Spin-polarization and spin-memory effects in the F-center absorption and F' conversion of NaI and NaBr crystals

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(Received 1 September 1982)

The low-temperature optical conversion of F centers in NaBr and NaI into defects with absorptions at equal or higher energies was studied under magnetic fields up to 80 kG. A strong reduction of the optical conversion was observed under fields giving clear evidence that the reaction product of the conversion is an F' center with two electrons in a singlet state, the formation of which becomes forbidden in spin-polarized F-center systems. This magnetic field quenching of the F' conversion ("Porret-Luty effect"), however, is incomplete even under full spin polarization indicating the existence of some loss mechanisms. To clarify the latter, we measured the spin-memory loss during the optical cycle by monitoring the magnetic circular dichroism (MCD) under known pumping conditions, obtaining spin-mixing parameters of $\epsilon=0.03$ and 0.12 for NaBr and NaI, respectively. These ϵ values can explain only in part the incompleteness of the magnetic field effect, hinting towards the existence of a bound triplet F' state. From the MCD measurement, the spin-lattice relaxation time of the F ground state as a function of magnetic field and the spin-orbit—splitting parameter Δ of the F center were determined too.

I. INTRODUCTION

The mainstream of color-center research in alkali halides has involved hosts with comparable cation and anion size ($r_+:r_- > 0.5$) and has left out the materials with small ($r_+:r_- < 0.5$) ratios, like the sodium and lithium bromides and iodides. This is mostly due to the extremely hygroscopic nature of these hosts, the difficulties of pure crystal growth and production of F centers by the usual additive or irradiation coloration technique, and the strong extrinsic influence of oxygen-containing impurities on the behavior of F centers.[1] In spite of these difficulties, F-center studies in these latter hosts (which we call for convenience "group II") are important and attractive scientifically, because several intrinsic F-center properties are predicted—or have been found—to be distinctively different from the "normal" F-center properties ("group I") for which KCl is the most widely investigated prototype.

Some of these characteristic differences, as far as they have been studied, are summarized below.

(1) While F centers in group I couple to phonons of a wide frequency range and of A_{1g}, E_g, and T_{2g} symmetry with comparable strength, F centers in NaI couple predominantly ($\sim 80\%$) to a single sharp A_{1g} phonon band (at 116 cm^{-1}), as seen by Raman experiments.[2] The description of the electron-phonon coupling with a configurational coordinate diagram involving a single breathing mode, which is a gross oversimplification for normal F center of group I, should therefore be a rather good approximation in NaI.

(2) The Dexter-Klick-Russel (DKL) criterion for the occurrence of luminescence,[3] as applied to all available F-center data by Bartram and Stoneham,[4] predicts luminescence quenching by crossover between the excited- and ground-state curves for group-II hosts. Indeed, a study in zone-refined NaI and NaBr found the F-center luminescence to be extremely weak (quantum efficiency ~ 0.2—0.8%).

(3) The same study[5] showed that dilute F centers in both NaI and NaBr can be converted by optical excitation reversibly into F' centers via a thermal activated process which leads at high enough temperature to a full conversion efficiency. The measured activation energies (30 and 60 meV for NaI and NaBr) fit very well in the trend for the energy gap ΔE between the relaxed excited state ($\tilde{F}^*$) and the conduction band, established with the effective-mass model for other alkali halides.[6] Electron ionization therefore occurs in the relaxed excited $\tilde{F}^*$ state in NaBr and NaI, as it does in normal F centers of group I. As apparently all optically excited electrons can reach this state from which ionization occurs, it must be deduced that the observed strong nonradiative deexcitation must take place in the same state as well. The main conclusion from the previous study[5] is therefore that the nonradiative decay occurs not *during* relaxation by a crossover process, but rather *after* relaxation from the relaxed $\tilde{F}^*$ state by a rate process which competes with the much weaker radiative and with the thermally activated ionization process.

(4) While in the group-I materials the main F' band lies at considerably lower energies compared to the F band, the F' band in NaBr overlaps mostly the F band while in NaI it even is located at the short-wave side of the F band.[5] This trend towards a very strong binding of the second electron in the vacancy when going from group-I to group-II hosts is not yet understood and has remarkable consequences, as seen under (5).

(5) It is known that for high F-center densities a tunneling process from the relaxed excited $\tilde{F}^*$ state can occur which transfers the electron into a neighboring F center forming the F' state.[7] In group-I systems a back-tunneling into the ground state of the original F center occurs subsequently, such that the F' state in a neighboring F center works only as a *short-lived intermediate state* in the nonradiative deexcitation of the excited F center. In NaBr and NaI, the same $\tilde{F}^* \rightarrow F'$ electron tunneling into a neighboring F center occurs at high F-center densities. The back-tunneling, however, is not possible due to the very low-lying F' state, so that the F' center produced by low temperature $\tilde{F}^* \rightarrow F'$ tunneling is not a short-lived intermediate but a *totally stable reaction product.*[5]

The tunneling process (5) can be strongly influenced by high magnetic fields at low temperatures.[8] Spin polarization of the ground-state F electron in connection with a high spin memory in the optical cycle produces a quenching of the $\tilde{F}^* \rightarrow F'$ tunneling transition, as the only bound F' state is a singlet state requiring two electrons with antiparallel spins. In group-I F centers the two-step tunneling process through the intermediate F' state and its magnetic field quenching can be observed (in static experiments) only indirectly by its effect on the F luminescence.[8]

In NaI and NaBr where *stable* F'-center formation is possible by $\tilde{F}^* \rightarrow F'$ tunneling, a possible quenching of the one-step tunneling process by spin polarization should be observable directly by F and F' absorption experiments. We test in the following these expectations and the whole underlying framework of concepts and conclusions about the group-II F and F' centers by static and dynamic low-temperature absorption experiments in high magnetic fields. Besides tests on the concepts these experiments are intended to clarify the unknown spin-lattice relaxation and spin-memory effects of the F center in NaI and NaBr.

II. EXPERIMENTAL PROCEDURES AND APPARATUS

The NaBr and NaI crystals were grown in the Utah Crystal Growth Laboratory from ultrapure and partially from zone-refined material. F centers were produced by a two-step process. Firstly, U centers were produced by heating the crystals in approximately 6 atm of hydrogen and sodium vapors at about 600 °C for about 5 d. The crystals were afterwards stored in a dry, dark environment until the time of being used for the experiment. A small piece was then cut and mounted as quickly as possible in an optical cryostat containing a superconducting magnet. F centers were obtained by irradiating the crystals for approximately 1 h with uv light from a deuterium lamp filtered for visible light. This procedure was followed for NaI but was slightly modified for NaBr, where it was previously found[5] that F centers in hydrogenated samples are produced only in a layer approximately 2 mm thick. Moreover, perturbed F centers can be produced in this layer, especially near the surface of the sample. Consequently, approximately 1 mm of the top surface was always ground off to eliminate as far as possible any potential contamination of the F centers by surface impurities. A NaBr sample (grown by Korth-Kiel) colored by γ-ray irradiation from a ^{137}Cs source was also utilized.

Absorption measurements and $F \leftrightarrow F'$ conversions were performed by means of an optical apparatus with the magnetic field produced by a superconducting solenoid directed along the light path and normal to the (100) face of the crystals. During the experiment, the samples were immersed in liquid helium pumped below the λ point.

Magnetic circular dichroism (MCD) was mea-

sured through the differential absorption of circularly polarized light σ^+ and σ^- propagating through the sample parallel to an external magnetic field. The polarization of the monitoring light is periodically switched between σ^+ and σ^- by means of a linear polarizer followed by an acousto-optical $\lambda/4$ modulator.

III. EXPERIMENTAL RESULTS

Figures 1 and 2 show the F absorptions (solid curves) of two typical NaI and NaBr crystals. The average F concentrations are approximately 4×10^{16} and 8×10^{16} cm^{-3}, respectively, for the two samples. The observed halfwidths of the two absorptions, approximately 0.23 V and 0.29 eV, ensure the existence of good unperturbed F centers, as previously demonstrated.[5] Under illumination at 600 nm for NaI, and 520 nm for NaBr (arrows in Figs. 1 and 2), the F band decreases and a new band appears, well resolved in NaI and strongly overlapped by the F band in NaBr (dotted curves in Figs. 1 and 2). By illuminating the samples of NaI at 500 nm and those of NaBr at 630 nm, where the F' band does not strongly overlap the F band, the previous process is reversed, and the original absorption curves are almost completely restored. This result again points to the existence of unperturbed F centers, as demonstrated previously.[5]

By detecting the pump beam transmitted through the crystal and properly attenuated before the photomultiplier, it was possible to follow the $F\rightarrow F'$ conversion. Figure 3 shows the results for NaI. The optical density of the F absorption band at 600 nm is plotted as a function of irradiation time for various values of the magnetic field. These measurements indicate clearly that *increasing magnetic fields decrease the low-temperature $F\rightarrow F'$ conversion by tunneling.* Figure 4 shows analogous results for NaBr with the additional feature that the magnetic field was turned off after 11 min of irradiation time. This produces immediately a considerable increase of the conversion, particularly when the original magnetic field was very strong. The conversion reported in Figs. 3 and 4 have been obtained with a pump power of ~50 $\mu W/cm^2$ at 600 nm in NaI and 25 $\mu W/cm^2$ at 520 nm in NaBr. These values refer to the intensities incident on the sample, without taking into account reflection and scattering losses at the surfaces.

MCD signals in NaBr and NaI are displayed in Fig. 5. The derivative-shaped spectral curves are centered around the F bands and no contribution has been observed in the region of the F' band. The MCD signals were measured both before and after the $F\rightarrow F'$ conversion, and in no case did they show any appreciable spectral variation, confirming the

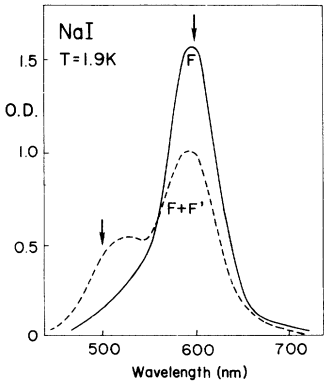

FIG. 1 Absorption spectra of colored NaI at 1.9 K. Solid curve, pure F centers; dotted curve after F light bleaching. Arrows indicate the wavelengths of the spectral irradiation used for the reversible optical conversion between the two bands.

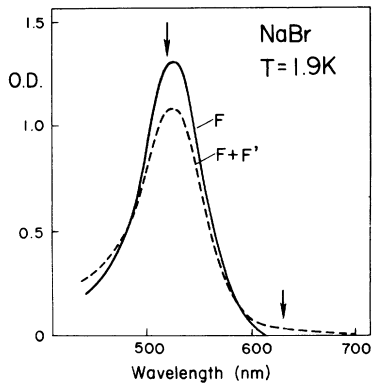

FIG. 2. Absorption spectra of colored NaBr at 1.8 K. Solid curve, pure F centers; dotted curve after F light bleaching. Arrows indicate the wavelengths of the spectral irradiation used for the reversible optical conversion between the two bands.

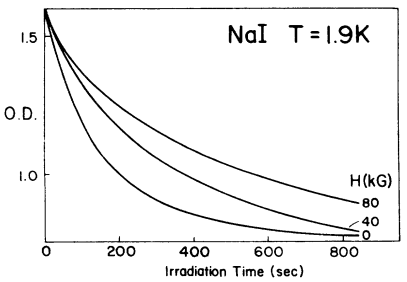

FIG. 3. Decrease of the F-band absorption (at 600 nm) in NaI under constant light irradiation at 1.9 K, measured at various values of magnetic fields H.

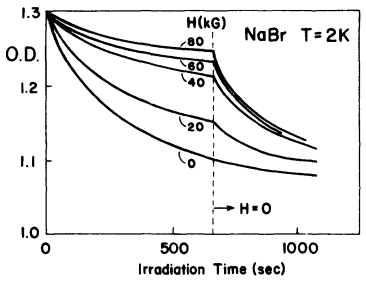

FIG. 4. Decrease of the F-band absorption (at 530 nm) in NaBr under constant light irradiation at 2 K, measured at various values of the magnetic field. After 660 sec irradiation time, the magnetic fields were switched to zero.

spinless nature of the ground state of the F' center ($S=0$, $L=0$).

At a given wavelength the MCD signal depends linearly on the steady magnetic field and on the polarization P of the F-center ground state. The latter parameter can be varied if an intense pump beam of appropriate wavelength is simultaneously aimed at the sample. The maximum variation occurs when the pump beam is tuned to one of the dichroic peaks in Fig. 5. We chose the line of an He-Ne laser ($\lambda=6328$ Å) for the measurements in NaI and the $\lambda=5145$ Å line of an Ar^+ laser for the measurements in NaBr. Using various pump intensities and a large variation of magnetic fields, we have recorded a large quantity of time-dependent MCD signals on a memory oscilloscope. Figure 6 gives typical traces for a sudden switch-on (a) and switch-off (b) of the pump light in NaBr.

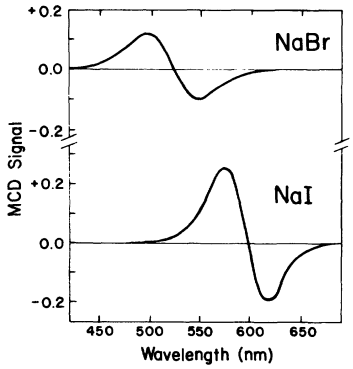

FIG. 5. Spectral dependence of the MCD of the F band in NaBr and NaI at $T=1.85$ K and $H=30$ kG. The MCD signal is given in terms of the normalized intensity ratio $(I^+-I^-)/(I^++I^-)$.

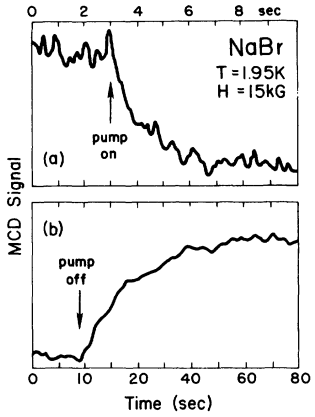

FIG. 6. Time dependence of the MCD signal (at 500 nm) measured in NaBr at $T=1.95$ K and $H=15$ kG under (a) sudden switch-*on* of pump light and (b) sudden switch-*off* of pump light. Note different time scale in (a) and (b).

IV. DISCUSSION AND INTERPRETATION OF EXPERIMENTAL RESULTS

Although the *average* F-center concentration (as measured by the absorption constant of the F band) was rather low (in the 10^{16}-cm^{-3} range), the *local* concentration must have been considerably higher. This is clearly seen by the fact that a sizable fraction ($\sim 50\%$) of the F centers present in the crystal could be converted under low-temperature light excitation by tunneling into F' centers.[5] Owing to this unknown nonstatistical distribution of the F centers (which is an inherent consequence of the production process used), we refrain from attempts to analyze the tunneling behavior itself with an interaction model, involving a "critical distance" for the tunneling process as done in Mielich's work.[9] Instead we accept phenomenologically that in a given sample with a particular F-center density and distribution, a sizable fraction of the F centers have separations which are smaller than the relevant "critical distance" such that they can produce electron tunneling and $F^*\rightarrow F'$ conversion after optical excitation. We then concern ourselves only with the *effect of the magnetic field on this tunneling process.*

The measurements in Figs. 3 and 4 indicate clearly that the bleaching rate of the F band under light excitation becomes effectively reduced by applied magnetic fields. The initial slopes of the F bleaching curves in Figs. 3 and 4 reflecting the tunneling rate w from the excited F state ($\widetilde{F}^*\rightarrow F'$) are plotted in terms of this normalized magnetic field dependencies $w(H)/w(0)$ in Figs. 7(a) and 7(b) for NaI and NaBr, respectively. If a full memory of the spin

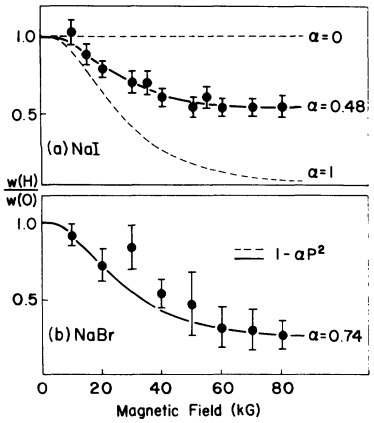

FIG. 7. Initial rate of F band decreases under light irradiation $w(H)$ as a function of magnetic field, normalized to $w(0)$, for NaI (a) and NaBr (b). Measurements (points with error bars) are compared to calculated $1-\alpha P^2$ curves with different α parameters.

polarization of the F ground state (P) is preserved during the optical cycle, and F' centers can be formed only in a singlet (antiparallel spin) state,[10] the expected behavior would be[8]

$$w(H)/w(0)=1-P^2 , \tag{1}$$

as indicated in Fig. 7 with a dotted line. Evidently, the observed behavior deviates considerably from this ideal case but can be well represented with a relation

$$w(H)/w(0)=1-\alpha P^2 \tag{2}$$

using a "loss factor" $\alpha=0.48$ and 0.74 for NaI and NaBr, respectively (solid lines in Fig. 7). The physical origin of this loss factor can be twofold:

(a) A *loss of spin memory* can occur during the optical excitation cycle, as expressed by a spin-mixing parameter ϵ, which gives the relative probability for a spin flip during the optical cycle.[11]

(b) The probability to form F' centers by tunneling will not be completely quenched by spin polarization if F' centers can be formed in a *stable triplet state* with certain relative probability δ.

These two effects will produce a loss coefficient

$$\alpha=(1-2\epsilon)\left[\frac{1-\delta}{1+\delta}\right] , \tag{3}$$

as was shown in the previous work by Porret and Luty.[8] It is evident that separate experiments on the spin-mixing effects (ϵ) and a possible F' triplet formation (δ) must be conducted in order to interpret the measured α values in Fig. 7.

The spin-memory loss in the optical cycle can be determined from MCD experiments monitoring the ground-state spin polarization P under intense optical pumping, a technique first applied in Ref. 12. When the pump light is turned on suddenly at time $t=0$, the ground-state polarization P changes as follows[12]:

$$P(t)=P_f+(P_i-P_f)\exp(-t/T_R), \tag{4}$$

where P_i and P_f are the initial and final values of the spin polarization and T_R is given by

$$\frac{1}{T_R}=\frac{1}{T_1}+\epsilon U . \tag{5}$$

U is the sum of the pump rates out of the ground-state magnetic sublevels and can be obtained from the measured absolute pump light intensity using the relation between absorption coefficient and center concentration (Smakula equation). This requires the knowledge of the oscillator strength of the F absorption, which we assumed (in analogy to other F-center systems) to be 0.8.

Measurements of T_1 can be done directly and accurately by experiments of the type in Fig. 6(b), in which the pump intensity is suddenly *turned off*, and the spin system returns to equilibrium with time constant T_1. Measurements of the type in Fig. 6(a) with sudden *turn-on* of pump light of various intensity U allows the determination of ϵ. In Fig. 8 we illustrate typical results obtained for both NaI and NaBr with four pump intensities U and at $U=0$, showing the linear variation of T_R^{-1} with U. It should be noted that the plotted pump rate U is obtained from the measured light intensity at the entrance surface of the sample. Owing to the variation of U in different layers of the absorbing sample, a correction must be applied,[13] before obtaining ϵ from the slope of the $T_R^{-1}(U)$ curves. The error in determining ϵ is rather large due to the experimental difficulties in measuring the absolute absorbed pump light intensity and hence U. In order to further check our experimental procedure, we have therefore determined with the same optical pumping technique the value of ϵ for F centers in KI and found $\epsilon=0.22$, very close to the previously determined value[12] of $\epsilon=0.24\pm30\%$.

The obtained result is a value of $\epsilon=0.03\pm0.01$ for NaBr and $\epsilon=0.12\pm0.04$ for NaI, similar magnitudes as observed for F centers in other alkali halide hosts. These rather small spin-mixing effects ϵ would produce a loss factor α in the $w(H)$ experiment [Eqs. (2) and (3)] of $\alpha=0.94$ and 0.76 for NaBr and NaI, respectively, if we assume that spin mixing is the *only* origin of loss in the magnetic field dependence of the F' formation. Obviously,

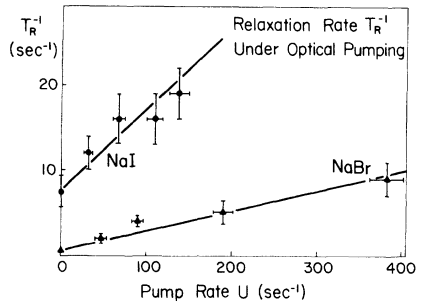

FIG. 8. Relaxation rate T_R^{-1} of the F ground-state spin polarization measured in NaI and NaBr at 2 K as a function of the optical pump rate U.

the experimentally observed values, $\alpha=0.74$ and 0.48 for NaBr and NaI, respectively, are considerably lower indicating the presence of another loss mechanism. Owing to the exceptionally low-energy position of the singlet F' level in NaI and NaBr, one could suspect that—different from other alkali halides—a bound triplet state of the F' center could exist in NaI and NaBr. This would give rise to an additional contribution to the loss factor α according to Eq. (3). A systematic search for such an F' triplet absorption was therefore started, and first indications for its existence and behavior in magnetic fields have been obtained.[14] A full discussion of the magnetic field effects on the $\tilde{F}^* \rightarrow F'$ tunneling will only be possible after a quantitative account on the F' triplet properties is available.

Beyond the physical properties discussed so far, our measurements supply information on two quantities important for the characterization of F centers in the two hosts investigated.

(a) The *spin-lattice relaxation time* T_1 of the F ground state was determined from the decay of the MCD signals [Fig. 6(b)] at various magnetic fields. Figure 9 shows the obtained T_1^{-1} values at 1.9 K as a function of the magnetic field in double logarithmic scale for NaBr and NaI. If the hyperfine mechanism is the dominant one in determining the spin-lattice relaxation we expect a dependence of the form[15]

$$T_1^{-1}=AH^3\coth\left[\frac{g\mu_B H}{2kT}\right] \tag{6}$$

(g is the Landé factor and μ_B is the Bohr magneton). The solid curves in Fig. 9 represent a plot of Eq. (6) with $A=1.5\times10^{-14}$ and 15×10^{-14} sec^{-1} G^{-3} for NaBr and NaI, respectively. These A values are of the same order of magnitude as the ones found for KI and KBr. A very good fit is obtained for NaBr over the whole observed magnetic field range, while

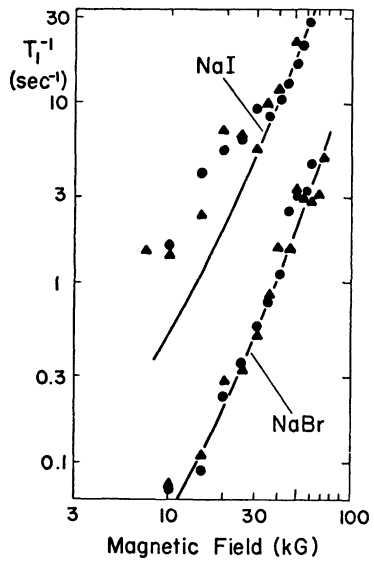

FIG. 9. Spin-lattice relaxation rate T_1^{-1} of F centers in NaBr and NaI at 1.9 K as a function of the magnetic field, measured in two different samples (circles and triangles). Curves represent fittings with Eq. (6).

the data for NaI fit well only above 30 kG. Obviously, some other mechanism with a weaker magnetic field dependence becomes operative in the lower field range for NaI.

(b) The *spin-orbit splitting* Δ of the F center can be obtained from the measured MCD signals as a function of wavelength (Fig. 5). By applying the method of moments one can evaluate the change of the first moment $\langle\Delta E\rangle$ of the shape function of the F band due to the magnetic field.[16] $\langle\Delta E\rangle$ is related to the magnetic field and to the temperatures as

$$\langle\Delta E\rangle_{\pm}=\pm(g_o\mu_B H+\tfrac{1}{3}\Delta P)$$
$$=\pm\left[g_o\mu_B H-\tfrac{1}{3}\Delta\tanh\frac{g\mu_B H}{2kT}\right], \tag{7}$$

where g_o is the orbital g factor. At the low temperature used ($T\leq4.2$ K), the first term is always less than 1% of the second, so that the experimental uncertainties did not allow the determination of g_o. From $\langle\Delta E\rangle$ values obtained at different fields (15–40 kG) and temperatures (1.5–4.2 K), we calculated values for the spin-orbit splitting Δ. The results are summarized in Table I and compared to values obtained in previous work.[17,18]

V. CONCLUSIONS

The observed reduction of the optical F-center conversion at low temperatures by magnetic fields has definitely confirmed the previous assignment[5] of

TABLE I. Measured values of the spin-orbit splitting Δ in meV for F centers in NaBr and NaI.

	This work	Previous work
NaBr	-40 ± 4	-28.2 ± 6 (Ref. 17)
NaI	-50 ± 4	-53.5 ± 1 (Ref. 18)

the reaction product to be an F' center with the two electrons in a singlet state. The fact that the F' band in NaI lies at higher energies than the F band remains a puzzle and a challenge to the theory to explain. The incompleteness of the magnetic field quenching of the $F \rightarrow F'$ process *cannot* be explained on the basis of spin-memory loss in the optical cycle, because the measured spin-mixing parameters ϵ are too small. To explain the difference, the existence of a bound F' triplet state is suspected, which is under present study. The measured magnetic field dependence of the F ground-state spin-lattice relaxation time shows the predominance of coupling through the hyperfine mechanism. The spin-orbit coupling constant of the F center, obtained from MCD measurements, is in agreement with earlier results.

ACKNOWLEDGMENTS

The authors are indebted to Dr. L.Bosi of the Politecnico di Milano for NaBr samples irradiated with γ rays and for stimulating discussions. U. M. Grassano is grateful to the Centro di Frascati for the hospitality during completion of this work. The work of F. Luty was supported by NSF Grant No. 81-05332.

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