PHYSICAL REVIEW B VOLUME 24, NUMBER 6 15 SEPTEMBER 1981

Decay properties of the F center in additively colored NaF:Li

L. Bosi and M. Nimis
Gruppo Nazionale di Struttura della Materia del Consiglio Nazionale delle Ricerche, and Istituto di Fisica del Politecnico, Piazza Leonardo da Vinci, 32-20133 Milano, Italy

P. Gagliardelli
Istituto di Fisica del Politecnico, Piazza Leonardo da Vinci, 32-20133 Milano, Italy
(Received 8 January 1981)

Accurate measurements show that the F-center lifetime, in NaF samples, does not depend on the coloration technique. The anomalous behavior of the F-center decay in NaF is confirmed: In particular, light irradiation in the F band does not produce F' centers.

Although F-center luminescence and lifetime in NaF (Refs. 1–4) is far from clear, few studies have been made on the subject.

The activation energy of the deexcitation for the luminescence process does not correspond[1] to the energy required for the jump into the conduction band; the lifetime value τ (Refs. 2–4) is lower than expected[5] on the basis of the general rule[5] for the F-center lifetime in alkali halides. The first measurements[2,3] of the F-center lifetime in NaF were performed in 1969 by the Swank and Brown technique,[6] which gives reliable results if only one exponential decay is present. On the other hand, later data[4] show a strange knee near to 100 K.

Because of the difficulty of obtaining additive coloration, the samples used in previous experiments were always colored with x or γ rays. The main disadvantage with this technique is the formation of a large and noneliminable quantity of F_2^+ centers, whose luminescence is strong and partially overlaps the F-center luminescence (see Fig. 4 of Ref. 2 and Fig. 2 of Ref. 4); in addition, F_2^+ centers seem to be responsible for energy-transfer processes.[7] Another disadvantage is the presence[8] in the samples of several varieties of aggregate and ionized centers that make the luminescence study even more laborious.

New lifetime data in additively colored NaF samples are necessary even for an investigation of the influence of F_2^+ centers in the decay mechanism. In this field the technique of data acquisition has made considerable progress and the authors therefore feel it necessary to add further information to the paper previously published by one of them.[2]

In 1974, Collins, Schneider, Klein, and Johnson[9] performed the first successful additive and electrolytic coloration of NaF crystals, a success believed[9] to be due to the low OH^- content in the specimens. The electrolytic technique was also used by Jawad and Smith[10] to produce a homogeneous distribution of F centers in NaF samples containing mercury. Colloidal bands, however, were always present in the absorption spectra.[9,10] (Only NaF:Li-doped crystals seem[9] to avoid colloid formation.)

Starting from the above experimental results, we performed lifetime measurements in additively colored NaF:Li (≃1 mol% of LiF in the melt). The crystals and about one-tenth their weight of Na metal were sealed at room temperature under 1 atm of argon in a stainless-steel tube, then maintained at 830 °C for about 4 h. The sample we employed (3.5 mm thick) showed at liquid-nitrogen temperature a 0.75-OD (optical density) F band, together with a 0.5-OD colloid band.

Even if the coloration were not so successful as in the Collins, Schneider, Klein, and Johnson[9] experiments, we believe that the luminescence properties of the excited F center were not affected by the presence of colloids. Indeed, by using our technique of measuring the delay distribution of the single photons emitted after a pulsed excitation,[11] we obtained single exponential decay curves.

In Fig. 1, we present the lifetime $\tau(T)$ of the

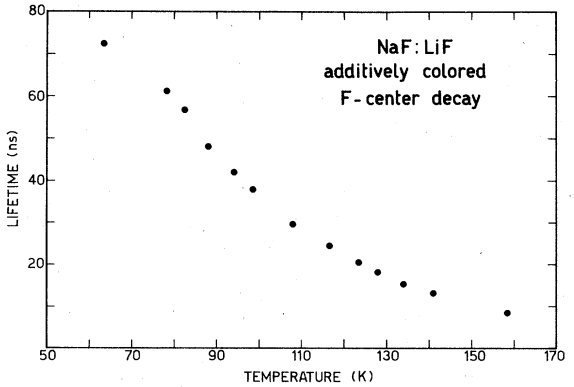

FIG. 1. The lifetime τ as a function of temperature. Data accuracy is 2%.

excited state of the F center as a function of the temperature T. The activation energy of the de-excitation, ΔE_L, for the luminescence process, is 0.050 ± 0.005 eV. Furthermore, quantum-yield analysis, as a function of the temperature, showed similar behavior to that observed for the $\tau(T)$ curve, even if the data are somewhat scattered due to fluctuations in flashlamp stability.

At every F-center concentration τ values, obtained by repeating the measurements in pure NaF samples (from Korth) after coloration with γ rays (from a ^{137}Cs source) are practically the same as those presented in Fig. 1. It may be noted, however, that F_2^+-center luminescence is always present in these samples; consequently, taking into account the F_2^+ lifetime value (33 ns),[7] only F-center lifetimes higher than 33 ns are accurate.

In our opinion, the knee observed by Stiles, Fontana, and Fitchen[4] in their $\tau(T)$ curve near to 100 K, could be due to the F_2^+-center component in the decay spectra, because of the similarity between the F and F_2^+ lifetimes. Nevertheless, since the lifetime data we found are the same for NaF samples colored additively as for those colored with γ rays, it seems that the possibility of an apparent change in the F-center lifetime due to the F_2^+ component (or to energy-transfer effects) can be disregarded. In fact our decay spectra, obtained in NaF:Li additively colored samples, does not show any F_2^+ component, but only the F center one.

In conclusion, our test of a possible lifetime change depending on the coloration technique was negative. Our measurements substantially confirm the results previously obtained.[1-4] The lifetime data are somewhat different, but the ΔE_L value is practically the same[1,2] and does not correspond to value $\Delta E_I = 0.12$ eV (Ref. 1) which is related to the jump into the conduction band, as pointed out by Podini.[1] This is because ionization has little[1] influence on the luminescence process in the temperature range below 200 K.

As further evidence of this, we have tried to form F' centers in additively colored NaF:Li with irradiation by F light as in NaF samples[1] colored with x rays, but no growth of the F' band was detected at any temperature investigated, not even at room temperature. It should be noted that F' centers are formed by light irradiation in the F band in all alkali halides, except NaF.

The results on the F-center decay in NaF might be interpreted by taking into account a possible radiationless transition, which involves an intermediate level situated between the relaxed excited state of the F center and the conduction band. Tunneling processes can be disregarded, because they would produce a change in the lifetime values as a function of the F-center concentration. The absence of F'-center formation might be related to the presence of this intermediate level, which would favor the recombination of the electrons released from the F centers into the conduction band during the photoionization process,[1] with the vacancies (α centers) so formed. However, it would seem that up to the present this effect has not been fully explained.

The authors are indebted to Professor G. Spinolo for kindly supplying the NaF:Li samples.

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