The F_A(II) centres of KCl:Li in a reoriented centre distribution

The $F_A(II)$ centres of KCl:Li in a reoriented centre distribution

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Abstract. The magnetic circular dichroism (MCD) spectra of $F_A(II)$ centres in KCl:Li crystals have been measured at a magnetic field of 11.5 kG at 17 K and room temperature. When a crystal is irradiated with linearly polarized F_{A1} light, a non-zero circular dichroism (CD) signal is detected at zero field. The MCD spectra are compared with the zero-field CD spectra, which were obtained in systems containing both a random distribution of centres and an aligned distribution. The meaning of the MCD signal obtained in the reoriented anisotropic system using a conventional CD polarimeter is discussed.

1. Introduction

One of the most important features of the F_A centre in alkali halide crystals is that it reorients under light excitation (Luty 1968). The F_A centres may be partially or completely aligned in a particular direction, depending on the polarization and wavelength of the exciting light. The reorientation can be detected by dichroism such as linear dichroism (LD) and magnetic circular dichroism (MCD). The observation of the MCD of the F_A centre and the analysis of MCD spectra have been made by Henry (1965) for KCl:Na, Smith *et al* (1983) for KCl:Li, Baldacchini *et al* (1990) for KCl:Na and KCl:Li, and recently by Tsuboi and Peiponen (1990) for KCl:Li.

The F_A centre exhibits a zero circular dichroism (CD) intensity at zero magnetic field when the measurement is made before any optical measurement such as MCD or absorption, indicating that the crystal has a random population of centres, i.e. an equal or isotropic distribution of the three possible ⟨100⟩ orientations. When the absorption and/or MCD measurements are repeated both with and without changing the magnetic field, however, it is found that the CD is not zero any longer at zero field. Moreover the CD spectrum, and eventually the MCD spectrum, change as time passes, as shown in figure 1. Because we have to illuminate the crystal and scan the wavelength of the source to obtain these spectra, even the F_{A1} and F_{A2} light used during the scanning gives rise to a partial reorientation of F_A centres.

To obtain a stable MCD spectrum is necessary to study the electronic state of the $F_A(II)$ centre. The present work was undertaken to obtain stable MCD spectra and to investigate the difference between the MCD lineshapes of the random distribution of $F_A(II)$ centres and the reoriented distribution. As seen in figure 1, the MCD signal of the
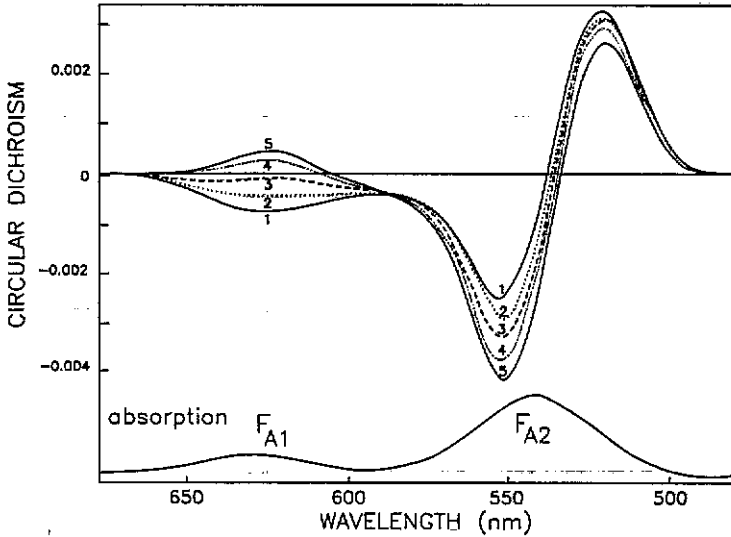
Figure 1. Time dependence of MCD spectra of F_A bands in KCl:Li at 11.5 kG at 17 K. The MCD measurement was done every 10 min after curve 1 which was obtained immediately after the crystal had been cooled to 17 K from RT. Several typical spectra are shown by curves 2, 3, 4 and 5 which were obtained 50 min, 70 min, 90 min and 120 min, respectively, after curve 1. The lower part of this figure shows the absorption spectrum measured after obtaining curve 5.

F_{A1} band changes its sign when the measurement is repeated. Therefore it is interesting to clarify whether the absorption-like magnetic-field-induced CD lineshape, which was obtained with the random F_A distribution, is obtained for the F_{A1} band with a reoriented and aligned distribution of centres.

2. Experimental procedure and results

Measurements were performed on additively coloured KCl crystals containing 0.02 mol% LiCl. Before measurement, the crystals were heated in a furnace at 500 °C for 1 min and quenched to destroy F-centre aggregates. After the quenching, the crystal was irradiated with white light emitted from a 50 W xenon lamp at room temperature (RT) for 10 min to produce the F-to-F_A conversion. We also performed this F-to-F_A conversion at about −20 °C, but no large differences were found in the intensity of the F_A band, compared with RT conversion. The MCD spectra were measured using a JASCO spectropolarimeter J-40A at KSU and J-500 at UWO. A magnetic field was applied using an electromagnet. The MCD signal is given here as the difference between the optical densities measured using the left- and right-circularly polarized light.

In the present work, we investigate the F_{A1}-band MCD spectrum produced by the F_{A1}-band optical excitation. Therefore we scan the wavelength from 700 up to 590 nm to obtain the MCD spectra of the F_{A1} band. We stop the scanning at 590 nm since the F_{A2}-band excitation induces a different reorientation from F_{A1}-band excitation. Another reason for concentrating our study on the F_{A1}-band MCD only was to avoid some of the complications which are involved in the F_{A2}-band MCD spectra. The MCD signal of the
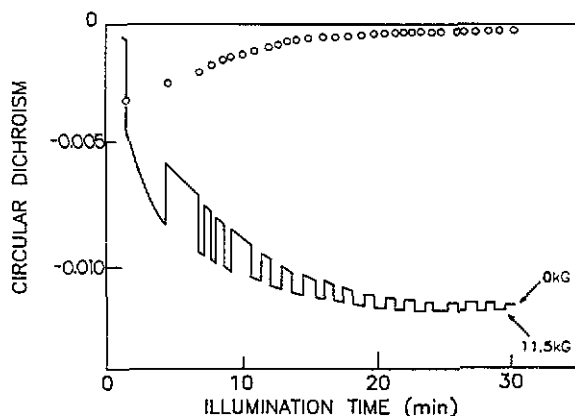
Figure 2. Illumination time dependence of the CD intensity at 625 nm at 17 K, which was measured at 0 and 11.5 kG alternately during the continuous illumination of 625 nm light (see text): O, difference between the CD at 11.5 kG and the zero-field CD.

F_{A2} band contains inevitably the MCD of the F band, which is located quite close to the F_{A2} band, since the F centres coexist along with the F_A centres.

A KCl:Li crystal was cooled to 17 K without any light illumination. An absorption-like MCD lineshape with a negative sign such as curve 1 of figure 1 was obtained for the F_{A1} band under a magnetic field of 11.5 kG in the first measurement. We then fixed the wavelength of the CD polarimeter at 625 nm where a high negative intensity was obtained corresponding to the F_{A1}-band peak position, and we then repeated the measurement of CD intensity at both 0 and 11.5 kG consecutively by changing the magnetic field. The zero-field CD intensity increases to a negative value as the illumination time increases as seen in figure 2, approaching saturation after about 30 min. Unlike the case illustrated in figure 1, where the crystal is illuminated with F_{A2} in addition to F_{A1} light, the CD at 625 nm never changes the sign. The MCD at 11.5 kG shows an exponential-like time dependence which is quite similar to CD at 0 kG. The two have a large intensity difference in the early stage of the experiment but this difference becomes much smaller as the illumination time with 625 nm light increases.

Similar behaviour was observed for the F_{A1} band at RT. Unlike the case at 17 K, however, both the MCD and the CD (strictly speaking, the CD at zero field) signals at RT begin to decrease immediately and approach a zero value after stopping illumination with F_{A1} light or after decreasing the intensity of the exciting light. This means that $F_A(II)$ centres at RT exhibit a thermal reorientation from an optically induced alignment of the centres into an equal distribution of centres in the three possible ⟨100⟩ directions. Such a thermal reorientation was never observed at 17 K, and the MCD and CD signals were quite stable at low temperatures even after the optical excitation ceased.

The CD and MCD spectra of the F_{A1} band at the early and late stages of 625 nm light illumination are shown in figure 3(a) and figure 3(b), respectively. The CD measurement was performed first immediately after cooling the crystal to 17 K. We obtained a zero CD signal for the whole of the F_{A1} band (curve 1). Next, we measured the absorption spectrum (curve 2), subsequently the MCD spectrum at 11.5 kG (curve 3) and then the CD spectrum (curve 4) immediately after obtaining curve 3. As already seen in figure 2, a large intensity difference is observed between the MCD and CD spectra at this early
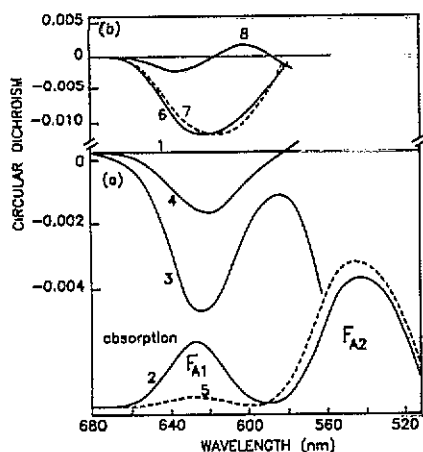
Figure 3. MCD (at 11.5 kG) and CD spectra of the F_{A1} band in KCl:Li measured at (a) the early stage and (b) the late stage after the crystal had been cooled to 17 K. Curves 1, 4 and 7 are CD spectra, while curves 3 and 6 are MCD spectra. The lowest curves show the absorption spectra. Curve 1 was obtained immediately after the crystal had been cooled to 17 K, and curves 2 and 5 immediately after curves 1 and 4, respectively. Curves 3, 4, 6 and 7 were obtained after 625 nm light illumination for 1 min, 2 min, 120 min and 121 min, respectively. Curve 8 was obtained by subtracting curve 7 from curve 6, whose spectrum has been magnified by a factor of 2.

stage. We then measured the absorption, MCD and CD spectra after a 2 h illumination with 625 nm light. Such a long illumination decreases the F_{A1} absorption band but increases the F_{A2} band as seen in curve 5. After the 2 h illumination, we obtained curves 6 and 7 as the 11.5 kG MCD and zero-field CD spectra, respectively. No changes were observed in these spectra when illumination was continued for longer than 2 h, indicating that curves 6 and 7 reflect a stable reoriented state.

Unlike the early stages of illumination with 625 nm light, no magnetic field effect seems to appear at a sufficiently late stage. The intensity is certainly not different between 0 and 11.5 kG, but the spectra are slightly different, for the MCD lineshape of curve 6 is found to be shifted from the zero-field CD lineshape of curve 7, the MCD peak being at 627 nm while the CD peak is at 618 nm. Such a shift is also observed in the early stages but is smaller than that observed in the late stage; the MCD peak is at 627 nm (curve 3), while the CD peak at 625 nm (curve 4). The MCD spectrum of curve 6 consists of the CD at zero field and the CD induced by only the magnetic field. To derive the latter magnetic-field-induced CD component, we must subtract the zero-field CD component of curve 7 from curve 6. In curve 8 of figure 3, we show a magnetic-field-induced CD lineshape in the reoriented F_A-centre distribution; a derivative-like lineshape is obtained for the F_{A1} band.

Next we illuminated the same crystal as used for figure 3 with linearly polarized light from 5 mW He–Ne laser. The laser light has a wavelength of 632.8 nm and is absorbed within the F_{A1} band. A 15 min illumination at 17 K produces a quite stable MCD or CD spectrum, exhibiting no more changes even after much longer optical excitation. Almost the same MCD and CD spectra as curves 6 and 7, respectively, of figure 3(b) are observed for the F_{A1} band; these are shown in figure 4. This figure shows the MCD spectrum of not only the F_{A1} band but also the F_{A2} band. A quite similar derivative-like magnetic-field-induced CD lineshape is found for both these two bands (see curve 4 of figure 4).

3. Discussion

Unlike the $F_A(I)$ centres formed in, for example, KCl:Na, $F_A(II)$ centres in KCl:Li have the so-called 'off-centre' symmetry. The substitutional Li^+ ions occupy four equivalent sites slightly shifted from the proper lattice sites and displaced along $\langle 110 \rangle$ directions
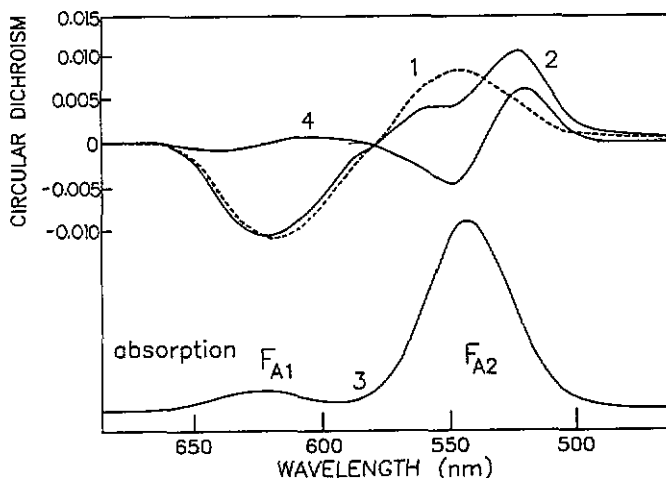
Figure 4. MCD (curve 1, at 11.5 kG), CD (curve 2) and absorption (curve 3) spectra of the F$_A$(II) centre in KCl:Li at 17 K measured after a 15 min irradiation with He–Ne laser light linearly polarized along the *y* ([010]) direction. Curve 4 was obtained by subtracting curve 2 from curve 1, magnified by a factor of 2.

with an off-axis angle θ from the $\langle 100 \rangle$ axis, lying on the (001) planes. Such an F$_A$(II) centre does not allow complete alignment along the other two perpendicular directions by the optical excitation of the F$_{A1}$ band with light polarized along one of the three $\langle 100 \rangle$ directions.

We can calculate the number N_i of centres lying along the four directions forming the angle θ with the crystal axis i ($i = x, y, z$; where x is in the [100] direction, y in the [010] direction and z in the [001] direction) under the excitation of the F$_{A1}$ band with light propagating along the z direction and linearly polarized parallel to the y axis. Using the result of an analysis by May *et al* (1988), N_x, N_y and N_z are given by

$$N_x = N_z = N_0[a - (1 - a)\exp(-t/T)]/3 \tag{1}$$

$$N_y = N_0[3 - 2a - 2(1 - a)\exp(-t/T)]/3 \tag{2}$$

where

$$a = 6\cos^2\theta/(4 - 3\sin^2\theta) \tag{3}$$

$$T^{-1} = Ib(4 - 3\sin^2\theta)/8 \tag{4}$$

b is a constant relative to the F$_{A1}$ band depending on the wavelength of the exciting light, N_0 is the total number of the centres in the crystal, I is the intensity of the exciting light and t is the time of illumination. In the above derivation, we assumed an isotropic distribution among N_x, N_y and N_z at $t = 0$. Such an assumption is consistent with our observation of zero CD signal before optical excitation. Equation (2) indicates that the number of 'y-oriented' F$_A$ centres never becomes zero even by y-polarized pumping light, as expected for an F$_A$ centre in which the Li$^+$ ion is off-centre.

The CD signal in our measurement is believed to be proportional to the difference between N_x and N_y. If we use $\theta = 17°$ as the off-axis angle (May *et al* 1988), this difference is given by

$$N_x - N_y = 0.466 N_0 [1 - \exp(-t/T)]. \tag{5}$$

The observed exponential time behaviour (shown in figure 2) is consistent with this theoretical expectation. Moreover, the relaxation time depends on the intensity of the exciting light, as seen from equation (4). We used two kinds of light source to excite the F_{A1} band: a Xe lamp and a 5 mW He–Ne laser. Almost 2 h were needed to obtain the steady state using Xe lamp excitation while less than 1 min was enough for excitation by the intense laser light. This is consistent with the result expected from equation (4).

By illumination with linearly y-polarized F_{A1} light, the KCl:Li crystal is no longer cubic but it becomes uniaxial since N_y is different from $N_x (= N_z)$. When linearly polarized light propagates along the z direction in a crystal with an anisotropic system in the x–y plane, one observes a strong LD and linear birefringence (Baldacchini *et al* 1986, May *et al* 1986, 1988). Special care is needed to analyse the MCD signal observed in the uniaxial or anisotropic system, because circularly polarized waves cannot propagate through the system without deformation (Piepho and Schatz 1983). If we measure the MCD for such a uniaxial system using light propagating along the z direction (i.e. a direction not parallel to the uniaxial axis), the signal obtained is no longer a pure MCD signal; it contains not only the CD but also the LD component (Jensen *et al* 1978, Shindo 1985, Shindo and Nakagawa 1985, Shindo *et al* 1985). Indeed, we obtained a zero CD signal for the crystal measured before light irradiation to induce the reorientation, but we obtained a non-zero-CD spectrum at zero field after light irradiation. This spectrum is quite similar to the LD spectrum obtained by May *et al* (1988). Therefore the CD signal obtained by the spectropolarimeter is not pure CD but is instead strongly affected by the LD signal, as expected by Shindo and Nakagawa (1985) and Shindo *et al* (1985).

In summary, when circularly polarized light propagates along the z direction into an isotropic system in the x–y plane, we obtain a zero CD signal (and also zero LD); eventually we can obtain a real MCD signal (e.g. curve 1 of figure 1) with its magnetic field applied parallel to the z direction. However, when there is an anisotropic system in the x–y plane, produced by the F_A centre reorientation or alignment, the conventional JASCO CD polarimeter yields a CD signal which is an artefact (Jensen *et al* 1978) and reflects the strong LD produced in the crystal. As a result, the MCD signal obtained in the anisotropic system contains not only the magnetic-field-induced CD but also the natural (i.e. zero-field) LD and MLD.

Baldacchini *et al* (1990) have observed the MCD spectrum of a KCl:Li crystal with an F_A population of $N_x/N_0 = 0.07$, $N_y/N_0 = 0.05$ and $N_z/N_0 = 0.88$, in addition to another MCD spectrum for a crystal with a population of $N_x/N_0 = 0.17$, $N_y/N_0 = 0.80$ and $N_z/N_0 = 0.03$. The former spectrum (labelled A) is similar to our curve 1 of figure 1, while the latter (labelled B) is roughly similar to our curve 2 of figure 4. Curve 1 was obtained after confirming a zero CD signal at zero field, i.e. after confirming the presence of an isotropic centre population in the x–y plane. The system of Baldacchini *et al* (1990) for $N_x/N_0 = 0.07$ and $N_y/N_0 = 0.05$ is assumed to be almost isotropic in the x–y plane. On the other hand, spectrum B and curve 2 of figure 4 were obtained in the anisotropic system which was produced by linearly polarized light irradiation. Therefore it is reasonable that the two spectra should be similar to one another.

In the present case where the LD is large because of the anisotropy of the system, severe problems and additional complications are anticipated in implementing the

theoretical analysis of the MCD spectrum (Piepho and Schatz 1983). Therefore, in this paper, we do not analyse the observed MCD spectrum of curve 8 in figure 3, but we note only that a different MCD lineshape from an absorption-like lineshape obtained in the isotropic system was obtained, thus reflecting the anisotropic aligned centre system.

Acknowledgments

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