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On the off-centre angle and the refractive index difference due to the birefringence of F_A (II) centres in KCl:Li crystals

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Abstract. Based on the dichroism of the F_A (II) KCl:Li centres the off-centre angle of the Li^+ ion was measured to be $13.5 \pm 1°$ at 26 K. Furthermore, the birefringence of the centres was verified and the difference between the refractive indexes relating to the two preferred directions was directly derived from the absorption spectra measured with polarized waves.

1. Introduction

The search for laser-active colour centres has been intensive during the last 15 years and several active units in different host materials have been discovered. The first colour centre laser ever built was based on the F_A (II) centre in Li-doped KCl crystals. The use of the anisotropic properties of F_A centres to create temporary optical memories has quite recently revived interest in the dichroic properties of these centres [1, 2].

The simplest colour centre in alkali halides is the F centre which consists of an anion vacancy occupied by one electron. This unit has a cubic O_h symmetry. If one of the six nearest neighbours of the vacancy is replaced by a smaller alkali cation, an F_A centre is formed. This unit has a C_{4v} symmetry, which allows the reorientation of the centre with polarized light and accordingly makes the crystal dichroic. The lowering of the symmetry leads to two absorption bands: F_{A1} relating to the optical dipole moment parallel to the symmetry axis of the centre, and F_{A2} relating to the direction perpendicular to the axis.

Based on their excited-state configuration and emission behaviour of the F_A centres are divided into two types, namely types I and II. Type I behaves very similarly to the F centre while type II is different because of its saddle-point configuration in its relaxed excited state. The latter type has an emission of high quantum efficiency and it forms an ideal four-level system for laser action. Questions regarding the structural properties of the F_A(II) KCl:Li centre, such as the magnitude of the off-centre angle θ, still remain open. It has been reliably shown that the Li^+ ion occupies an off-centre position, being shifted a small angle θ from the $\langle 100 \rangle$ crystal axis direction along the $\langle 110 \rangle$ direction. The ion performs a tunnelling motion between four equivalent positions at a frequency of the order 10^8 cycles s^{-1} [3]. Several studies have been made to determine the off-centre angle of the F_A(II) KCl:Li centre. A remarkable variation exists between the reported results. Firstly Lüty [4]

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reported a value of 2.5°. Baldacchini *et al* gave first a value of 6° [3] and later a value of 8° [5] after a careful study with both steady-state and transient emission and absorption measurements. Later they suggested values from 10° to almost 30° depending on the temperature. The result was achieved by comparing the emission and absorption behaviour of KCl:Li with that of KCl:Na which has no off-axis angle [6]. The last value given by them was 5° determined by photoinduced reorientation [7]. Quite recently May *et al* [8] reported a value of 17° at LNT determined from dichroic and birefringence measurements. This value has been used to explain the magnetic circular dichroism spectra of these centres by Tsuboi and Jacobs [9].

One may ask what is the reason for the diversity of the reported off-centre angle values. Baldacchini *et al* [6] have suggested that the overlapping of the F_{A1} and F_{A2} bands, which are not known exactly, may be the reason for the discrepancy. Recently this overlapping has been reliably measured by Silfsten and Tsuboi [10], which has induced us to make a new study of the off-centre angle. Thus, one object of the present study was to obtain a reliable value for the off-centre angle of the F_A(II) KCl:Li centre. This was possible by applying a new measuring geometry for the dichroic measurements. As shown by May *et al* [8] the F_A(II) KCl:Li centres have a birefringence behaviour as well as the dichroism. Another object of the present study was to verify this birefringence and to derive the corresponding refractive index change directly from the dichroic spectra.

2. Experimental details

The crystals were grown in an argon atmosphere by the Czochralski method. Before growth the starting material was thoroughly dried by evacuating the system at a temperature of 500 °C for 48 h. A Suprapur KCl material with 1 mol% LiCl in the melt was used as the starting material. Higher doping levels caused the crystal to become hazy. The crystals were additively coloured in a heat pipe oven having the construction proposed by Mollenauer [11]. The colouring pressure was 5 Torr, the temperature 680 °C and the colouring time 60 min for a sample 6 mm thick. After the coloration, samples of 1.0 mm thickness were heated at 580 °C for 2.5 min and quenched on a copper plate. After this treatment, the samples contained 1.2×10^{17} F centres cm^{-3} as calculated from Smakulas' equation, and their absorption spectra showed no sign of any other centres. Because the density of Li^+ ions is much higher than that of the F centres (around 30 times), it is highly possible that complete $F \rightarrow F_A$ conversion will occur. The conversion was made by illuminating the crystal with unpolarized F light at −20 °C. Before cooling, the randomness of the distribution was ascertained by delaying the thermal reorientation until no change occurred in the absorption spectrum. The randomness was also checked using the integrated area of the absorption curve. The cooling was performed with a closed-cycle He cryostat in darkness. To reorient the F_A centres, a geometry different from the previous studies was used, as presented in figure 1. The coordinate axes x, y and z correspond to the crystallographic directions [100], [010] and [001], respectively. For the reorientation a polarized and expanded beam of a 50 mW He–Ne laser, propagating in the y direction, was used. The electric vector formed an angle of 45° with respect to the x and z axes. Dichroic spectra of the crystal were measured with a beam propagating in the z direction which was polarized along the [100] (x axis) or the [010] (y axis) direction. For birefringence measurements the sample was mounted between an analyser and a polarizer, the geometry being otherwise similar to that described above. The analyser was at an angle of 45° with respect to the x and y axes whereas the angle of the polarizer was varied. The sample holder of the He cryostat and the polarizers were mounted in the sample compartment of the Perkin–Elmer Lambda 9 spectrophotometer, which was used to record absorption spectra. For manipulation of the spectra, Perkin–Elmer computerized spectroscopy software, including programs for addition, subtraction and multiplication with a parameter, was applied.

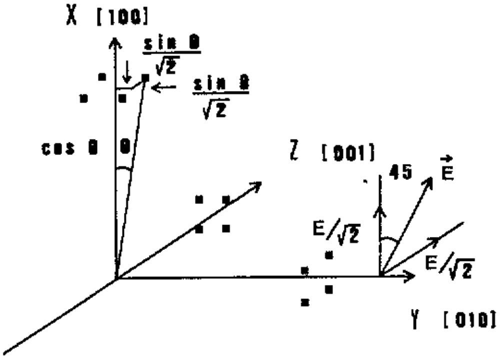

Figure 1. Exposure geometry for the reorientation of F_A centres, where E is the electric light vector used for reorientations: ■, equivalent off-centre positions.

3. F_A-centre distribution after excitation in the F_{A1} band

After the F → F_A conversion there is a random distribution of F_A centres in the crystal, which means that the numbers of F_A centres in different crystal axis directions are equal, i.e.

$$c_x = c_y = c_z . \tag{1}$$

The total amount of the centres is

$$c = c_x + c_y + c_z . \tag{2}$$

The excitation for the reorientation is made with the He–Ne 632.8 nm laser line, which coincides with the F_{A1} band only. As shown in figure 1, the excitation beam propagates along the y axis and is polarized at an angle of 45° with respect to the x and z axes. In this case we obtain the following equations for the time evolution of the concentrations:

$$\begin{aligned}
\mathrm{d}c_x/\mathrm{d}t &= aI[-(P/2)c_x\cos^2\theta - (P/4)c_x\sin^2\theta + (P/4)c_z\cos^2\theta \\
&\quad + (P/8)c_z\sin^2\theta + (P/4)c_y\sin^2\theta] \\
\mathrm{d}c_y/\mathrm{d}t &= aI[(P/4)c_x\cos^2\theta + (P/8)c_x\sin^2\theta + (P/4)c_z\cos^2\theta + (P/8)c_z\sin^2\theta \\
&\quad - (P/2)c_y\sin^2\theta] \\
\mathrm{d}c_z/\mathrm{d}t &= aI[(P/4)c_x\cos^2\theta + (P/8)c_x\sin^2\theta - (P/2)c_z\cos^2\theta - (P/4)c_z\sin^2\theta \\
&\quad + (P/4)c_y\sin^2\theta].
\end{aligned} \tag{3}$$

Here I is the light intensity, P the probability of reorientation and a a proportionality factor. Because of the exposure geometry most of the centres will become oriented along the y axis. However, because of the off-centre position the reorientation is not complete, and there will also be small distributions along the x and z axes. After reaching the saturation values we obtain

$$\mathrm{d}c_x/\mathrm{d}t = \mathrm{d}c_y/\mathrm{d}t = \mathrm{d}c_z/\mathrm{d}t \tag{4}$$

and furthermore

$$c_x = c_z \tag{5}$$

for reasons of symmetry. It follows from equations (3)–(5) that

$$c_x/c_y = \sin^2\theta/(\cos^2\theta + 0.5\sin^2\theta). \tag{6}$$

This result equals exactly the ratio of the peak absorptions A measured for the F_{A1} band with the [100]- and [010]-polarized beams. Further, for the F_{A2} band the ratio of peak absorptions measured with different polarizations will be

$$A[100]/A[010] = (c_z + c_y)/(c_x + c_z) = (c_x + c_y)/2c_x \qquad (c_x = c_z). \tag{7}$$

Thus we can state that by measuring the peak absorptions for the F_{A1} and F_{A2} bands using the [100]- and [010]-polarized beams the values for the off-centre angle θ can be calculated from equations (6) and (7).

4. Results and discussion

4.1. Gaussian fitting of the non-dichroic and dichroic spectra

Figure 2 shows the absorption spectrum of a KCl:Li crystal at 26 K measured after the F → F_A conversion. The separation of the different optical transitions in both the dichroic and the non-dichroic spectra was carried out by fitting with Gaussian line profiles. For the peak positions of the K, F, F_{A2} and F_{A1} bands the carefully measured respective values of 490 nm, 537 nm, 551 nm and 625.5 nm, respectively, were used. The half-widths of the bands used for fittings were 0.518 eV, 0.168 eV, 0.190 eV and 0.121 eV, respectively. Figures 3, 4 and 5 present the computer-fitted Gaussian curves together with the original absorption curves for a random F_A distribution, for a reoriented distribution measured with the [010]-polarized beam and for a reoriented distribution measured with the [100]-polarized beam, respectively. We can state that the spectra obey the Gaussian line profiles well. The curves show that in our case there is present a small amount (about 7%) of F centres, compared with the integrated absorption of the original F band. The dichroic behaviour of the K band is clearly visible in figures 4 and 5. Quite recently it has been shown by May *et al* [12] that the K band consists of two bands K_{A2} and K_{A1}, which have been proved to be higher excitations of F_{A2} and F_{A1} bands, respectively. For the ratio of full width H_2 at half-maximum of the F_{A2} band to the full width H_1 at half-maximum of the F_{A2} band (both expressed in electronvolts) we obtain

$$H_2/H_1 = 1.57. \tag{8}$$

This value is temperature independent and is in good agreement with the value of 1.58 given by Fritz *et al* [13]. This result also confirms the high purity of the F_A spectrum.

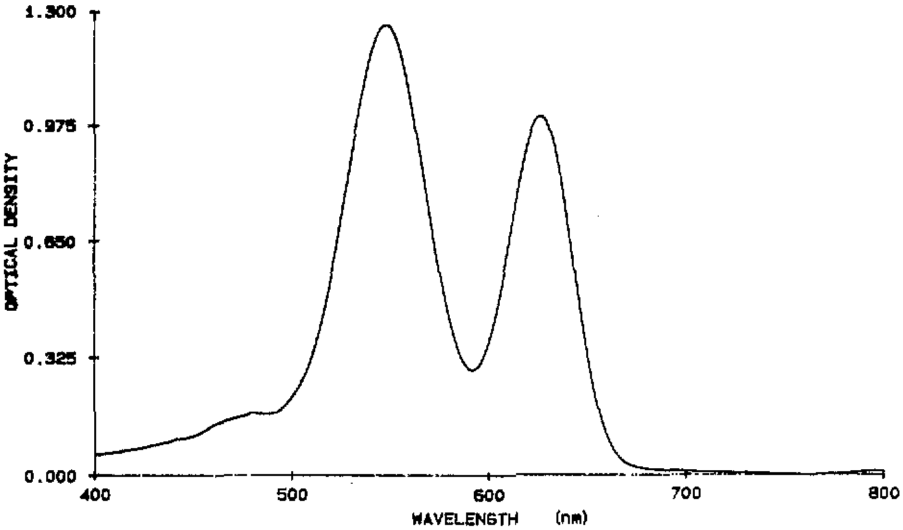

Figure 2. Absorption spectrum after the F → F_A conversion measured at 26 K.

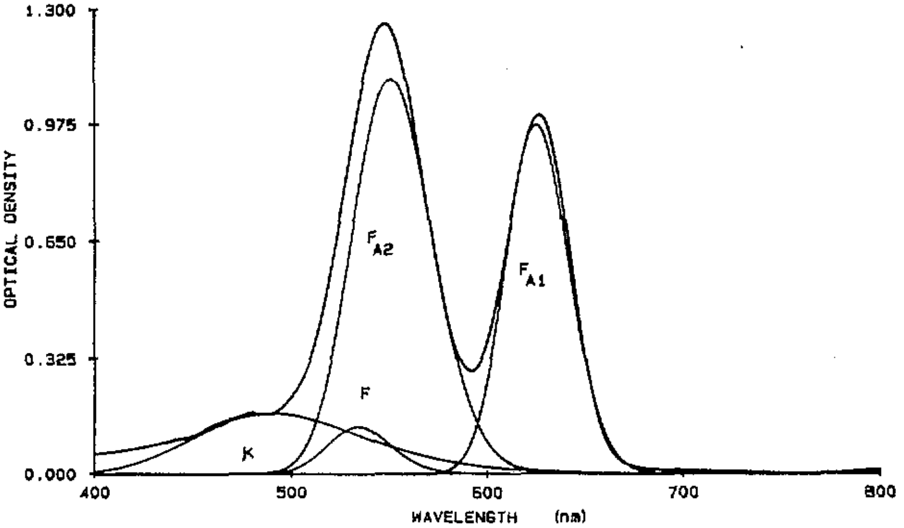

Figure 3. Gaussian fitting of the absorption curve with K, F, F_{A2} and F_{A1} transitions before the reorientation.

4.2. Determination of the off-centre angle

From equations (6) and (7) we can calculate the value for the off-centre angle, obtaining the result $\theta = 13°$ derived from the F_{A1}-band absorptions and $\theta = 14°$ derived from the F_{A2}-band absorptions. These results would be markedly affected if overlapping of the bands exceeds the tails of the Gaussian curves. Anyhow, it was shown in [10] that the tail of the F_{A2} band does not reach the wavelength value of the F_{A1} maximum. Hence, the use of F_{A1}-band absorption is justified. On the contrary, the tail of the F_{A1} band continues up to the wavelength of the F_{A2} maximum. Hence, the use of F_{A2}-band absorption will give too large an off-axis angle, just as it gave a

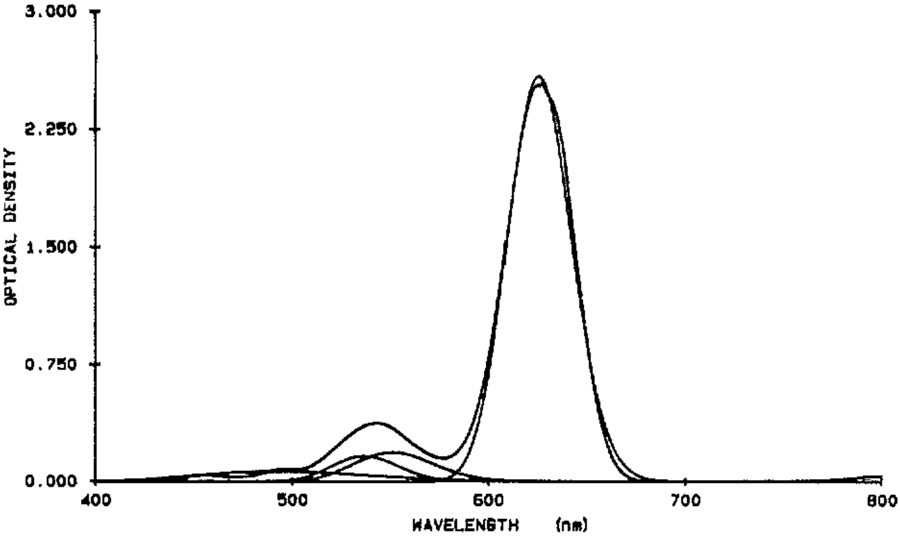

Figure 4. Gaussian fitting of the absorption curve after reorientation measured with the [010]-polarized wave.

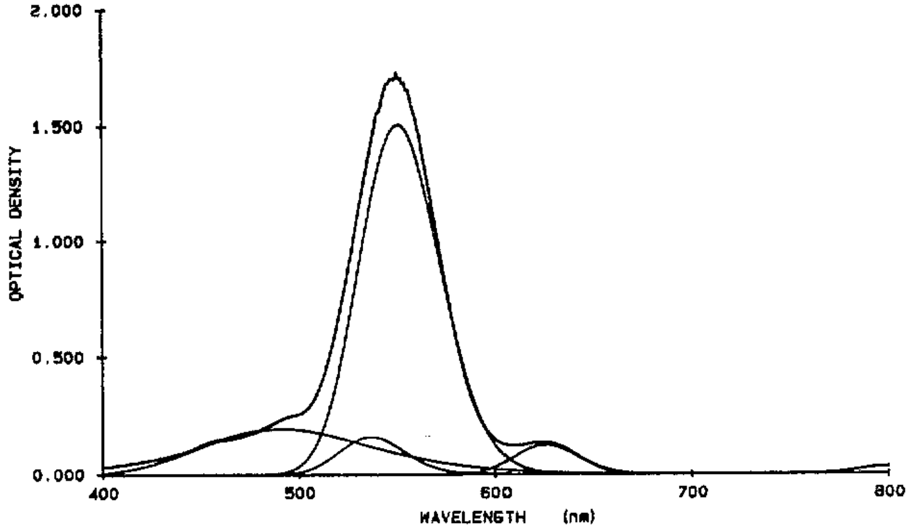

Figure 5. Gaussian fitting of the absorption curve after reorientation measured with the [100]-polarized wave.

larger value compared with that of the F_{A1} band. Estimating the sources of errors we obtain a value of 13.5 ± 1.0° for the off-centre angle θ of the F_A(II) KCl:Li centre measured at 26 K. Our result is in closest agreement with the data in [6], where the θ-values are given for different temperatures. An interpolation to 26 K gives a value of 13°. Unfortunately, [6] presents an absorption spectrum only for KCl:Na, showing a highly converted state of the $F \rightarrow F_A$ process. It is therefore reasonable to suppose that this is also valid in the case of KCl:Li.

4.3. Refractive index difference induced by the birefringence

As described in [8] the crystal will be optically uniaxial after the excitation with polarized light and shows a birefringence behaviour. In our case the birefringence equals the phase difference between the [100]- and [010]-polarized waves propagating in the z direction. In the case of colour centres the anomalous dispersion of the refractive index is related to the absorption. We can consider separately the dispersion of the refractive indices n_x and n_y corresponding to light polarizations in the [100] and [010] directions, respectively. We remember that in our case the centres are oriented along the y axis. In the [100] direction the dispersion is strong under the F_{A2} band and weak under the F_{A1} band. In the [010] direction the situation is the opposite. For this reason there exist two wavelength values, where the birefringence, proportional to $n_x - n_y$, has a zero value and changes its sign. One of the zero values is under the F_{A1} band and another under the F_{A2} band. The change in the sign of the birefringence near the peak positions of the F_{A1} and F_{A2} bands can be seen in such measurements, where the angle between the polarizer and the analyser is different from $\pi/2$ or zero. At such wavelengths where $n_x > n_y$, i.e. the refractive index for the [100]-polarized wave is higher, the rotation of the polarization is clockwise and correspondingly counterclockwise in the opposite case. To measure the phase difference we use the following method, the advantage of which is that the high absorption of crossed polarizers can be avoided. First an absorbance is measured, when both the analyser and the polarizer are parallel, at an angle of 45°. If the sample were not uniaxial, the spectrum measured would be a pure absorption spectrum and would consist of a linear combination of the dichroic spectra shown in figures 4 and 5. The proper linear combination of the dichroic spectra can now be formed using the information of two zero values and the change in sign of the birefringence in these points. Hence the absorption part can be subtracted from the spectrum recorded in the birefringence measurement. After the procedure described above and after converting the spectrum to the transmission spectrum, the curve corresponds to the intensity transmission through the sample modulated by birefringence effect alone according to the formula [13]

$$I = I_0[1 - \sin^2(\epsilon/2)] \tag{9}$$

where ϵ is the phase difference between the [100]- and [010]-polarized waves and can be expressed as

$$\epsilon = (2\pi d/\lambda)(n_x - n_y). \tag{10}$$

Here λ denotes the wavelength, d is the sample thickness and $n_x - n_y$ is the difference between the refractive indexes in the [100] and [010] directions. Using equations (9) and (10) and the manipulation procedure for the spectra described above, we can calculate the phase difference between the [100]- and [010]-polarized waves and further the difference between the refractive indexes in the x and y directions. The calculation procedure is explained in detail in [15]. The results calculated for a sample 1 mm thick are presented in figure 6. Both the phase difference and the difference between the refractive indexes have two minima and one maximum in the wavelength region of the F_{A1} and F_{A2} bands. The phase difference varies between +140 and −80° whereas for the refractive index difference the highest and lowest values are 23.2×10^{-5} and -14.3×10^{-5}, respectively.

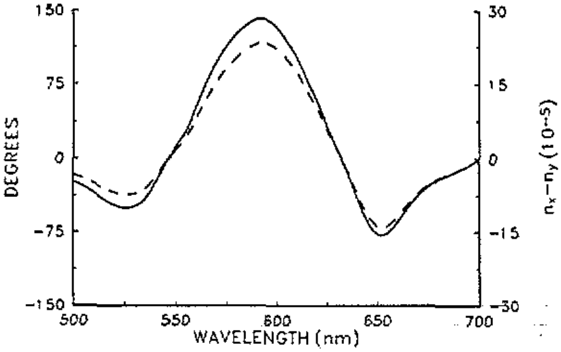

Figure 6. Phase difference (——) and refractive index difference $n_x - n_y$ (– – –) due to the birefringence as functions of wavelength for the [100]- and [010]-polarized waves.

As the phase difference caused by the birefringence is proportional to the concentration of the centres and to the sample thickness, the phase difference corresponding to a thickness of 1 mm is in our sample about three times that reported by May *et al* [8]. This is in good agreement, because the difference between the concentrations is of the same order of magnitude. May *et al* calculated the difference between the refractive indices from Dexter's [16] formula; here we have been able to derive it directly from the measured spectra. The method used in this study thus offers a direct way to determine even small changes (of the order of 10^{-5}) in the refractive index.

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