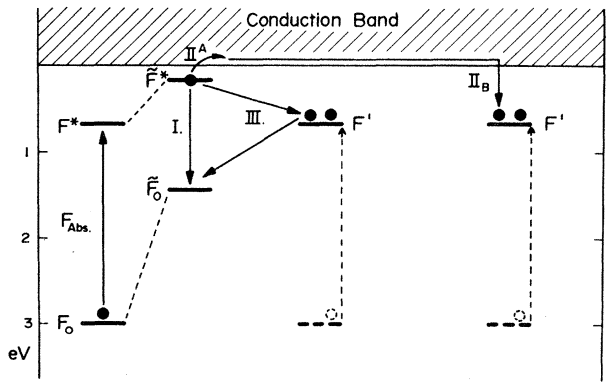

FIG. 1. Schematic representation of the three discussed processes for the transfer of the electron from the relaxed-excited $\tilde{F}^*$ state: (I) radiative transition into the $\tilde{F}_0$ ground state; (II) field ionization (II_A), conduction, and trapping in another F center, forming an F' center (II_B); (III) radiationless transfer from F^* to $\tilde{F}_0$ by tunneling through an intermediate F'-center state, formed at a nearby F center.

(b) With increasing F-center concentration the efficiency of the radiative process (I) decreases drastically.[4] A radiationless de-excitation process, produced by interaction among F centers, must therefore be present. For a phenomenological description of this process, Mielich[5] used a simple model, based on statistically distributed F centers and a "critical interaction distance" $R_c \approx 13$ lattice parameters. The measured concentration dependence of the luminescence could be explained by assuming that for F-center distances $R > R_c$ luminescence and for $R < R_c$ radiationless de-excitation occurs. As to the physical nature of the radiationless process, it was first proposed by Lüty[3] that the electron may tunnel from the $\tilde{F}^*$ state to a nearby F center, forming an intermediate F' center, from which it can tunnel back into the ground state of the original F-center site (process III in Fig. 1). Measurements with light-modulation spectroscopy by Chiarotti and Grassano[6] confirmed this picture.

Thus, for both processes II and III it is essential that an F center can trap a second electron and form an F' center. In the F' center the two electrons occupy a spin-antiparallel, singlet S state,[7] the spin-parallel arrangement being forbidden by the Pauli principle. The existence of a bound triplet state at higher energies is unlikely from theoretical arguments[8] and has not been detected experimentally. On the basis of the picture developed here, one can, therefore, ex-

pect that the whole kinetics of electronic processes should be changed in spin-polarized systems, because the processes II_B and III should become quenched. This expectation was fully verified by the following experiments.

KCl crystals additively colored with 5×10^{16} cm^{-3} F centers were immersed in superfluid He at 1.7°K in a cryostat with optical access. Spin polarization was achieved by a superconductive magnet, allowing the application of fields up to $H_{max} = 90$ kG. The spin polarization was monitored by the F-band circular dichroism,[9] measured with the help of a Pockels cell. The light intensity used for the F-band excitation was kept in all experiments at a level which avoided spin depolarization by optical pumping.[10] Application of high electric fields ($E_{max} = 2\times10^5$ V/cm) under F-light irradiation produces field ionization and $F \rightarrow F'$ conversion, which was monitored by measurements of the absorption height of the F band. Up to one-third of the F centers could be converted at 1.7°K into F' centers. As expected from the above discussion, the application of the magnetic field reduces the $F \rightarrow F'$ conversion, leading to a reduction of the steady-state ratio F'/F, as measured in Fig. 2 for various applied electric fields.

For interpretation we have to replace the electron-capture probability β by $\beta = \frac{1}{2}(\beta_{\uparrow\uparrow} + \beta_{\uparrow\downarrow})$. Here $\beta_{\uparrow\uparrow}$ stands for a capture process in which the conduction electron and the electron in the trapping F center have parallel spins, and similarly $\beta_{\uparrow\downarrow}$ for the antiparallel case. The steady-state ratio F'/F from Eq. (1) should then become dependent on the spin polarization p of the F-center system in the form

$$\left[\frac{F'}{F}(E,H)\right]^2 = \frac{F'}{F}(E,0)^2[(1-p^2)+\delta(1+p^2)],$$
$$\delta = \beta_{\uparrow\downarrow}/\beta_{\uparrow\uparrow} \ll 1. \quad (2)$$

From this relation the magnetic field dependence of the F-band reduction was calculated and plotted for $\delta = 0$ and 0.02. The agreement with the measured behavior can be regarded as very good. The high magnetic field range, which is extremely sensitive to the choice of δ, shows that $\delta \leq 0.01$ or $\beta_{\uparrow\downarrow} > 100\ \beta_{\uparrow\uparrow}$. Thus, for all practical purposes the triplet trapping process is negligible. While the observation of increased photoconductivity in magnetic fields by Hodby *et al.*[11] was first attributed to spin-dependent scattering effects, recent combined measurements of the photoconductivity and Hall effect[12] gave indication of the same spin-dependent trapping effect as derived directly in our experiment.

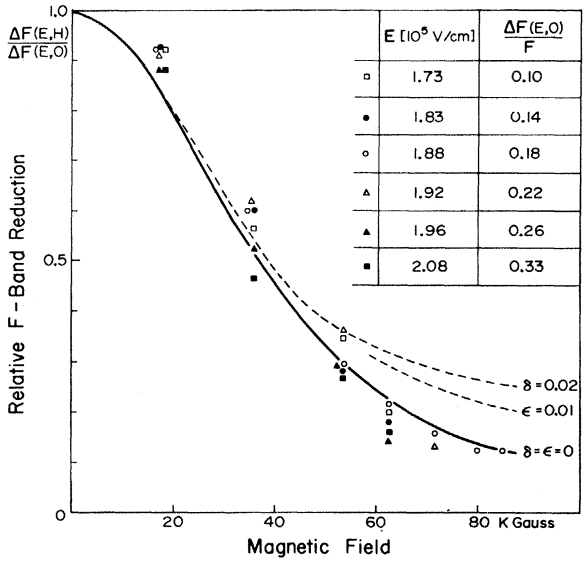

FIG. 2. Relative F-band bleaching under light irradiation and application of different electric fields at 1.7°K as a function of the applied magnetic field. The solid line is the expected behavior for full spin memory ($\epsilon = 0$) and zero triplet trapping ($\delta = 0$), while the dashed lines show the expectation for $\epsilon = 0.01$ and $\delta = 0.02$.

The expected relation (2) plotted in Fig. 2 is derived under the assumption that the spin polarization of the conduction electrons $p(e)$ is the same as that measured in the F ground state, $p_F = \tanh(g\beta H/2kT)$. If we assume a small loss (ϵ) of the spin memory, i.e., $p_e = p_F(1-\epsilon)$, we get from the appropriately modified relation (2) a predicted behavior which clearly deviates from the measured curve already for $\epsilon = 0.01$, as indicated in Fig. 2. It was shown recently[10,13] that during optical cycling of the F electron, the spin polarization is preserved nearly completely. For the interpretation of our results we must similarly conclude that the spin-memory loss of electrons field emitted from the $\tilde{F}^*$ state is less than 1%. Thus, practically fully spin-polarized conduction electrons can be produced by field ionization from optically excited spin-polarized F centers at lowest temperatures. This opens many possibilities for the study of spin-dependent photochemical processes, for which the quenched F' formation is a first example.

For the measurement of the expected spin-polarization effects on process III in Fig. 1, the electric field was removed and the F emission (process I) was monitored. Two separate flexible light pipes were used to supply the F-band ex-

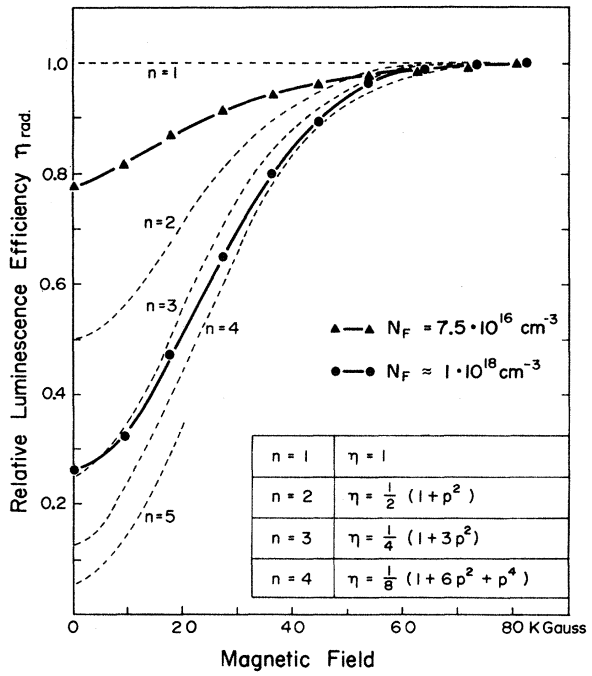

FIG. 3. Measured dependence of the F-center luminescence at 1.7°K as a function of the applied magnetic field for two crystals with different F concentrations. The dotted lines represent the expected behavior for clusters of $n = 1, 2, 3, 4$ interacting F centers calculated with the indicated relations $\eta(p)$, based on the model described in the text.

citation light to the crystal and to receive the F luminescence which was measured as a function of the magnetic field. Figure 3 gives the result for two crystals with different F-center concentrations, showing the expected increase of the emission with the spin polarization. While for low F-center concentration for maximum increase obtained is about 20%, for the heavily doped crystal the initial luminescence can be increased by a factor of 4. The measured relative luminescence efficiencies were normalized in Fig. 3 in such a way that for full spin polarization they are assumed to achieve full efficiency $\eta_{rad} = 1$. The resulting quantum efficiencies at $H = 0$ ($\eta_1 = 0.78$ and $\eta_2 = 0.26$) in Fig. 3 agree well with the average value $\bar{\eta}$ for the absolute quantum efficiency obtained from the various measurements[4,5] for the two F concentrations ($\bar{\eta}_1 = 0.80$ and $\bar{\eta}_2 = 0.20$). This shows that, under full spin polarization, approximately full quantum efficiency for the luminescence can be achieved for all F concentrations.

The interpretation can be based on the interaction model, mentioned above, in which an electron in an $\tilde{F}^*$ state can tunnel into another F center, which is choser than R_c, forming an intermediate F' center, thus quenching the F luminescence. We see now, however, that this radiationless process is possible only if the spin rule for the F' formation (spin antiparallel) is fulfilled. For an assumed "cluster" of $n = 2, 3, 4, \cdots$ F centers in an "interaction sphere" of radius R_c, the $n-1$ possibilities for a radiationless path III of an excited F-center electron are therefore restricted to the ones with antiparallel spin configurations. If all spins are parallel in the cluster, the radiationless path via an F' center is "blocked" and the radiative path I becomes effective. The probability for F luminescence in a cluster of n interacting centers is therefore equal to the (statistical or field-influenced) probability for parallel arrangements of all spins in the cluster. With spin polarization p this would give

$$\eta_{rad}(n) = [\tfrac{1}{2}(1+p)]^n + [\tfrac{1}{2}(1-p)]^n. \quad (3)$$

For clusters of $n = 1, 2, 3, 4, \cdots$ F centers, the luminescence efficiency at $p = 0$ should be $1, \frac{1}{2}, \frac{1}{4}, \frac{1}{8}, \cdots, 1/2^{n-1}$, increasing with p and reaching full efficiency at $p = 1$. This expected model behavior is plotted in Fig. 3 also as a function of the magnetic field for a cluster of $n = 1, 2, 3, 4$ centers.

The measured magnetic field dependence of the luminescence in Fig. 3 fits the predicted behavior from this model surprisingly well. Moreover, a temperature variation between 1.7 and 9°K showed the strong (about $\propto T^{-2}$) dependence of the effect, as predicted by Eq. (3). The measured $\eta(H)$ behavior of the lightly doped crystal in Fig. 3 could be accounted for by about 60% noninteracting ($n = 1$) and 40% interacting pair ($n = 2$) F-centers. The measured $\eta(H)$ for the high-F-concentration crystal follows very closely the predicted behavior of the $n = 3$ cluster and can even be better described by a superposition of the effects from $n = 2, 3, 4, 5$ clusters. For statistically distributed centers of known concentration and a given interaction distance R_c, the relative number of $n = 1, 2, 3, \cdots$ clusters can be calculated, so that this model can be tested more rigorously. Work is in progress to establish such a phenomenological treatment and to "calibrate" the effect for statistically distributed (additively colored) F centers. Measurements and analysis of $\eta_{rad}(H)$ could then become a powerful tool to determine the spatial distribution of F-center systems produced by other mechanisms (like radiation damage), for which F-center formation in correlated clusters can be anticipated.

Our experiment and its interpretation can contribute to the explanation of the puzzling result of the combined ESR and F-luminescence experiment by Ruedin and Porret.[14] They observed a decrease of the F luminescence (linear with the irradiated microwave power) when the system was tuned with the magnetic field into the resonance condition with $g = 1.984$. So far this effect could be ascribed only phenomenologically to the excitation of spin transitions in the F-center ground and/or relaxed excited state. The physical origin of this effect can now be understood to be the same as in our experiment: the presence of interacting F centers with reduced luminescence efficiency. As we showed that spin polarization *increases* the F luminescence, any microwave-induced spin flips—in the ground *or* excited F state—will *decrease* it. ESR experiments detecting microwave-induced luminescence decrease should be most promising for large magnetic fields (K-band) and F-center systems with strongly concentration-quenched luminescence.

A more detailed account of the experimental details, the derivation of the equations for the electron kinetics, and further experiments involving the magnetic-field–induced F-luminescence change will be published soon.

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Energy-Dependent Photoemission Intensities of "f" States in EuS, GdS, and US†

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Photoemission measurements of f states and valence-band energies of EuS, GdS, and US for photon energies from 5 to 41 eV show characteristic energy-dependent emission strengths of "p," "d," and "f" states. These energy dependences permit the "l" character of various levels to be identified in many cases. For example, the emission strength of the $4f^7$ level in EuS increases about 100-fold relative to the 3-eV wide valence "p" band which lies just below the $4f^7$ level. GdS shows a deep $4f^7$ level at about 9 eV below the Fermi level E_F, and US shows an "f-d" band at E_F.

We report the extension of ultraviolet photoemission spectroscopy measurements of "f"-state energy levels in several NaCl-type rare-earth and uranium compounds (EuS, GdS, and US) up to photon energies of $\hbar\omega = 41$ eV. Previously, measurements were limited to 11.6 eV (LiF window cutoff) and $4f$-state emission was found to be weak for such energies.[1,2] The availability of a wide range of photon energies ($\hbar\omega = 16.8$, 21.2, 26.9, and 40.8 eV as well as $\hbar\omega$