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Magneto-Optical Properties of F_2^+ Center in KCl:SH$^-$

By

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The magnetic circular dichroism (MCD) of F_2^+ centers in KCl:SH$^-$ has been measured in absorption in the $1s\sigma_g \rightarrow 2p_y\pi_u$ transitions at 493 and 509 nm, with fields up to 5 T and in the temperature range 1.5 K $< T <$ 77 K. Within the limit of detection, no MCD is observed in the near infrared transition $1s\sigma_g \rightarrow 2p\sigma_u$ as well as in both emissions $2p\pi_u \rightarrow 1s\sigma_g$ and $2p\sigma_u \rightarrow 1s\sigma_g$. The optical detection of EPR in the F_2^+ ground state presents an isotropic single band with $g = 1.965 \pm 0.007$. The spin–lattice relaxation measured at $H = 0.32$ T is typical of a direct process $T^{-1} = 4.3 \times 10^{-2}$ coth $(g\mu_B H/2k_B T)$. The spectral variation of the MCD is calculated using perturbation theory to first order. The Hamiltonian includes the spin–orbit interaction in the $2p\pi_u$ excited state and the orbital molecular wave functions are obtained by a linear combination of 1s and 2p atomic orbitals. The calculated MCD is in good agreement with the observed one, for the spin–orbit interaction strength $\pounds_z = 3.6$ meV.

Le dichroisme circulaire magnétique (DCM) des centres F_2^+ a été mesuré en absorption dans KCl:SH$^-$ pour les transitions $1s\sigma_g \rightarrow 2p_y\pi_u$ localisées à 493 et 509 nm. Le champ magnétique extérieur a été varié de 0 à 5 T et le domaine de température étudié de 1,5 à 77 K. Aucun DCM n'a été observé dans les limites de détection pour la transition proche infrarouge $1s\sigma_g \rightarrow 2p\sigma_u$ ainsi que pour les deux émissions $2p\pi_u \rightarrow 1s\sigma_g$ et $2p\sigma_u \rightarrow 1s\sigma_g$. La détection optique de la résonance paramagnétique électronique (DORPE) étudiée pour l'état fondamental des centres F_2^+ présente une seule bande de résonance isotrope avec une valeur de $g = 1,965 \pm 0,007$. La relaxation spin–réseau mesurée sous champ $H = 0,32$ T est typique d'un processus de relaxation direct caractérisé par $T_1^{-1} = 4,3 \times 10^{-2}$ coth $(g\mu_B H/2k_B T)$. La variation spectrale du DCM a été calculée utilisant la théorie de perturbation au premier ordre. L'Hamiltonien inclut une interaction spin–orbite $\pounds_z$ pour les états $2p\pi_u$ et les functions d'onde des orbitales moléculaires ont été obtenues comme combinaison linéaire des orbitales atomiques 1s et 2p. Un bon accord entre la théorie et l'expérience est obtenu pour $\pounds_z = 3,6$ meV.

1. Introduction

The F_2^+ center in alkali halide crystals is a defect consisting of an electron bound to the double well potential created by two [110] nearestneighbor anion vacancies. Its formation kinetics and optical properties in absorption and emission have been studied in detail in KCl crystals by Aegerter and Lüty [1 to 3]. They showed in particular that the energy position and the oscillator strength of the absorption bands can be described by the simple model of the H_2^+ molecular ion embedded in a dielectric matrix [1]. Fig. 1 shows schematically the six possible orientations of the defect in a KCl crystal and their allowed optical transitions (x, y, z). Fig. 2 shows a comparison of the main optical transitions with
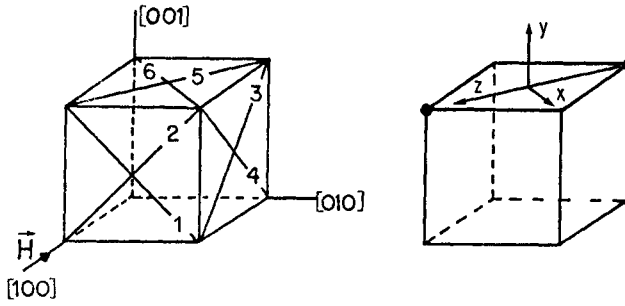
Fig. 1. The six possible orientations of the F_2^+ center in a KCl matrix and their allowed optical dipole transitions (x, y, z)

their polarization properties as observed in KCl and the H_2^+ model best fit obtained from the relation

$$E_{H_2^+}(R) = \varepsilon_0^2 E_{F_2^+}\left(\frac{r_{AB}}{\varepsilon_0}\right),$$ (1)

where $\varepsilon_0 = 2.33$ is the dielectric constant of the medium (2.19 for KCl) and $r_{AB} = 0.396$ nm is the separation of the double well potential (0.444 nm for the anion–anion KCl lattice), and $R = 0.17$ nm is the H_2^+ separation in free space (from [1]).
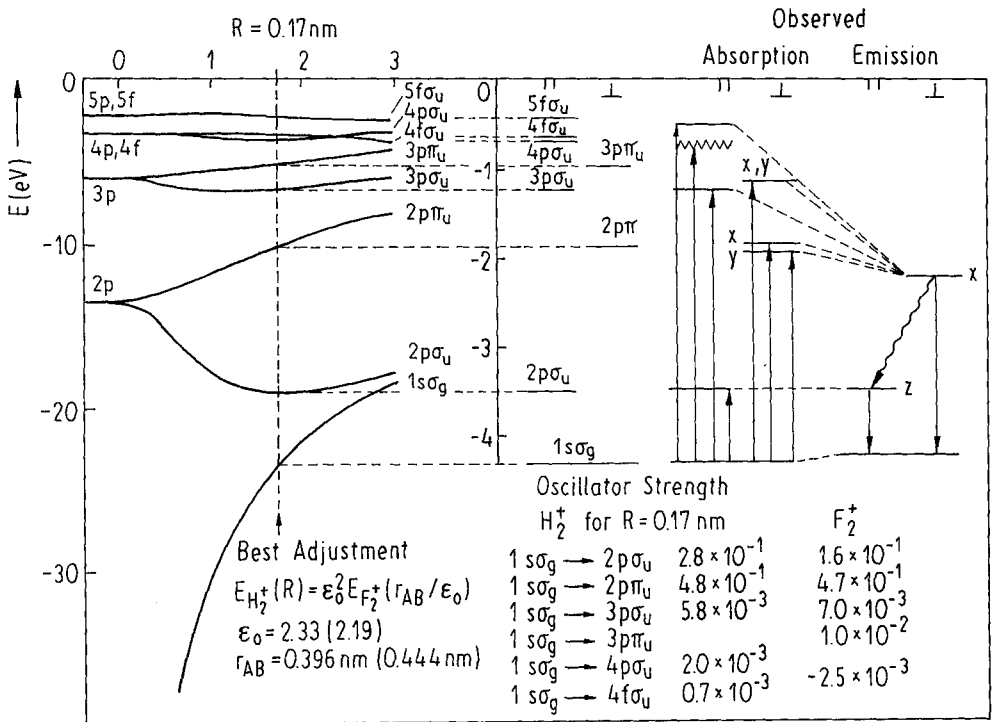

Fig. 2. Comparison of the energy scheme and oscillator strength of the experimentally observed polarized F_2^+ center transitions ($\|(z)$ and $\perp(x, y)$) and those determined by best fitting the H_2^+ model (from Aegerter and Lüty [1]). The labeling of the states is the united atom notation

F_2^+ centers were initially produced in additively colored crystals by direct photoionization of the neutral aggregate F_2 centers, via optical excitation in the so-called L_{F_2} bands. The free electrons captured by existing F and F_2 centers lead to the formation of F$^-$ and F_2^- centers [2]. The introduction of extra electron traps with higher electron capture cross-section and better thermal stability leads obviously to an increase of the amount of F_2^+ centers without changing the spectral dependence of the production process. Such traps can be introduced by X-irradiation of the crystal at liquid helium temperature as intrinsic anion vacancies of unassociated Frenkel pairs ($\boxminus$ + Cl_{int}^-) or as H centers forming Cl_{int}^-, [1]. On the other hand, extrinsic Frenkel pairs such as H$^-$ interstitials and anion vacancies can be formed by UV radiation of hydrogen doped crystals [1]. With these techniques of preparation, F_2^+ centers are always accompanied by other defects such as F, F_2, hole-type defects or interstitials which have usually absorption bands overlapping the F_2^+ transitions. Some of these defects exhibit large magneto-optical effects which prohibit any magneto-optical studies of the F_2^+ centers.

A decade ago, Gellerman et al. [4, 5] developed a new way to produce very stable electron traps which allows to obtains a F_2^+ center system with complete elimination of perturbing and unwanted optical transitions of other defects in the wavelength range of interest. The technique was successfully used for KCl crystal doped with OH$^-$ and SH$^-$. The F_2^+ center creation process is basically similar to the earlier processes but the nature of the electron traps is different. Electron or X-irradiation decomposes these substitutional OH$^-$ or SH$^-$ molecules in chalcogenide entities such as O$^-$, O_2^-, S$^-$, S_2^-, etc. which occupy mainly substitutional sites, and hydrogen-type interstitial defects such as H_2 molecules (optically inactive) and H$^-$ substitutional defects. The creation of S_2^- or O_2^- defects is accompanied by the simultaneous creation of anionic vacancies. These vacancies and especially the singly charged chalcogenide defects S$^-$ or O$^-$ are very good electron traps and can be created with a high concentration. The formation of F_2^+ centers is made at relatively high temperature ($-40\,°C$) by F light irradiation. During this process the F centers are ionized and their electrons are immediately trapped preferentially at the S$^-$ or O$^-$ defects as stable entities S$^-$ or O$^-$; at this temperature the anion vacancies migrate and aggregate to existing F centers forming F_2^+ centers.

This technique has been used to prepare F_2^+ centers for a study of the magneto-optical properties of F_2^+ in KCl:SH$^-$ crystals. In this paper we present the results of the magnetic circular dichroism measured in absorption in the $1s\sigma_g \rightarrow 2p\sigma_u$ and $1s\sigma_g \rightarrow 2p\pi_u$ transitions and in emission in the $2p\pi_u \rightarrow 1s\sigma_g$ transition, and of the optical detection of the electron paramagnetic resonance (ODEPR) and spin–lattice relaxation time T_1 of the F_2^+ center ground state ($1s\sigma_g$). A theoretical model is finally developed and is shown to be in good agreement with the experimental data.

2. Preparation of the Samples

KCl:SH$^-$ single crystals have been grown at the University of Utah (USA) by the Czochralsky method in a 0.45 Pa H_2S atmosphere. Samples cleaved into small platelets $10 \times 10 \times 2$ mm^3 were submitted in a specially designed cryostat to a 2 h X-ray irradiation on both faces at $(-40 \pm 2)\,°C$, (Phillips Müller model 150 equipped with a tungsten anode, 1 mm Al filter, working at 90 kV, 20 mA), creating a high concentration of F centers (absorption constant $\alpha \approx 250$ cm^{-1} measured at $T = 77$ K). After transferring the crystal into an optical cryostat (without intermediate treatment) a high concentration of "pure"

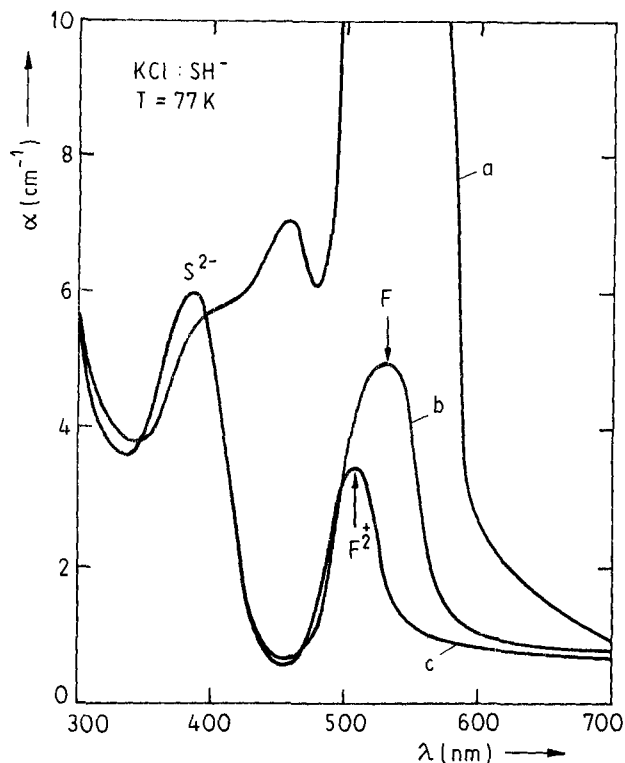D. A. Donatti, M. A. Aegerter, and T. Iida

Fig. 3. Absorption spectra measured at $T = 77$ K of KCl:SH$^-$ after the following treatments — (a) X-irradiation (90 kV, 20 mA, Mo + 1 mm Al) at -40 °C during 4 h, (b) after subsequent white light irradiation at -40 °C during 30 min, (c) after subsequent white light irradiation at -40 °C during 15 min. The $1s\sigma_g \rightarrow 2p\pi_u$ transition of F_2^+ centers appears completely free of other transitions

F_2^+ centers was achieved by illuminating the sample at the same temperature, with white light from a 100 W halogen lamp (slide projector) filtered by a Schott KG 3-2 mm filter in order to eliminate the infrared heat radiation. In order to obtain a homogeneous concentration of F_2^+ centers, the light irradiation was done on both faces for equal periods of time; the illumination system was also constantly rotated around its axis in order to eliminate any birefringence effect which would create preferentially oriented F_2^+ centers. The duration of illumination depends on the amount of light received by the sample, the temperature of the crystal, and the initial concentration of F centers; it is typically of the order of 45 to 60 min.

Fig. 3 shows the change of the optical absorption measured in the visible range after various treatments. We see in particular that the high F center band disappears completely at the profit of a pure F_2^+ system (transition $1s\sigma_g \rightarrow 2p\pi_u$) and other bands which are well separated. The F_2^+ centers are stable in the dark till -50 °C, but are rapidly destroyed if the crystals are heated to around 0 °C. At this temperature we observe the appearance of a small F band, a small decrease of the S^{2-} band, and the presence of a new band of unknown origin at $\lambda = 1.1$ μm having a half-width $\Delta\lambda \approx 0.3$ μm and which is thermally stable up to 50 °C. Under light irradiation, the F_2^+ centers are totally destroyed for $T > 120$ K; during this process no other defects can be detected optically and we assume

that the light dissociates the F_2^+ into two anion vacancies (with absorption in the UV region), and one electron which is probably trapped at a S$^-$ site.

F_2^+ centers prepared with this technique occupy equally all the $\langle 110 \rangle$ possible directions. However, they can easily be aligned along particular directions down to 1.5 K by a proper linear polarized excitation in their 2pπ levels, as already observed by Aegerter and Luty [2] and Schneider [6]. The reorientation efficiency increases with the temperature. The linear dichroism is stable in the dark up to 240 K.

3. Experimental

The measurements of the magnetic circular dichroism have been made using the arrangement scheme shown in Fig. 4. The light (Oriel light source model 7340, 100 W) passed through
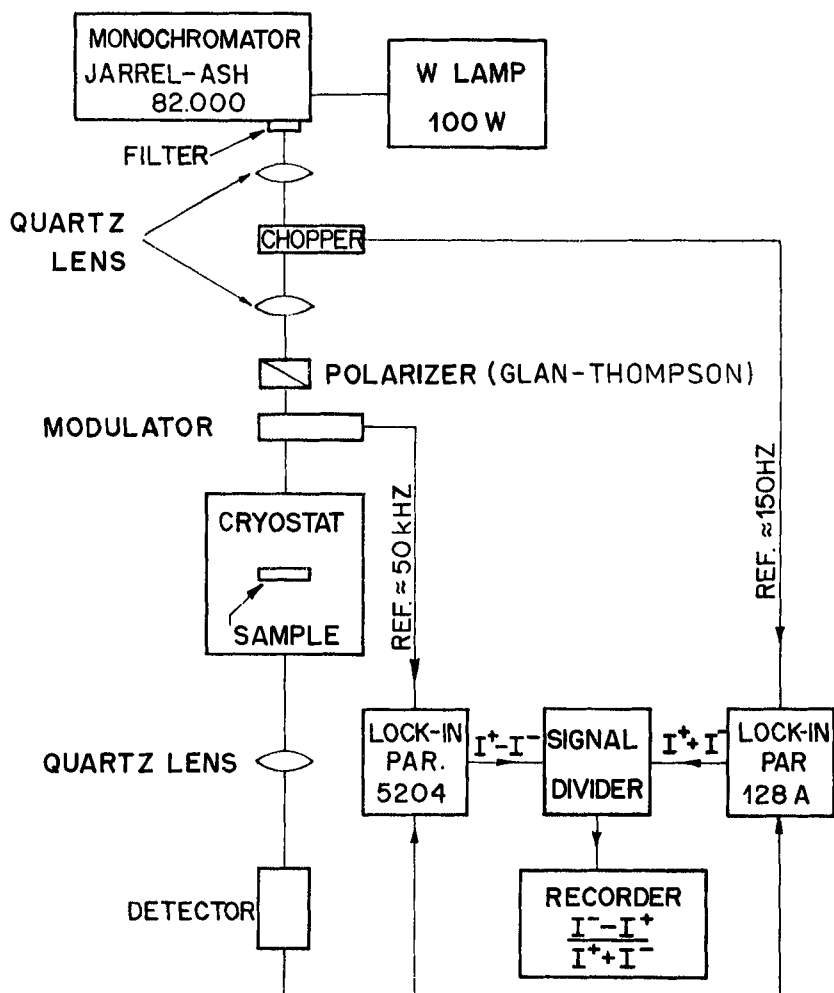
Fig. 4. Scheme of the experimental arrangement used for measuring the magnetic circular dichroism in absorption (see text)

a 50 cm Jarrel-Ash Model 82000 monochromator having a dispersion of 1.6 nm/mm in the visible and 3.2 nm/mm in the infrared region. Before reaching the sample its intensity is first modulated at frequency $v_1 = 150$ Hz by a PAR chopper Model 192 and then by a light modulator at frequency $v_2 = 50$ kHz (Morvue Model PEM-3) in order to obtain the σ^+ and σ^- polarizations. The intensity reaching the detector (EMI 9558 QA photomultiplier for the visible region or Judson Model J16D germanium cell for the near infrared) is the sum of the intensity transmitted through the crystal

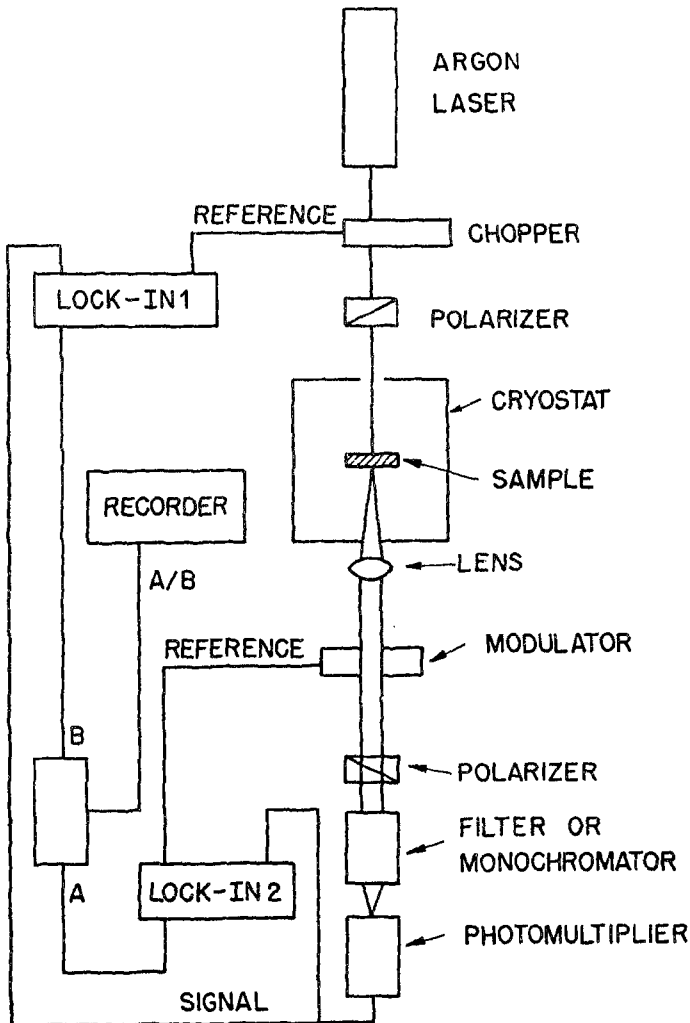$$I^+(t) + I^-(t) = f(t)\,(I^+ - I^-)\,(1 + \sin 2\pi v_2 t)\,,$$ (2)

Fig. 5. Scheme of the experimental arrangement used for measuring the magnetic circular dichroism in emission (see text)

where the first factor $f(t)\,(I^+ - I^-)$, corresponds to the ac value of the intensity modulated by the chopper at frequency v_1 and the last one corresponds to the ac value of the intensity modulated at the frequency v_2. By using two lock-in synchronized at the frequency v_1 and v_2, respectively, it is possible to separate both signals. As $f(t)$ is practically a square wave function, the values of the signals are given by

$$f(t)\,(I^+ - I^-)\sin(2\pi v_2 t) = \left(\frac{\sqrt{2}}{8}\right)(I^+ - I^-),$$

$$f(t)\,(I^+ + I^-) = \left(\frac{\sqrt{2}}{\pi}\right)(I^+ - I^-). \tag{3}$$

The ratio of these two values gives the signal effectively recorded (SER)

$$\text{SER} = \left(\frac{(I^+ - I^-)\sin(2\pi v_2 t)}{I^+ + I^-}\right) = \frac{\pi}{8}\left(\frac{I^+ - I^-}{I^+ + I^-}\right) = \frac{\pi}{8}\,S, \tag{4}$$

where S is taken as the measure of the MCD in absorption

$$S = \frac{8}{\pi}\,(\text{SER}). \tag{5}$$

A test made by introducing at the place of the crystal a component composed of a $\lambda/4$ plate (B. Halle) followed by a Glan-Thompson linear polarizer (B. Halle) gives a value $S = 0.993$ showing that the whole optical system has a good optical quality.

For the measurements of the MCD in emission we used basically the same set-up and optical components arranged according to Fig. 5. A normalization test using a circular polarizer placed before the photoelastic modulator gives a value $S = 0.993$. In both experiments the samples were placed in a superconducting magnet cryostat (Oxford Instrument Model Spectromag 4), giving a maximum field of 5 T with a homogeneity of 1 in 10000 in a 1 cm sphere, and allowed temperature variation between 1.2 (pumped helium) and 300 K. The sample temperature was monitored by a calibrated thermistor (Lake Shore Model GRG-1-1000).

All the conventional absorption measurements were done using a home-made double-beam spectrometer built around the large tail of the Spectromag cryostat.

EPR measurements have been performed by optical detection (ODEPR), monitoring the MCD during the application of microwave power. The sample holder has been replaced by an X-band wave guide to which is attached a small cavity operating in the TE101 mode with a Q value of 2200 at liquid helium temperature. Two small 3×3 mm^2 apertures have been made on the large side of the cavity for optical access.

Measurements of the spin–lattice relaxation in the $1s\sigma_g$ ground state of the F_2^+ center have been obtained by monitoring at resonance the variation of the MCD induced by periodical modulation of the microwave power by a pin modulator (HP-8735b) at frequencies varying between 10^{-3} and 10^5 Hz. The signal $(I^+ - I^-)$ was measured directly by a lock-in or a PAR-Model 4202 signal averager.

4. The F_2^+ Model

As shown by Aegerter and Lüty [1], the simple model of the H_2^+ molecular ion immersed in a dielectric medium, originally proposed by Herman et al. [7], is in excellent agreement with the optical properties of the F_2^+ center in alkali halides.

The ground state and the first excited states are identified as linear combination of 1s and 2p-type hydrogenic atomic orbital states located at the site of the two vacancies. They are labeled $1s\sigma_g$ (ground state), $2p\sigma_u$ and $2p\pi_u$ (first excited states). In KCl crystals, the F_2^+ center belongs to the D_{2h} group. Let us denote the wave functions of $1s\sigma_g$ state by $|g\rangle$, $2p\sigma_u$ state by $|z\rangle$, and $2p\pi_u$ state by $|x\rangle$ and $|y\rangle$, which have the same symmetries as the irreducible representations Γ_1^+, Γ_3^-, Γ_2^-, and Γ_4^- of the group D_{2h}, respectively. Here x, y, and z axes are taken as shown in Fig. 1.

The linear polarized absorptions due to the transitions from the ground state $|g\rangle$ to the excited states $|z\rangle$, $|x\rangle$, and $|y\rangle$ have been observed [1]; the peak positions of the absorption bands are 1.4 μm (0.886 eV) for the transition $|g\rangle$ to $|z\rangle$, 509 nm (2.435 eV) for $|g\rangle$ to $|y\rangle$, and 493 nm (2.515 eV) for $|g\rangle$ to $|x\rangle$.

In order to calculate the magnetic circular dichroism (MCD), we take into account the spin–orbit interaction, written in the form

$$H_{so} = \sum_{i=x,y,z} \hat{L}_i \hat{s}_i , \tag{6}$$

$\hat{L}_i$ being a tensor operator which belongs to the same irreducible representation as the i-th component of the angular momentum and $\hat{s}_i$ the spin operator. To the first order of the spin–orbit interaction, the wave functions for the excited states are given as follows:

$$\psi(x, \pm) = \left\{ |x\rangle \pm i\frac{\pounds_z}{2D} |y\rangle \right\} |\pm\rangle ,$$

$$\psi(y, \pm) = \left\{ |y\rangle \pm i\frac{\pounds_z}{2D} |x\rangle \right\} |\pm\rangle , \tag{7}$$

$$\psi(z, \pm) = |z\rangle |\pm\rangle ,$$

where $\pounds_z$ is the matrix element of the tensor operator $\hat{L}_z$ with respect to the excited states, i.e., $i\pounds_z = \langle y| \hat{L}_z |x\rangle$, $|\pm\rangle$ are the spin up and down states and $D = 80$ meV is the energy separation between $|x\rangle$ and $|y\rangle$ states. Here we have assumed that the spin–orbit interaction is sufficiently small compared with the energy separation between $|z\rangle$ and $|y\rangle$ states, $D' = 1.55$ eV, to ignore the admixture of $|z\rangle$ and $|x\rangle$ or $|y\rangle$. Actually $\pounds_z$ will be estimated to be 3.6 meV which is much smaller than D'.

We consider the transitions from the ground states $\psi(g, \pm) = |g\rangle |\pm\rangle$ to the excited states given by (7) via the interaction with the circularly polarized light propagating along the axis parallel to the applied magnetic field. In the presence of the magnetic field, the wave functions (7) are modified by the Zeeman interaction. This effect, however, can be ignored, since we confine our attention to the paramagnetic part of the MCD. For the centers aligned along the directions $\{1, 2\}$, the light propagation is parallel to the $\hat{y}$ direction, and the electric dipole operators can be written as

$$\hat{\sigma}^\pm = \frac{1}{\sqrt{2}} (\hat{d}_z \pm i\hat{d}_x) , \tag{8}$$

where $\pm$ refers to the right (σ^+) and the left (σ^-) circular polarizations, respectively. Using (2) and (3), the probabilities of the transitions from the ground state to the excited states can be calculated easily. The result shows that

$$P_i^+(\sigma^+) - P_i^+(\sigma^-) = 0 ; \qquad P_i^-(\sigma^+) - P_i^-(\sigma^-) = 0 ; \qquad i = x, y, z , \tag{9}$$

where $P_i^\pm(\sigma^\pm)$ are the probabilities of the transitions from $\psi(g, \pm)$ to the excited states $\psi(i, \pm)$ for the $\sigma^\pm$ polarized light. Therefore the centers aligned along the directions $\{1, 2\}$ yield no MCD signal in absorption.

For the centers aligned along the directions $\{3, 4, 5, 6\}$, the light propagation is parallel to the $(\hat{x} + \hat{z})$ direction and the electric dipole operators are written as

$$\hat{\sigma}^\pm = \left(\frac{\hat{d}_x - \hat{d}_z}{2} \pm i \frac{\hat{d}_y}{\sqrt{2}} \right). \tag{10}$$

Calculating the transition probabilities within the first order of $£_z/D$, we have

$$P_x^\pm(\sigma^+) - P_x^\pm(\sigma^-) = \pm \frac{£_z}{\sqrt{2}\,D} d_x d_y ,$$

$$P_y^\pm(\sigma^+) - P_y^\pm(\sigma^-) = \pm \frac{£_z}{\sqrt{2}\,D} d_x d_y ,$$

$$P_z^\pm(\sigma^+) - P_z^\pm(\sigma^-) = 0 , \tag{11}$$

where $d_i = \langle i | \hat{d}_i | g \rangle$ is supposed to be real.

Now, we introduce the absorption spectra normalized by the dipole-transition probability for the transitions to the states $\psi(x, \pm)$ and $\psi(y, \pm)$. Within the rigid-shift approximation, they are written as $f_i(E - E_i - \delta E_i^\pm) = F_i(E - E_i - \delta E_i^\pm)/d_i^2$, where i is x, y, $F_i(E - E_i)$ is the absorption spectrum in the absence of the magnetic field and $\delta E_i^\pm$ stands for the rigid shift due to magnetic field effects.

Taking into account the thermal distribution of spins in the ground state, $N^\pm$, and using the approximation $F_i(E - E_i - \delta E_i^\pm) \approx F_i(E - E_i)$ the MCD spectra, for the transition $1s\sigma_g \to 2p\pi_u$, is obtained from (11) as follows:

$$S_{MCD}(E) = \{N^+(P_x^+(\sigma^+) - P_x^+(\sigma^-)) + N^-(P_x^-(\sigma^+) - P_x^-(\sigma^-))\} f_x(E - E_x)$$

$$+ \{N^+(P_y^+(\sigma^+) - P_y^+(\sigma^-)) + N^-(P_y^-(\sigma^+) - P_y^-(\sigma^-))\} f_y(E - E_y)$$

$$= (N^- - N^+) \frac{£_z}{\sqrt{2}\,D} d_x d_y \{f_y(E - E_y) - f_x(E - E_x)\} \tag{12}$$

with

$$(N^- - N^+) = \tanh\left(\frac{g\mu_B H}{2k_B T}\right), \tag{13}$$

where g is the g-value in the ground state observed with the magnetic field making an angle of $45°$ with the principal axis of the defects (g_{45}). On the other hand, from (11), we have

$$S_{MCD}(E) = 0 \tag{14}$$

for the transition $1s\sigma_g \to 2p\sigma_u$.

In summary, the calculation shows that:

(i)   the MCD can be observed only for the transitions $1s\sigma_g \to 2p\pi_u$;

(ii)   when the light and the magnetic field are along the $\langle 100 \rangle$ directions, only centers aligned along the directions $\{3, 4, 5, \text{and } 6\}$ contribute to the MCD;

(iii)   alignment of the centers does not change the first moment of the MCD but only its intensity.

5. Experimental Results

The MCD equipment was first tested with a KCl pure single crystal containing F centers. The MCD spectrum measured at liquid helium temperature is shown in Fig. 6 and presents good agreement with the literature [8].

Fig. 7 shows the MCD and the absorption spectra in the visible region of a $KCl:SH^-$ sample containing a system of unaligned F_2^+ centers and a very small amount of F centers
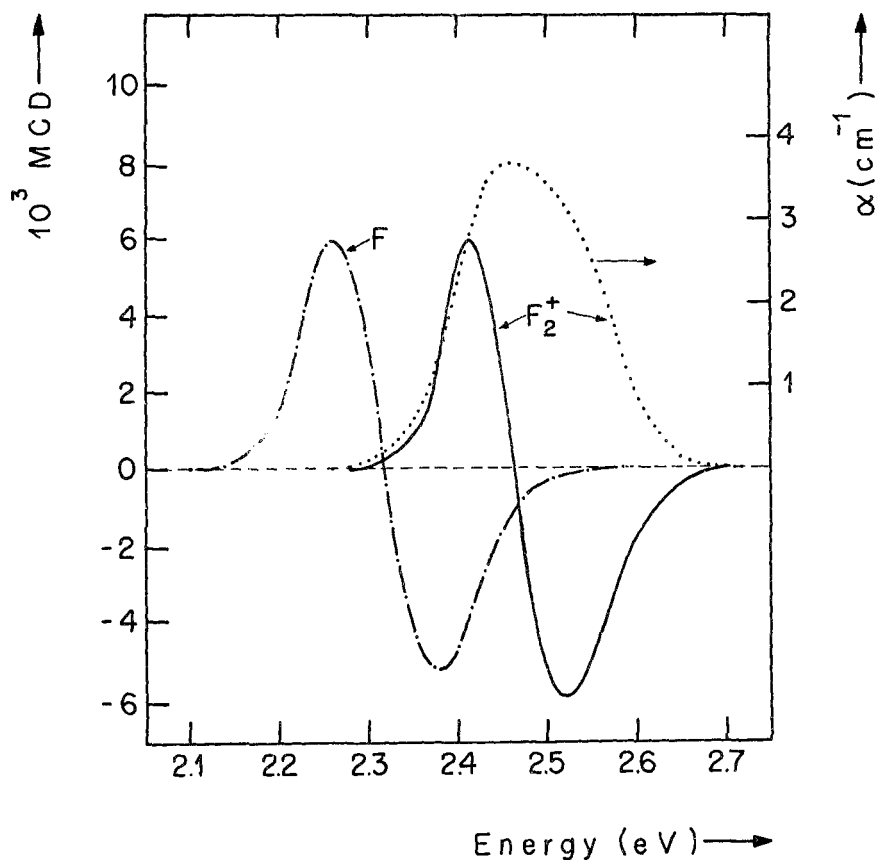

Fig. 6. Magnetic circular dichroism spectrum of F centers in pure KCl ($\alpha = 4.12\,\text{cm}^{-1}$) observed at 4.2 K and 0.983 T ($- \cdot - \cdot -$), and absorption ($\cdots\cdots$) and magnetic circular dichroism (————) spectra observed at 4.2 K and 1.97 T for a system of randomly oriented F_2^+ centers in $KCl:SH^-$
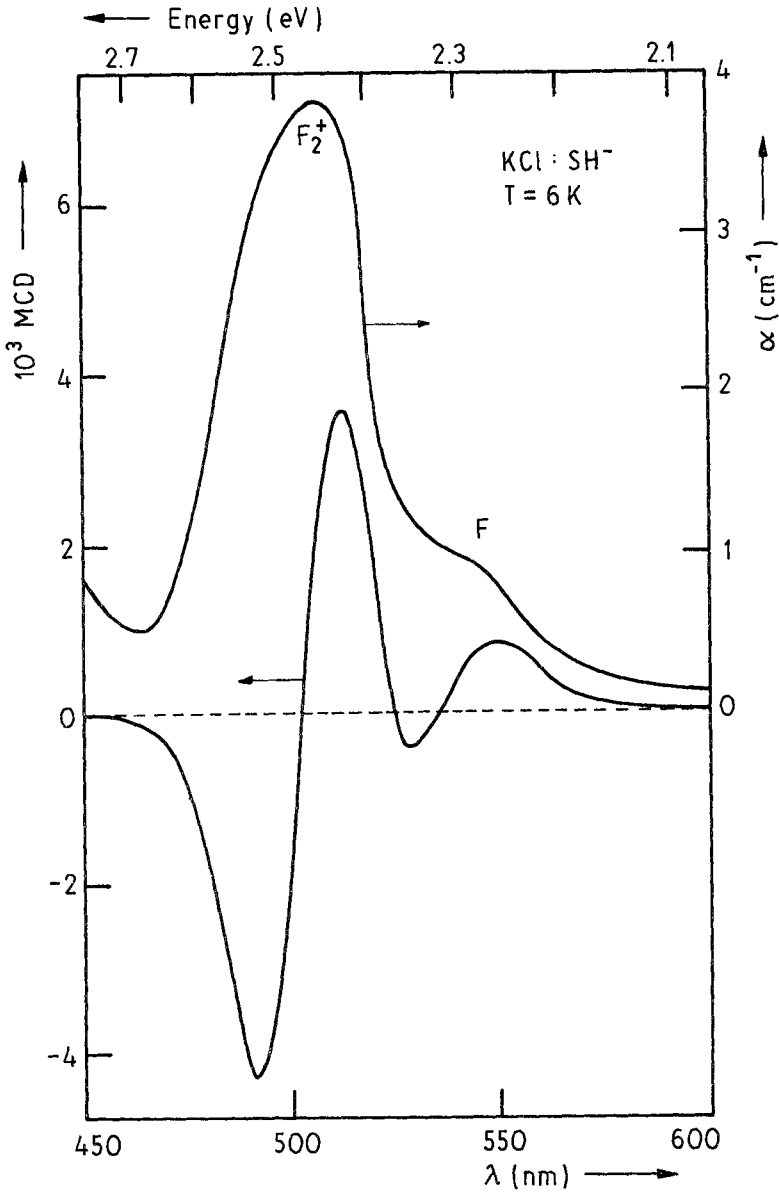
Fig. 7. Magnetic circular dichroism and absorption spectra of a mixed system of F and F_2^+ centers in KCl:SH⁻ observed at 6 K and 1.97 T

measured at 6 K. Both signals are well separated and easy to identify. For larger F center concentrations, the F_2^+ centers MCD will be completely masked by the F center MCD.

In Fig. 6 we show the $1s\sigma_g \rightarrow 2p\pi_u$ absorption band of a pure unaligned F_2^+ center system produced according to Section 2, and its MCD measured at liquid helium temperature

under a magnetic field of 1.97 T. The MCD lineshape is not altered by increasing the magnetic field up to 4.8 T in the temperature range 1.5 to 80 K.

In the proposed model, the MCD signal of the $1s\sigma_g \to 2p\pi_u$ transition is only due to the population difference of the Zeeman sublevels of the ground state (13) and should vary linearly with tanh $(g\mu_B H/2k_B T)$. Fig. 8 drawn for a F_2^+ system having an absorption constant $\alpha = 1$ cm^{-1} confirms this linear behavior. Utilizing the experimental lineshape function of the $1s\sigma_g \to 2p\pi_u$ transitions ($\langle x \rangle$ and $\langle y \rangle$), obtained by Aegerter and Lüty [1], the MCD signal can be best fitted for a spin–orbit coupling constant $£_z = 3.6$ meV. For comparison, the MCD behavior of a pure F center system having the same absorption constant is also shown.
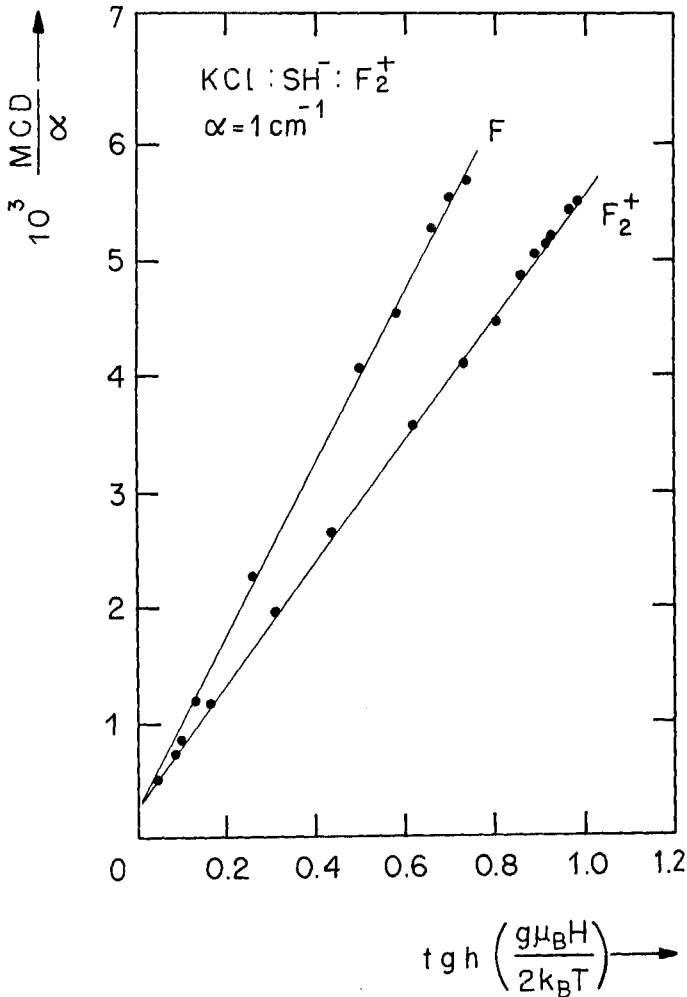

Fig. 8. Behavior of the magnetic circular dichroism vs. tgh $(g\mu_B H/2k_B T)$ for F and F_2^+ centers, when the absorption coefficient α is 1 cm^{-1} at band maximum $E = 2.5$ eV (F_2^+ centers) and $E = 2.32$ eV (F centers). The MCD was measured at $E = 2.234$ eV and $E = 2.515$ eV for F and F_2^+ centers, respectively
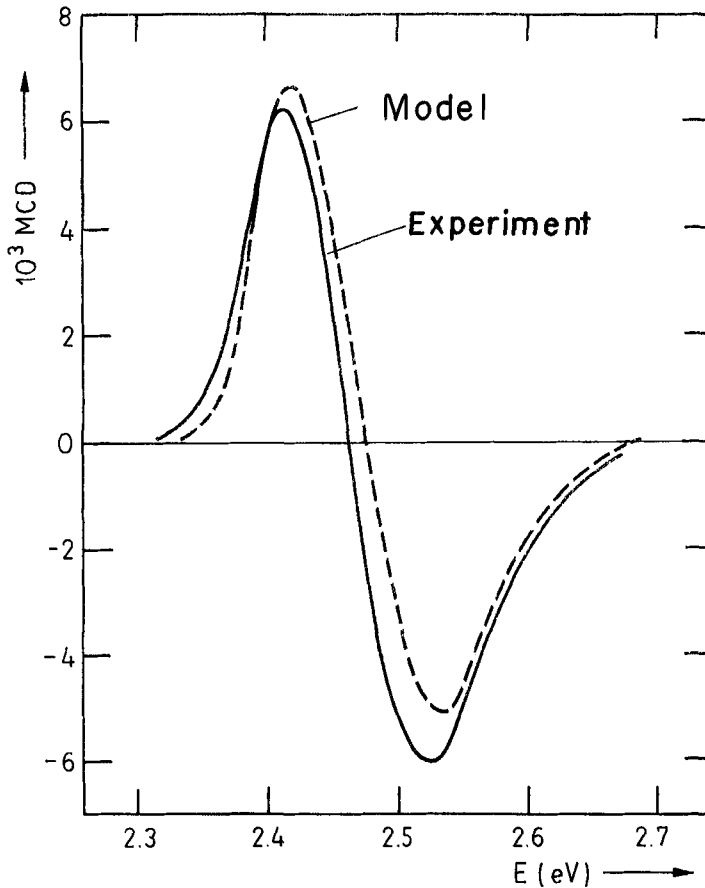
Fig. 9. Magnetic circular dichroism spectra of F_2^+ centers in KCl:SH$^-$ observed at 4.2 K and 1.97 T (————) and model prediction using a spin–orbit coupling constant $\mathcal{L}_z = 3.6$ meV (- - - -)

Fig. 9 shows a comparison of the experimentally determined MCD with the MCD spectrum predicted by the model when $\mathcal{L}_z = 3.6$ meV. Both spectra are in good agreement.

Symmetry consideration of the defects (see Fig. 1), shows that F_2^+ centers aligned along the directions {1} and {2} contribute of identical form for the MCD. The same condition applies for defects oriented along the directions {3, 4, 5, 6}. Therefore, from the MCD band absorption measurements and with a partially aligned F_2^+ center, it is possible to calculate the true MCD contribution of the $\langle x \rangle$ and $\langle y \rangle$ transitions for both groups of defects. Fig. 10 shows this effective MCD measured at liquid helium temperature and at 2.95 T. We see that there is no contribution to the MCD for defects oriented along the directions {1, 2} and only defects oriented along the directions {3, 4, 5, 6} are responsible for it. A confirmation of this result is shown in Fig. 11, where the MCD appears as a linear function of the relative number of defects in the {3, 4, 5, 6} positions.

No MCD signal has been observed in emission in the $2p\pi_u \rightarrow 1s\sigma_g$ transition for fields up to 3 T and at $T = 4.2$ K. As the limit of detection of the MCD signal S is 2×10^{-4}
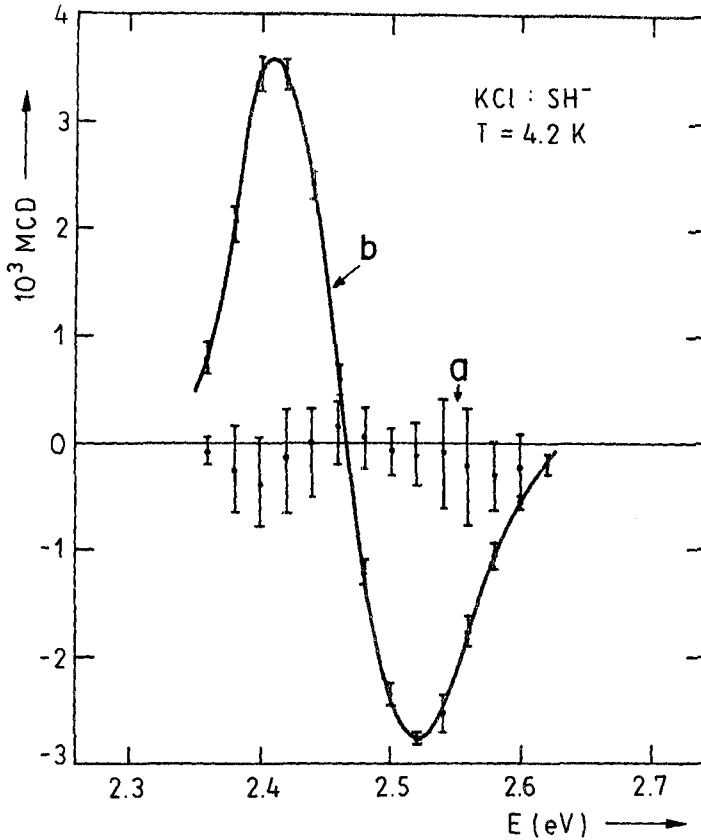
Fig. 10. Magnetic circular dichroism behavior for (a) $\langle x \rangle$ transitions of F_2^+ centers aligned along the directions $\{1, 2\}$ (see Fig. 1) and (b) $\langle x \rangle$ and $\langle y \rangle$ transitions of F_2^+ centers aligned along the directions $\{3, 4, 5, 6\}$ (see Fig. 1)

(signal-to-noise ratio $= 1$) this result suggests that

$$\frac{\pounds_z'}{D'} < 5.8 \times 10^{-5} \, . \tag{15}$$

Utilizing the previously described technique for optical detection of electronic paramagnetic resonance (ODEPR), we have observed only one resonance band at 0.32 T having a half-width of 8.0 mT at liquid helium temperature (Fig. 12), whatever the magnetic field direction is. For a magnetic field in the [110] direction, three bands should be observed corresponding to g_{zz}, g_{60}, and g_{xx}, where g_{zz} is the Landé factor in the ground state observed with the magnetic field making an angle of zero degree with the principal axis of the defects, g_{xx} and g_{60} making an angle of 90° and 60°, respectively, with the principal axis of the defects. The g_{xx} resonance cannot be observed with this technique as the F_2^+ center system does not present any MCD signal in this configuration. As only one resonance band is observed, the two other resonances are therefore superimposed implicating that $g_{zz} = g_{60}$. When the magnetic field is in the [100] direction, only one resonance is observed allowing the
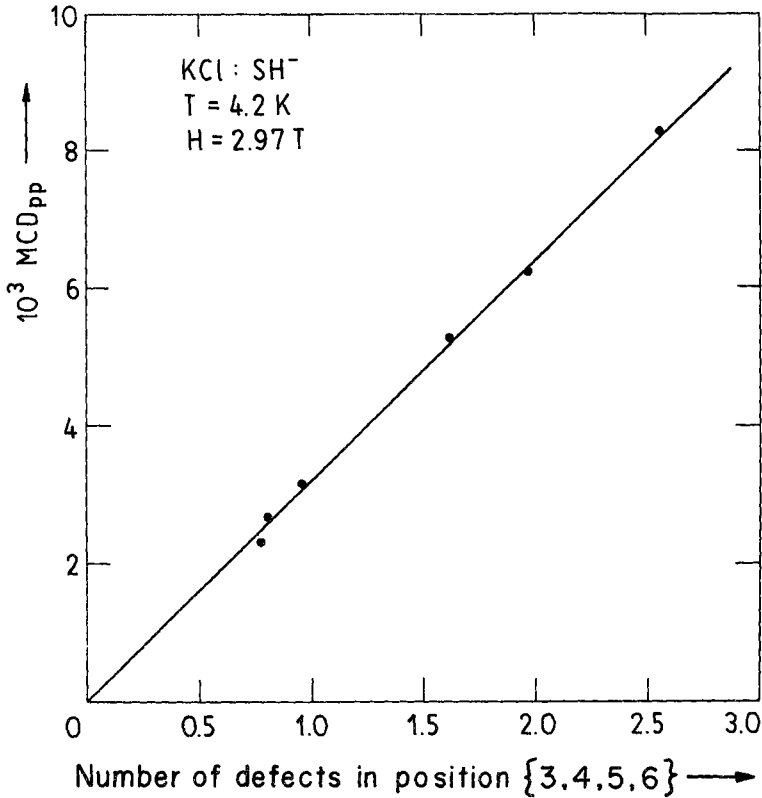
Fig. 11. Peak to peak values of the magnetic circular dichroism as a function of the relative number of F_2^+ centers aligned along the directions {3, 4, 5, 6}, measured at 4.2 K and 2.97 T

determination of g_{45}. Analyzing various measurements with different samples and different magnetic field configurations, we encountered that $g = 1.965 \pm 0.007$, implying that $g = g_{zz} = g_{60} = g_{45}$.

The determination of the spin–lattice relaxation time was obtained by switching off the microwaves under resonance conditions. Measurements performed at various temperatures show that the MCD signal recovery at 2.515 and 2.41 eV can be fitted by an exponential function: $S_{MCD} = a \exp(T_1/t)$. Fig. 13 shows a plot of T_1^{-1} as a function of temperature obtained at 0.32 T. Within the temperature interval 3 to 11 K, a good fit is obtained with

$$T_1^{-1} = 4.31 \times 10^{-2} \coth\left(\frac{g\mu_B H}{2k_B T}\right) \tag{16}$$

implying a direct relaxation process [9].

6. Conclusions

We have presented an experimental and theoretical study of the magneto-optical properties of F_2^+ centers in KCl:SH$^-$. The experimental results are in good agreement with the
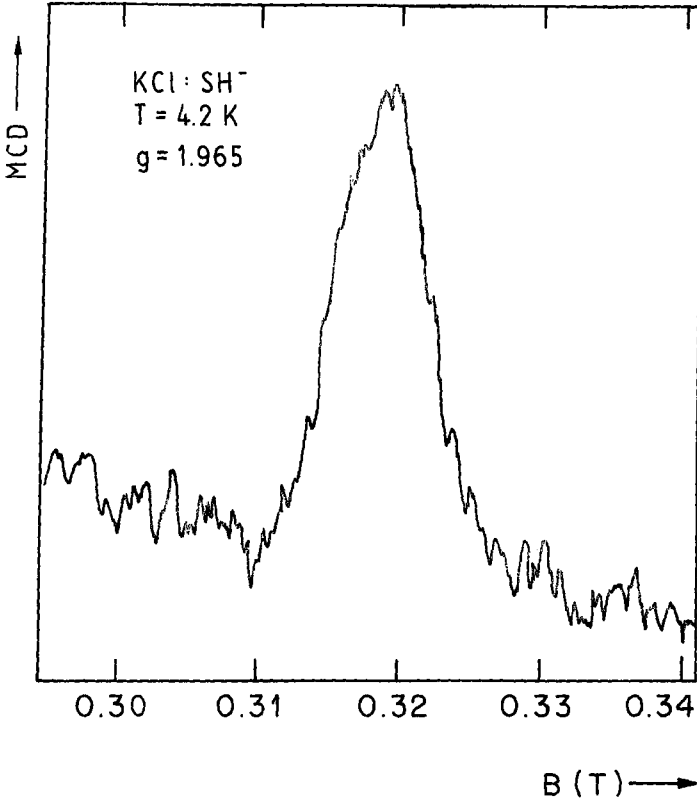
Fig. 12. Magnetic circular dichroism signal variation of F_2^+ centers measured at 2.515 eV and 4.2 K. The magnetic field sweep rate is 5.9×10^{-4} T/min around the resonance condition

prediction of the model. The MCD is only observed in absorption for the transition $1s\sigma_g \rightarrow 2p\pi_u$ (around 500 nm). When light and applied field are aligned along the [100] direction, only the centers for which their transitions $|x\rangle$ and $|y\rangle$ can be attained simultaneously will contribute to the signal (positions 3, 4, 5, 6, Fig. 1). Good agreement is obtained between the results and the theoretical model if we assume a spin–orbit coupling $\pounds_z = 3.6$ meV. The alignment of the defects does not change the first moment of the MCD but only its intensity. Within the detection limit (signal/noise = 1) no MCD was observed in emission either for the $2p\pi_u \rightarrow 1s\sigma_g$, $2p\pi_u \rightarrow 2p\sigma_u$ or $2p\sigma_u \rightarrow 1s\sigma_g$ transitions in the excited states.

Measurements of optical detection of electronic paramagnetic resonance (ODEPR) of F_2^+ centers in their ground state ($1s\sigma_g$), show that the Landé factor is isotropic and equal to $g = 1.965 \pm 0.007$. This is in agreement with the model prediction as the states envolved are symmetric. The half-width of the resonance band is 8.0 mT at 4.2 K and for a field of 0.32 T. Between 3 and 11 K and for an applied field of 0.32 T, the spin–lattice relaxation time in the ground state is typical of a direct process and follows the law $T^{-1} = 4.3 \times 10^{-2} \coth (g\mu_B H/2k_B T)$.

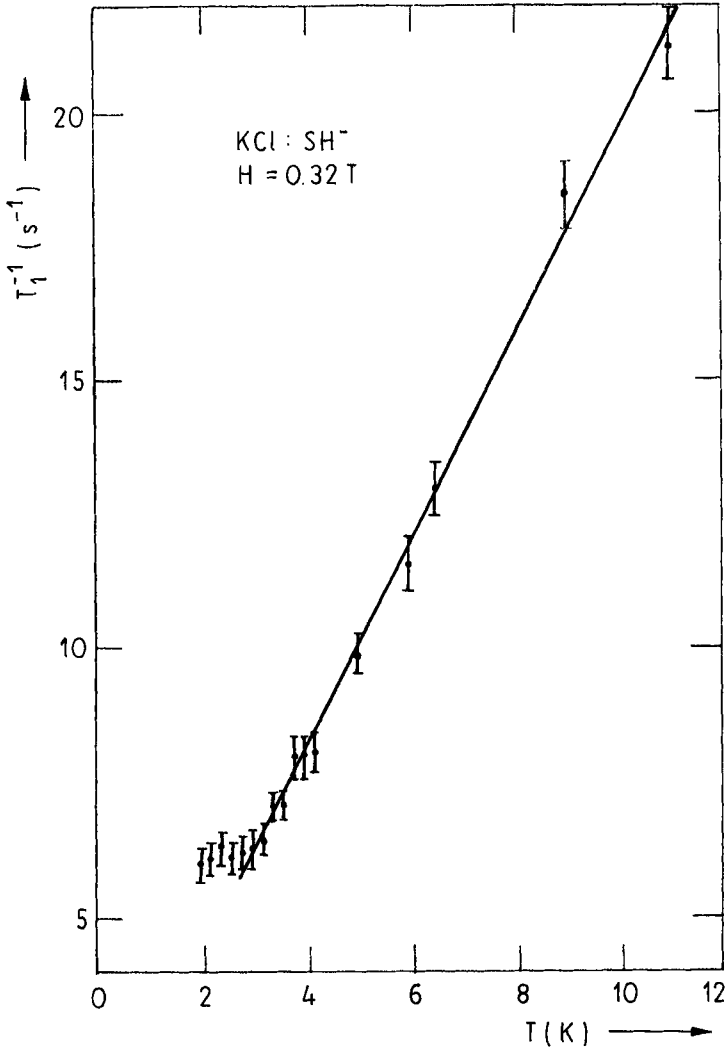The results also indicate that there is a perfect spin memory during the optical pumping.

Fig. 13. Reciprocal of the spin–lattice relaxation time (T_1^{-1}) of F_2^+ centers vs. temperature measured at 0.32 T

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