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OPTICAL DETECTION OF THE EPR OF LOOSE F AGGREGATE CENTERS IN KCl†

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In order to explain the quenching of the luminescence of F centers in alkali halide crystals (concentration effect), the following mechanism was proposed [1, 2]: after optical excitation, a relaxed excited F center ($\tilde{F}^*$) may transfer its electron non-radiatively via a tunneling process toward a neighboring F center in its ground state (F_0). This process leads to the momentary formation of an anion vacancy (α center) and F′ center. Since this last defect can only be a spin singlet, such an electron tunneling will be possible only if the spins of the $\tilde{F}^*$ and F_0 centers are antiparallel [2], otherwise the disexcitation mechanism will be radiative. This process induces a population difference between the parallel and the antiparallel spin states of the excited pairs and provides a new way to detect optically the occurring resonance phenomena, either in the excited state or in the ground state of the F center pairs. The competitive influence of the different local hyperfine fields and of an applied magnetic field causes a decrease of the tunneling probability, i.e. an increase of the luminescent yield. On the other hand, spin–lattice relaxation (in this case an Orbach process) and EPR in the ground and in the excited state reduce this effect by mixing between the spin state populations (fig. 1a). Both effects can be explained quantitatively [3, 4].

After a short controlled F center aggregation, performed optically in KCl at $T = 283$ K, new effects appear. The luminescent yield η is depressed by a magnetic field ($0 < H < 6$kG) and a new single gaussian EPR line appears together with the former resonances. It corresponds however to an increase of η. This new line is characterized by a g-value of 2.001 and a halfwidth of 64 G. After a longer bleaching the luminescence yield decreases still more and a new well separated EPR line, with similar optical characteristics, appears at nearly half field. Its g-value is 4.019 and its halfwidth is 37 G (fig. 1b).

These phenomena are tentatively attributed to the presence in the crystal of

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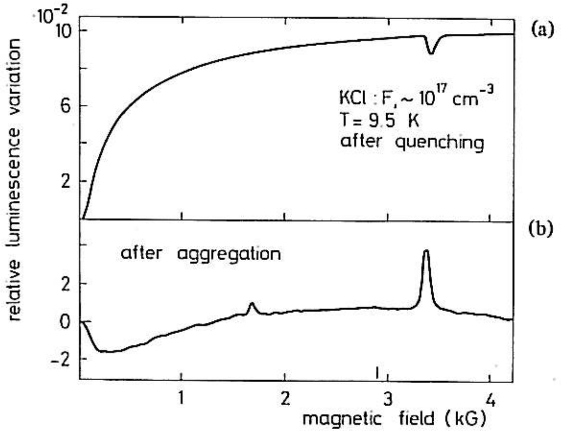

Fig. 1. (a) Relative luminescence variation $\Delta I/I$ of a KCl crystal containing ~ 10^{17} quenched F centers/cm^3 at $T = 9.5$ K measured as a function of an applied magnetic field. The EPR line (microwave field at 10 GHz) is composed of 2 superimposed gaussian lines attributed to resonances in the ground state ($g = 1.985$, $\Delta H_{\frac{1}{2}} = 65$ G) and in the excited state ($g^* = 1.981$, $\Delta H^*_{\frac{1}{2}} = 79$ G) of F centers pairs. (b) Relative luminescence variation $\Delta I/I$ of the same crystal in the same experimental conditions after a long and controlled F center aggregation. The two new single gaussian EPR lines are respectively characterized by $g = 2.001$, $\Delta H_{\frac{1}{2}} = 64$ G and $g = 4.019$, $\Delta H_{\frac{1}{2}} = 37$ G. The high field line is attributed to resonances in the ground state of loose aggregates of F centers. The former resonances do not appear in this case.

loose aggregates of F centers, i.e. pairs of F centers separated by just a few interionic distances. Using the previous model [3] and taking into account, in the magnetic hamiltonian, an exchange interaction between the two spins of the close pair $JS_1 \cdot S_2$, it is found that this interaction modifies especially the energy levels of the excited state of the pairs, because of the large overlap of the orbital wave functions; the energy levels are given schematically in fig. 2. For not too high values of J^* the antisymmetric states are favoured at the expense of the symmetric ones. Therefore the populations n_i of the ground state levels are modified during each optical cycle, so that in stationary state $n_2 + n_3 > n_1 + n_4$. This causes an appreciable transient decrease of the F center luminescence yield, which can be observed immediately after an optical excitation with a time constant of the order of 0.1 s. A microwave field of suitable frequency shall cause an increase of the luminescence intenstity by mixing between the spin state populations. In this way the new high field EPR line, which behaves optically as described above, is attributed to transitions occurring in the ground state of the close pairs from the levels 2 and 3 to the level 4, ($\Delta m = 1$). The origin of the low field EPR line, which has a similar optical behavior, cannot be explained in the framework of this model.

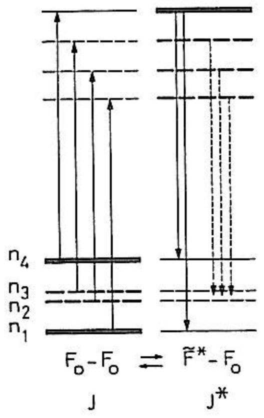

Fig. 2. Diagram of the energy levels of a loose aggregate of F centers in its ground state ($F_0 - F_0$) and its excited state ($\tilde{F}^* - F_0$). The full lines represent symmetric states (low tunneling probality in the excited state) while the dashed lines characterized antisymmetric states (high tunneling probability in the excited state). The optical cycle, in which other intermediate states are omitted, is represented by the vertical lines; full lines: radiative transitions; dotted lines: radiationless transitions.

Long bleaching is known to create more complex loose aggregates of F centers as well as F_2, F_3, etc., centers. Therefore additional EPR lines should be detected by using the same technique.

This new way to detect the EPR of F centers complexes should give a better knowledge of their spatial distribution and the aggregation mechanism occurring in alkali halide crystals where numerous questions are left open [5].

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