†Paper based on a dissertation submitted by R. W. Dunham to the faculty of the Department of Physics and Astronomy, Rensselaer Polytechnic Institute, Troy, N. Y., in partial fulfillment of the requirements for a Ph. D. degree.

*Work supported in part by the National Aeronautics and Space Administration and in part by the National Science Foundation.

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PHYSICAL REVIEW B VOLUME 2, NUMBER 4 15 AUGUST 1970

Magnetic Circular Dichroism of the *F* Band in KF and Quenching of *F*-Center Spin Polarization by Optical Pumping*

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(Received 27 January 1970)

The magnetic circular dichroism (MCD) of the *F* absorption band in KF has been detected. The field and temperature dependence of the MCD signal yielded $g_{orb} \sim 1$ and $\Delta = -3.2 \pm 0.4$ meV for the orbital *g* factor and spin-orbit splitting of the excited state of the *F* center. The effect of unpolarized optical pumping on the MCD signal was investigated, with the result that at the maximum power level used ($\sim 10^{15}$ photons/sec) approximately 75% of the signal was quenched. The data have have been interpreted using a simple model involving a small (efficiency $\epsilon \sim 0.01$) spin-memory loss while the *F*-center electron is in the excited state. The fact that the spin polarization of the *F* center can be completely quenched if the pumping intensity is high enough is sufficient to explain the absence of a spin-dependent contribution to the magnetic circular polarization of the *F*-center emission observed by Fontana and Fitchen.

1. INTRODUCTION

Recently, the effect of a magnetic field on the emission of the *F* center in KF was successfully detected.[1] The effect, a small circular polarization of the emission, was independent of temperature and was assigned to orbital Zeeman mixing in the relaxed excited state. The absence of a contribution due to the spin polarization in the ground state of the *F* center was peculiar, since for all the alkali halides studied in absorption,[2] the paramagnetic contribution to the magnetic circular dichroism (MCD) was dominant for $T < 4.2$ °K. Also, in the case of KCl, the *F* electron has been shown[3,4] to preserve spin memory during an optical pumping cycle with an efficiency better than 95%. On the other hand, there is a small spin-memory loss during a pumping cycle, and the light levels used to excite the *F* luminescence in KF were sufficiently high ($> 2\times10^{15}$ photons/sec) to expect that any given *F* center would undergo many optical cycles in a time short compared with the spin-lattice relaxation time. In fact, Schmid and Zimmerman[3] have already shown qualitatively for the *F* center in KCl that optical pumping can destroy up to 95% of the EPR signal due to spin polarization of the ground state. This spin polarization can also be observed by monitoring the paramagnetic component of the MCD of the *F* absorption band to which it gives rise.[4]

We have used this latter method to study the effect of optical pumping with unpolarized light on the spin polarization of the ground state of the *F* center in KF.

Since data on the MCD of the *F* band in KF are not available in the literature, we first detected and determined the basic properties of the MCD of the F band in KF, such as temperature and field dependence, thus obtaining values for g_{orb} and for the spin-orbit splitting Δ in the unrelaxed excited state. The study of the effect of unpolarized optical pumping on the paramagnetic component of this MCD signal showed that at the light levels previously used to observe the magnetic circular polarization of the F-center emission in KF, [1] the ground-state spin polarization was almost completely quenched.

2. THEORY

An external magnetic field H_z induces a first moment change in the F absorption band given by[2]

$$\langle \Delta E \rangle_{\pm} = \pm (g_{orb}\beta H_z + \tfrac{2}{3}\Delta \langle S_z \rangle) \tag{1}$$

for left (+) and right (−) circularly polarized incident light, respectively. Δ is the spin-orbit splitting in the excited state, and the spin polarization $\langle S_z \rangle$ is given by

$$\langle S_z \rangle = -\tfrac{1}{2}\tanh(\beta H_z/kT) . \tag{2}$$

Since $\Delta < 0$ for the F center, the two contributions to $\langle \Delta E \rangle$ will have the same sign. On the other hand, it is possible to separate them since the spin-dependent contribution will build up with a time constant related to the spin-lattice relaxation time T_1 when the magnetic field is turned on. [2] Apart from the determination of Δ and g_{orb} for the F band of KF, in what follows, we shall be mainly concerned with the effect of optical pumping on $\langle S_z \rangle$, and, therefore, shall limit our considerations to the paramagnetic component of the MCD signal, which we shall denote by S. As we stated before, the time constant τ of the buildup of S when H_z is turned on is related to T_1. It is not equal to T_1 since the spin system is not in thermal equilibrium due to the small spin-memory loss during the pumping cycle caused by the monitoring light. In fact, the relationship between τ and T_1 is[3,5]

$$1/\tau = 1/T_1 + u\epsilon , \tag{3}$$

where u is the pumping rate and ϵ is the spin-flipping efficiency per pumping cycle. Therefore, only if $u\epsilon \ll 1/T_1$ will the buildup time constant be equal to T_1. The validity of Eq. (3) has been tested experimentally for KCl, [3] and in this paper for KF, yielding a measurement of ϵ, the spin-flipping efficiency in the excited state.

Once T_1 and ϵ have been determined, the effect of optical pumping on $\langle S_z \rangle$ can be predicted quantitatively. For pumping with unpolarized light, the rate equations of Mollenauer *et al.* [6] yield for the spin polarization of the ground state

$$\langle S_z \rangle_p = \frac{T_p/T_1}{1 + T_p/T_1} \langle S_z \rangle_0 , \tag{4}$$

where $\langle S_z \rangle_0$ is the thermal equilibrium value of the spin polarization, and $1/T_p = u\epsilon$. The relative spin depolarization due to optical pumping then is

$$\delta = (\langle S_z \rangle_0 - \langle S_z \rangle_p)/\langle S_z \rangle_0 = T_1\epsilon u/1 + T_1\epsilon u . \tag{5}$$

Equation (5) clearly indicates that, for the pumping rate u sufficiently high, the spin depolarization δ can be complete, resulting in the destruction of the paramagnetic component of the MCD signal.

3. EXPERIMENTAL

The MCD of the F band was detected with now conventional techniques. A diagram of the main components of the experimental setup is shown in Fig. 1. The details of the apparatus and of the measuring technique are described elsewhere. [7] The pumping light was furnished by the 2.84-eV line of a 200-W Hg lamp. Its intensity at the crystal site was measured with a calibrated photocell. The introduction of the total reflection prism and other optical surfaces in the light path reduced the light intensity by a factor of 2.

F centers were produced by x raying KF samples at 77 °K for typical concentrations of 5×10^{15} (F centers)/cm^3. The samples (~ $8\times8\times2$ mm^3) were situated in the bore of a small superconducting magnet in a liquid-helium immersion cryostat. The sample temperature could be varied from 4.2 to 1.3 °K with magnetic fields up to 25 kG. In the optical pumping experiment, a typical measurement consisted of recording the MCD signal at 2.95 eV as the pumping was started and then of following the signal decay until a new equilibrium value had been reached. The pump was then turned off and the signal recorded as it regained its original level. This operation was repeated at various temperatures and field intensities. From this set of measurements we can obtain directly the spin-lattice relaxation time T_1, the spin-memory loss efficiency per optical cycle ϵ, and the spin depolarization δ. Although the precision of the data is fairly good (~ 10%), the accuracy of the value of ϵ is poor, since it depends on the precise knowledge of the pumping rate, the measurement of which in turn depends on the calibration of the pumping source, the F-center concentration, and various geometrical factors. Therefore, the value for ϵ reported below is intended to have only order-of-magnitude significance.

4. RESULTS

The first set of measurements consisted of the detection of MCD in the F band of KF and of its study as a function of temperature and field. In Fig. 2, we show a typical dichroism spectrum obtained with a field $H_z = 15$ kG and at a tempera-

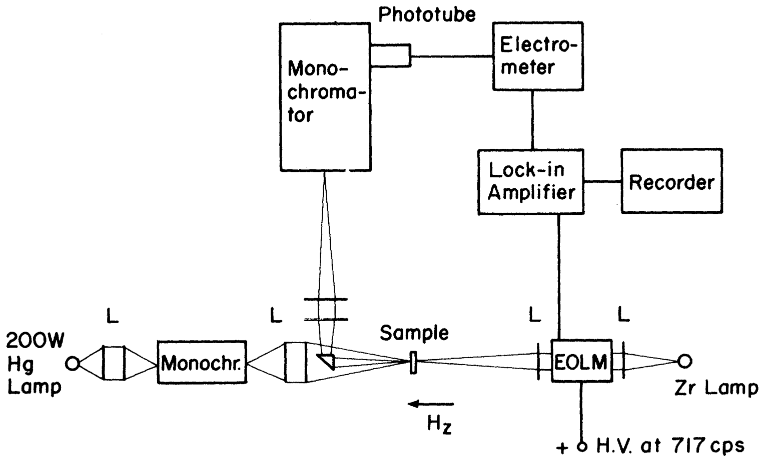

FIG. 1. Schematic diagram of the experimental apparatus and optical pumping geometry.

ture of $T = 1.3$ °K. The data were analyzed with the method of moments.[2] The zero-moment change of the F band was found to be negligibly small (< 0.01%). The temperature and field dependence of the magnetic-field-induced first moment change are shown in Figs. 3(a) and 3(b), respectively. In both cases, note the deviation from linearity indicative of the saturation of the paramagnetic term. A fit of (1) to the data yields the following values for g_{orb} and Δ:

$$g_{orb} \sim 1,$$
$$\Delta = -3.2 \pm 0.4 \text{ meV}. \qquad (6)$$

In the second set of measurements, the effect of optical pumping on the MCD signal at 2.95 eV was studied. When the optical pump was turned on, the MCD signal was found to decrease to a new equilibrium value with a characteristic time τ. $1/\tau$ was found to increase linearly with the pumping rate u. A plot of $1/\tau$ versus u yields the following values for T_1 and ϵ for a magnetic field of 13 kG and a temperature of 1.3 °K:

$$T_1 = 90 \pm 15 \text{ sec},$$
$$\epsilon \sim 0.01. \qquad (7)$$

The value of T_1 thus determined was the same,

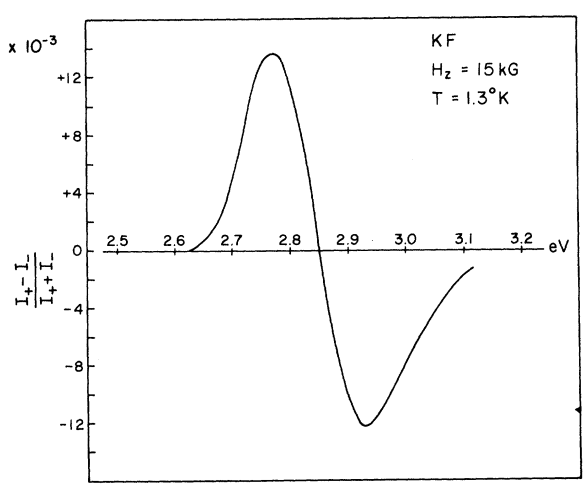

FIG. 2. A typical dichroism signal obtained for a field of 15 kG and a temperature of 1.3 °K.

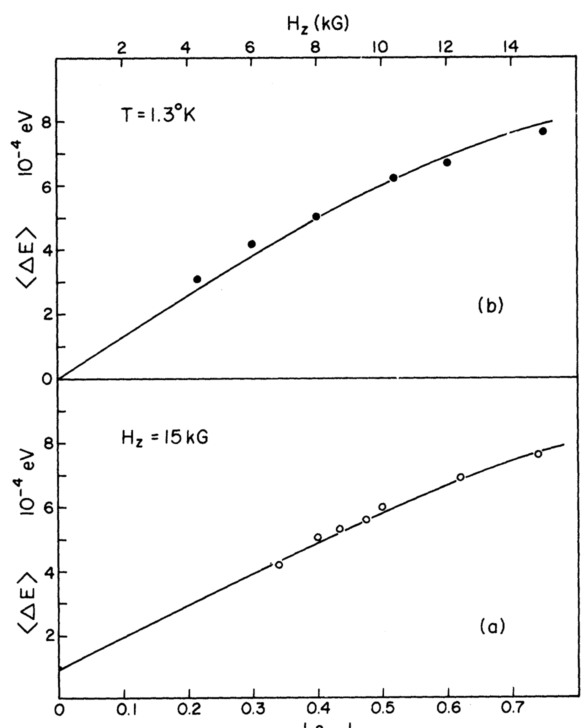

FIG. 3. Temperature (a) and field (b) dependence of the field-induced first moment change of the F band. The solid lines represent Eq. (1) with $g_{orb} = 1$ and $\Delta = 3.2$ meV.

within experimental accuracy, as that measured directly from the buildup of S when the magnetic field is suddenly turned on. The paramagnetic signal attenuation as a function of relative pumping intensity is shown in Fig. 4. The minimum pumping intensity used (3.3×10^{13} photons/sec, corresponding to a pumping rate of ~ 0.08 sec^{-1}) is arbitrarily given the value of 0 dB. At the maximum pumping intensity, S is ~ 75% quenched. Since for the emission experiment[1] the light intensity is ~ 3 times larger, we can see that (see vertical dash line in Fig. 4) at that power level the spin polarization is almost completely destroyed.

5. DISCUSSION

The model for the effect of optical pumping on $\langle S_z \rangle$ which was discussed in Sec. 2 can now be tested quantitatively. This model leads to Eq. (5), which involves the pumping rate u, the spin-memory loss efficiency ϵ, and the spin-lattice relaxation time T_1. All these quantities have been determined independently. Substituting their values in Eq. (5), we should be able to predict the behavior of the relative attenuation δ as a function of u without need of any fitting or normalization. The solid line of Fig. 4 represents the prediction of Eq. (5), and it is seen to be in excellent agreement with the data. The quantitative confirmation of the model for spin depolarization by optical pumping is sufficient to explain the absence of a

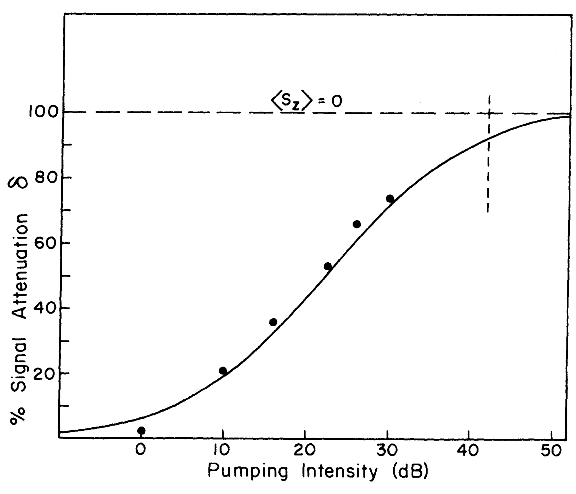

FIG. 4. Relative attenuation of the paramagnetic component of MCD signal as a function of pumping intensity. The filled circles are the experimental points, and the solid line plots the prediction of Eq. (5) with $T_1 = 90$ sec and $\epsilon = 0.01$. The short vertical dash line represents the pumping rate corresponding to the intensity of the light used to excite the F-center luminescence in Ref. 1.

paramagnetic contribution to the magnetic circular polarization of the F-center emission in KF.[1] It also implies that such a paramagnetic contribution should be observed if the effect of spin flipping due to optical pumping can be partially neutralized by using circularly polarized light for the excitation of F-center luminescence. Panepucci and Mollenauer[6] have already shown that under circularly polarized optical pumping the ground-state spin polarization tends towards an optical saturation value

$$\langle S_z \rangle_p^{\text{sat}} = \frac{1}{2} \frac{u^- - u^+}{u^- + u^+}, \tag{8}$$

where $u_+(\lambda)$ and $u_-(\lambda)$ are the transition probabilities for the absorption of, say, left circularly polarized light of wavelength λ by the $+\frac{1}{2}$ and $-\frac{1}{2}$ levels of the Kramers ground-state doublet, respectively. Therefore, the use of circularly polarized pumping allows the use of the high excitation intensities necessary to detect the magnetic circular polarization of the F-center emission, without completely quenching an eventual spin contribution. Use of circularly polarized excitation is nevertheless only a necessary condition to observe such a contribution. Clearly, its size will be proportional to the spin-orbit splitting in the relaxed excited state Δ^*. In the case of KF, Δ^* is expected to be approximately one order of magnitude smaller than Δ, because the measured value $g^*_{\text{orb}} = 0.04$ for the relaxed excited state indicates a strong angular momentum quenching.[1] Since $\Delta = -3.2$ meV, then we expect that Δ^* will be no larger than approximately 0.3 meV. Therefore, we may expect that the detection of the spin-dependent contribution to the magnetic circular polarization will be difficult in KF due to the small expected size of Δ^*. We are currently improving our apparatus in order to detect this spin-dependent contribution to the magnetic circular polarization of the F-center emission in KF as well as in other alkali halides. Its successful detection would be very interesting, because it would yield the first direct measurement of the spin-orbit coupling in the relaxed excited state of the F center.

6. CONCLUSION

We have detected the MCD of the F band in KF, and from the field and temperature dependence of the signal have determined values for the spin-orbit splitting Δ and g_{orb} for the unrelaxed excited state. By studying the effect of optical pumping on the buildup time of the paramagnetic component of the MCD signal, we have determined the spin-memory loss probability for one optical pumping cycle. Finally, the attenuation of the MCD signal due to optical pumping was studied and found to be in good agreement with the predictions of a simple model based upon the small, but non-negligible, loss of spin memory during an optical cycle. This latter result shows that, in general, excitation with circularly polarized light is a necessary, although not sufficient, condition to observe the spin-dependent contribution to the MCD signal in emission.

ACKNOWLEDGMENT

The author wishes to thank Professor D. B. Fitchen for many interesting and informative discussions.

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*Work supported by the Advanced Research Projects Agency through the Materials Science Center at Cornell University, MSC Report No. 1301.

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PHYSICAL REVIEW B VOLUME 2, NUMBER 4 15 AUGUST 1970

M Centers in MgF_2 Crystals†

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(Received 9 March 1970)

A study of the optical absorption and emission of the $M(C_{2h})$ center in MgF_2 has been made. It is shown that excitation of the 370-nm absorption band due to these centers gives rise to polarized emission bands at 420 and 861 nm. Narrow-line transitions are observed both on the low-energy side of the 370-nm absorption band and the high-energy side of the 420-nm emission band. These lines have almost a mirror symmetry about the zero-phonon line which occurs at 387.3 nm and are attributed to transitions involving the lattice vibration modes of the crystal.

INTRODUCTION

In the cassiterite structure of MgF_2, there are four different *M*-center configurations each with its own symmetry. In this paper, we will differentiate between these configurations by designating the symmetry of the center in parentheses immediately after the *M* notation, i.e., $M(C_{2v})$, $M(D_{2h})$, $M(C_{2h})$, and $M(C_1)$. Figure 1 illustrates the location of these various centers in the MgF_2 lattice. Little work has been done on either $M(C_{2v})$ or $M(D_{2h})$ centers,[1] but it has been established[1–3] that $M(C_{2h})$ centers absorb light of 370 nm (3.35 eV) and emit light of 420 nm (2.96 eV). The absorption band due to these centers also shows fine structure on the low-energy side that has been attributed to transitions associated with lattice phonons. The $M(C_1)$ center absorbs light of 400 nm (3.10 eV) and has an emission peak at 600 nm

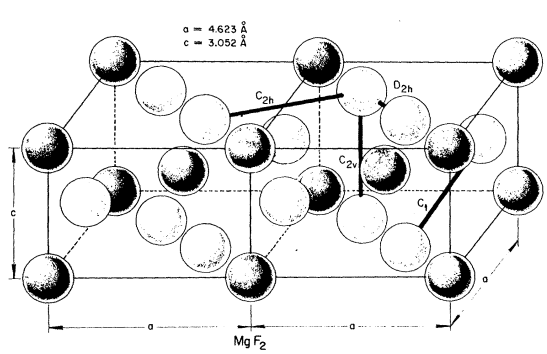

FIG. 1. MgF_2 lattice. The four possible *M*-center configurations are shown by the solid lines.