# Effects of X-irradiation on the Principal Uranium Centre in Alkali Fluorides

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*Abstract*

When fluorescing crystals of LiF and NaF containing hexavalent uranium and oxygen are X-irradiated the fluorescence is quenched and new absorption centres are created. There are strong absorption lines created at 562·8 nm in LiF:U,O and at 580·6 nm in NaF:U,O. These and other absorption lines have been studied by magnetic circular dichroism (MCD). A temperature independent MCD was observed, indicating an upper state degeneracy. A Fano antiresonance is observed in the absorption spectrum. No splitting was observed for the lines under uniaxial stress at 10 K. A model for these new centres is proposed.

## 1. Introduction

Uranium-doped lithium fluoride or sodium fluoride grown in an atmosphere containing oxygen produces crystals with an intense green or yellow luminescence respectively. The fluorescent centres are hexavalent uranium–oxygen complexes, and the principal centre is a tetragonal $UO_5F$ group which has been extensively studied both experimentally (Srinivasan *et al.* 1985) and theoretically (Runciman *et al.* 1986).

Electron paramagnetic resonance (EPR) studies on new paramagnetic centres created by X- or γ-irradiation at room temperature in LiF:U,O and in NaF:U,O showed the presence of a prevailing centre with tetragonal symmetry which has been associated with a $U^{5+}$ centre resulting from a radiation induced change in the principal centre (Lupei *et al.* 1976).

The low temperature absorption spectrum of X-irradiated LiF:U,O shows new lines appearing in the visible and infrared region (Parrot *et al.* 1977). The new lines in the infrared region were attributed to two different centres using excitation techniques and the energy levels of these two centres were obtained. Using the growth curves of these centres and the growth curve of the predominant EPR signal with X-irradiation, the 2·09 μm absorption centre created by X-irradiation was identified as the $UO_5F$ centre found in EPR measurements (Lupei *et al.* 1976).

Parrot *et al.* (1977) mentioned the presence of a strong new line at 562·8 nm in X-irradiated LiF:U,O crystals, but surprisingly have not made a study of this centre in detail, although this is the predominant new absorption line created by X-irradiation. Hence, a study of the optical and MCD spectra of X-irradiated LiF:U,O and NaF:U,O was undertaken to find more information on these new centres.

More recently the structure of the main luminescent centre has been confirmed (Lupei *et al.* 1982), and the effects of impurities have been studied (Lupei *et al.* 1977, 1985; Lupei and Lupei 1979). Some of these centres are charge compensated $(UO_6)^{6-}$ complexes as previously proposed (Runciman 1956) and supported by polarisation measurements (Runciman and Wong 1979; Srinivasan *et al.* 1985).

## 2. Experimental Details

Crystals used in this study had either 0·005 or 0·01 at.% of uranium and were grown in oxidising atmospheres, except the reference crystals which were the undoped LiF and NaF crystals grown in air. The crystals were X-irradiated at low temperatures, either at 77 K using a cryostat cooled by liquid nitrogen or at about 20 K using a continuous flow cryostat (Air Products and Chemicals Inc.). This was done to try to avoid or reduce electron trapping and creation of colour centres (Parrot
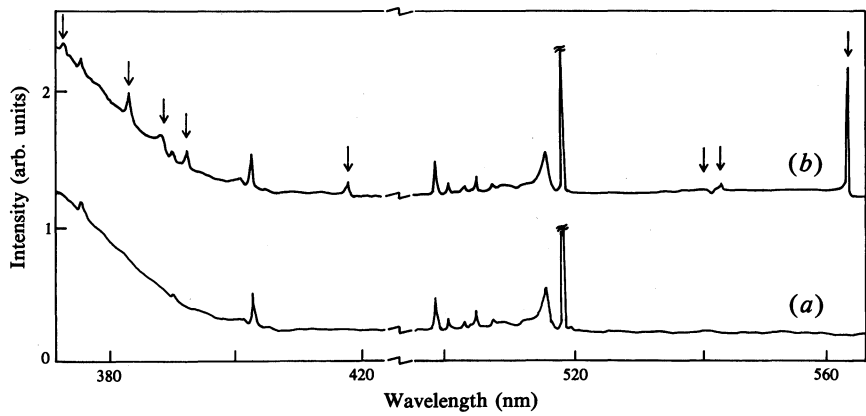


**Fig. 1.**   Absorption spectrum of a LiF:U, O crystal: (*a*) before X-irradiation and (*b*) after 1 hour of X-irradiation at 77 K. The new lines appearing in the irradiated crystal are indicated by arrows.
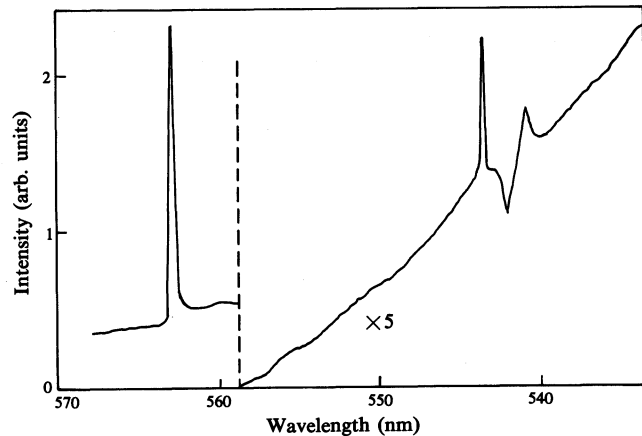


**Fig. 2.**   Absorption spectrum of an irradiated LiF:U, O crystal in the 530–70 nm region.

*et al.* 1977). The cryostats were fitted with three optical windows and one aluminium window to enable the irradiation and observation to be done simultaneously. The radiation consisted of 40 keV X-rays from a molybdenum target. Unless mentioned otherwise, the absorption spectra were recorded using a Cary 17 spectrophotometer. All the MCD experiments were carried out with a field of 5 T, using an Oxford Instruments superconducting magnet.

## 3. Results for X-irradiated LiF:U,O

### (a) Absorption of the New Centres

Fig. 1 presents the absorption spectra of LiF:U,O in the visible region before and after X-irradiation. Several new lines can be observed in the absorption spectrum of X-irradiated LiF:U,O, including a strong signal at 562·8 nm. Fig. 2 shows the region 530–70 nm in more detail. There is a broad new absorption band together with new sharp lines. The dip in the spectrum at 543·2 nm is an indication of an anti-resonance (Fano 1961) occurring in this region. An anti-resonance can occur when a sharp absorption line is overlapped by a broad vibronic band (Sturge *et al.* 1970). It is interesting to note that the dip shown in Fig. 2 is more pronounced than the anti-resonance feature at 14 800 cm$^{-1}$ in the absorption spectra of Cr$^{3+}$ doped glasses, which has been claimed as a striking example of anti-resonance in solid state physics (Lempicki *et al.* 1980). After X-irradiation this sample showed the presence of the 2·091 $\mu$m centre, previously reported by Parrot *et al.* (1977) and denoted as the C$_1$ centre, but there were no other new centres in the infrared region.

Table 1.   **Peak positions and relative heights of centres created by X-irradiation of LiF:U,O**

| Peak position (nm) | Relative peak height in Sample 1[A] | Relative peak height in Sample 2[B] | Ratio of peak heights in the two samples |
|---|---|---|---|
| 562·9 | 1·75 | 4·20 | 2·40 |
| 543·3 | — | 0·25 | — |
| 540·8 | — | 0·15 | — |
| 418·4 | 0·20 | 0·45 | 2·25 |
| 393·6 | 0·28 | 0·53 | 1·90 |
| 389·6 | 0·25 | 0·60 | 2·40 |
| 384·5 | 0·32 | 0·92 | 2·90 |
| 374·3 | 0·18 | 0·45 | 2·60 |
| 2091·1 | 0·20 | 1·50 | 7·50 |

[A] Sample 1 was irradiated for 30 minutes.
[B] Sample 2 was irradiated for 200 minutes.

To find whether the 562·8 nm absorption line was correlated with the C$_1$ centre, a crystal of LiF:U,O was irradiated at 15 minute intervals at liquid nitrogen temperature and the growth rates of the 562·8 nm line and the 2·09 $\mu$m line were simultaneously measured. Whereas the 562·8 nm line started growing almost immediately with irradiation of the sample and reached saturation after one hour of X-irradiation, the 2·091 $\mu$m line started growing only after about 45 minutes and reached saturation level after 200 minutes of X-irradiation. This clearly showed that the 562·8 nm absorption line is not due to the C$_1$ centre. The absence of other lines, except those due to the C$_1$ centre in the infrared region excludes the possibility of any of the newly

created lines in the visible region being due to the $C_2$ centre of Parrot *et al.* (1977). Hence, we shall denote the centre giving the 562·8 nm absorption as the $C_3$ centre.

More experiments were carried out to find whether the new lines created by X-irradiation near the ultraviolet region of the absorption spectrum were associated with either the $C_1$ or $C_3$ centres. For this purpose two adjacent parts of a LiF : U, O crystal were X-irradiated for different periods of time under similar conditions at liquid $N_2$ temperature, and the absorption spectra before and after radiation were measured. After X-irradiation new lines were found in the same positions for both samples, but with different intensities due to the difference in irradiation times. Table 1 gives the locations of these new lines, their peak heights in each sample and the ratio of the peak heights in the two samples for each line. Since the linewidths of these new lines were not significantly different, the ratio of the peak heights is a good approximation of the ratio of the concentration of the centres. It can be seen from the data presented, that the new lines near the ultraviolet region are definitely not due to the $C_1$ centre. They could be correlated with the $C_3$ centre and this is discussed later.
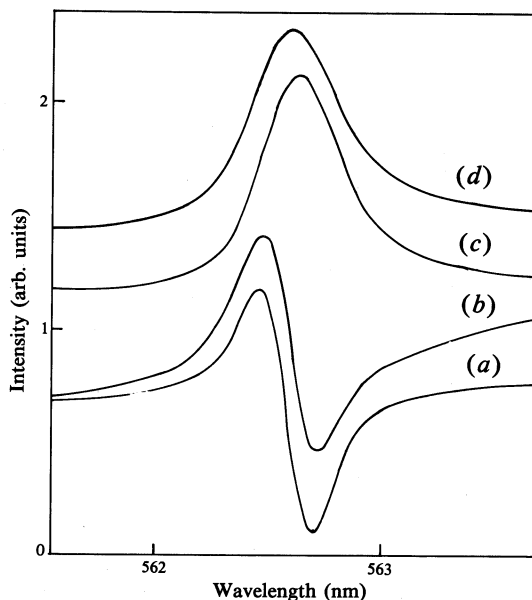


Fig. 3. Absorbance and MCD spectra of the 562·8 nm line in LiF : U,O: (a) MCD at 8 K; (b) MCD at 50 K; (c) absorbance at 8 K; and (d) absorbance at 50 K.

To test the relation of the new lines shown in Fig. 1 with the presence of uranium, an undoped LiF crystal grown in air and a LiF crystal doped with 0·01 mol.% $MgF_2$ and grown in air were X-irradiated at low temperatures for one hour, and the absorption spectra were measured. None of the new lines shown in Fig. 1 were present in these spectra. This shows that the new centres are not colour centres, nor are they associated with magnesium, which is the only significant impurity present in the LiF crystals. Hence, it can be concluded that the new lines are associated with uranium complexes.

*(b) MCD of the New Centres*

Although the data given in Table 1 suggest that the new lines around the ultraviolet region could be associated with the $C_3$ centre, further experiments were required to attribute these lines unambiguously to the $C_3$ centre. For this purpose absorption and MCD experiments were carried out on a LiF : U, O crystal X-irradiated at liquid nitrogen temperature for 30 minutes. The MCD is proportional to the difference between the absorptions of right- and left-circularly polarised light, $I^+ - I^-$. The MCD signals were calibrated against the diamagnetic MCD signal of the 403 nm (24798 cm$^{-1}$) line of unirradiated LiF : U, O, which has been found to have a $g$-value of $-0.82$. It was originally ascribed a $g$-value of $-0.41$ (Srinivasan *et al.* 1985), but recent research (Runciman and Manson 1988) shows that the $g$-values were undervalued by a factor of 2. The formula for the first moment of the MCD $\langle \Delta A \rangle_1$ divided by the absorption $\langle A \rangle_0$ for a distribution of tetragonal centres in a cubic crystal is $\langle \Delta A \rangle_1 / \langle A \rangle_0 = g\beta H$, instead of the formula $\langle \Delta A \rangle_1 / \langle A \rangle_0 = 2g\beta H$ applicable for a tetragonal centre with the magnetic field oriented along the principal axis. The $g$-values were calculated using the method of moments. The irradiated crystal had also a broad temperature-dependent MCD band in the 560–70 nm region. The MCD results for the lines given in Table 1 are summarised below:

*562· 8 nm line.* Fig. 3 shows the MCD and the absorbance of this line for different temperatures. It can be seen that there is no significant temperature dependence of the derivative shaped MCD signal, other than a slight broadening and shifting. This shifting could be due to the shifting of the absorption line which can be seen in the figure. Hence, the MCD signal is associated with a splitting in the degenerate excited state having a $g$-value of $-0.10$.

*418· 4 nm line.* Fig. 4 depicts the absorbance and MCD spectra of this line for different temperatures. At low temperature this line gives an asymmetric MCD signal occurring on the higher energy side of the absorbance peak. As the temperature is increased, the MCD signal changes lineshape and at higher temperature gives a derivative shaped signal. This indicates a splitting in the ground state due to the magnetic field. At lower temperatures only the lower level is populated and gives the asymmetric MCD signal on the higher energy side of the zero field absorption signal. As the temperature is increased the upper component of the ground state becomes populated and a signal of opposite sign appears on the lower energy side. This degenerate ground state has a $g$-value of $0.88$.

*393· 6 nm line.* Similar to the 562·8 nm line, the 393·6 nm line gave a temperature-independent derivative shaped MCD signal except for slight broadening of the signal with increasing temperature. Hence, this MCD signal is attributed to a degenerate excited state having a $g$-value of $0.24$.

*384· 5 nm line.* Fig. 5 presents the absorbance and MCD of this line at different temperatures. The MCD signal is asymmetric at low temperatures and becomes derivative shaped at high temperatures; but unlike the MCD signal of the 418·4 nm line, at low temperatures, the 384·5 nm line gives the absorption-like band shaped MCD signal to the lower energy side of the absorbance peak. This signal loses intensity as the temperature is increased with a signal of opposite sign appearing on the higher energy side. It is concluded that both the ground state and the excited
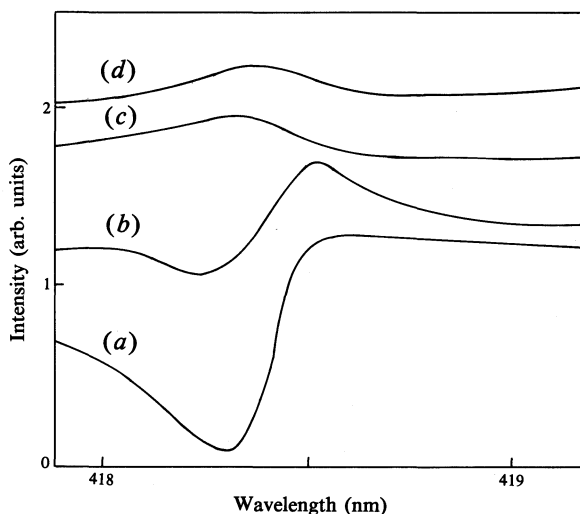
**Fig. 4.** Absorbance and MCD spectra of the 418·4 nm line in LiF:U,O: (a) MCD at 7 K; (b) MCD at 50 K; (c) absorbance at 7 K; and (d) absorbance at 50 K.
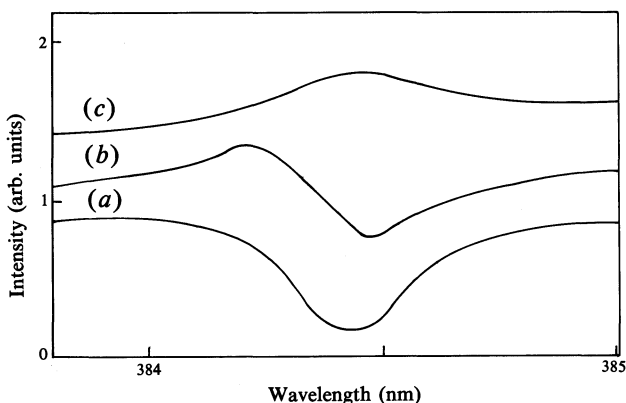


**Fig. 5.** Absorbance and MCD spectra of the 384·5 nm line in LiF:U,O: (a) MCD at 8 K; (b) MCD at 50 K; and (c) absorbance at 8 K.

state associated with the 384·5 nm line are degenerate. At high temperatures the $g$-value was found to be $-0·62$ using the method of moments. This will relate to the difference of the two individual $g$-values of the ground and excited states. The 543·3, 540·8 and 389·6 nm lines were too weak to give any appreciable signals.

### (c) Fluorescence and Uniaxial Stress Experiments on the 562·8 nm Line

To find the position of the fluorescence, if any, associated with the $C_3$ centre, an X-irradiated LiF:U,O crystal in which the 562·8 nm line was strongly present was cooled by helium gas in a flowtube to about 10 K and pumped at 562·8 nm using a dye laser for excitation. There was no visible fluorescence. A lead sulfide detector was used to look for emission in the infrared, but none was detected.

Uniaxial stress experiments were tried on an X-irradiated LiF:U,O crystal which showed the presence of the 562·8 nm line. The sample was mounted on a sample holder attached to a piston and was cooled to about 10 K by helium gas flow in a flowtube. White light, after being dispersed by a monochromator, was allowed to enter the sample in the ⟨100⟩ direction and on passing through the sample was detected by a S-20 photomultiplier and displayed on a chart recorder. The pressure on the sample was increased from zero to 9 kg mm$^{-2}$ in steps of 3 kg mm$^{-2}$ with the compression axis along the ⟨001⟩ direction, and the absorption spectrum was recorded at each interval. No splitting of the 562·8 nm line was observed. The cracking of the sample prevented measurements being made with sample pressure greater than 9 kg mm$^{-2}$.
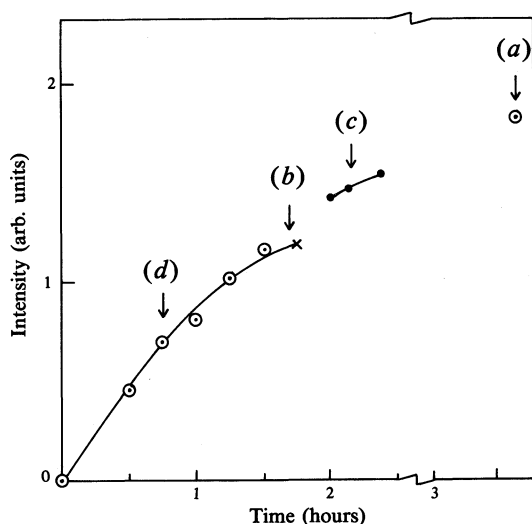


**Fig. 6.** Growth curve of the 562·8 nm line in LiF:U,O: (*a*) the open circles indicate X-irradiation of the sample at 15 K; (*b*) the cross indicates keeping the sample at 15 K after stopping irradiation; and (*c*) the closed circles indicate warming the sample to ~295 K.

### (d) Growth of the 562· 8 nm Line

A single beam set up was used, adjacent to the X-ray generator to enable the growth rate to be monitored while the sample was being irradiated. A LiF:U,O sample was cooled to about 20 K in the continuous flow cryostat. White light from a tungsten lamp was filtered before entering the cryostat, to cut off light in the blue and ultraviolet regions which might 'bleach' the newly formed centres. The incident light on passing through the sample was analysed using a Spex 0·75 m monochromator and detected by a S-20 photomultiplier. The signal was displayed on a chart recorder.

The sample was X-irradiated and the growth of the 562·8 nm line was measured simultaneously at about 15 minute intervals. The effect of time lapse after irradiation on the signal was observed by measuring the line just after irradiation is stopped and at a later time, keeping the sample under the same conditions all along. After nearly

90 minutes of total irradiation time, radiation was stopped and the sample warmed to and held at room temperature ($\sim 295$ K) for the different periods of time. Each time, the sample was cooled to $\sim 15$ K and the absorption spectrum was recorded (see Fig. 6).
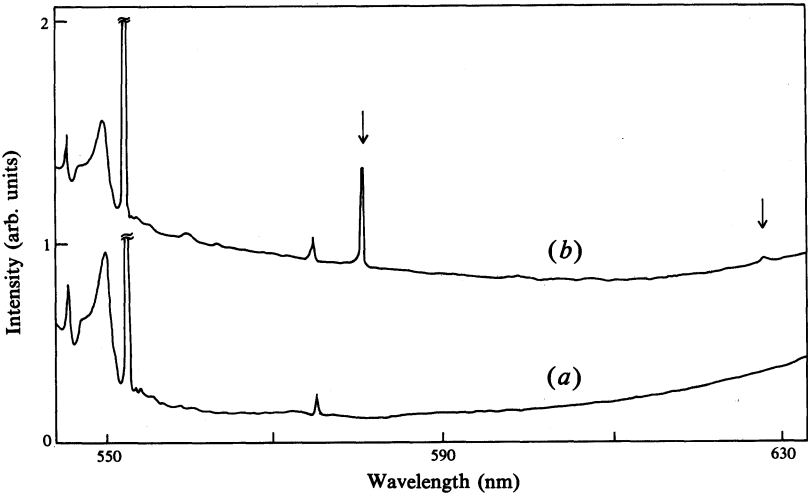


**Fig. 7.**   Absorption spectra of a NaF : U, O crystal: (*a*) before X-irradiation and (*b*) after 1 hour of X-irradiation at 20 K. The new lines appearing in the irradiated crystals are indicated by arrows.
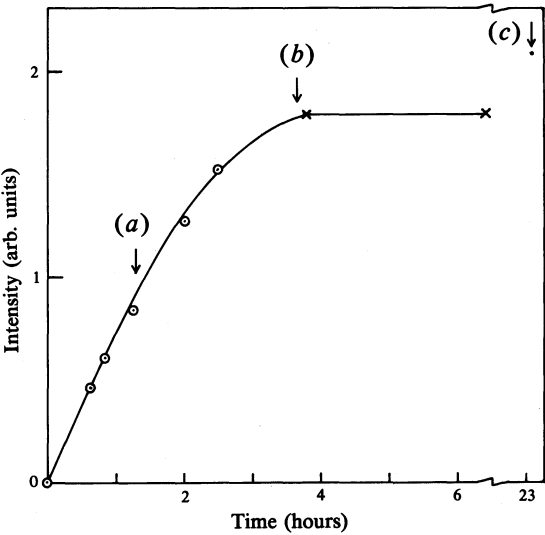


**Fig. 8.**   Growth curve of the 580·6 nm line in irradiated NaF : U, O: (*a*) open circles indicate X-irradiation at 20 K; (*b*) crosses indicate keeping the sample at 20 K after stopping the X-irradiation; and (*c*) the closed circle indicates warming the sample to $\sim 295$ K.

*(e) Heat Treatment of the 562·8 nm Line*

The absorption spectrum of an irradiated LiF:U, O sample was measured to ensure the presence of the 562·8 nm line. The sample was then annealed in a furnace, starting with two hours at a temperature of 200°C and increasing the temperature by 100°C every two hours, for a total annealing period of six hours. Then the sample was allowed to cool gradually by switching the current supply to the furnace and leaving the sample in the furnace until the temperature cooled down to room temperature. The absorption spectrum of this sample taken under similar conditions as the previous spectrum showed no sign of the 562·8 nm line.

*(f) The 547·2 nm Absorption Line in some X-irradiated LiF:U, O Crystals*

A LiF:U, O crystal which was grown from an impure LiF melt and showed strong absorption at 518·5 and 505·2 nm, indicating the presence of the principal and tetragonal impurity centres, possibly containing the hydroxyl ion, was X-irradiated at liquid nitrogen temperature for one hour. The absorption spectrum after X-irradiation in the 500–600 nm region showed the presence of a sharp new line at 547·2 nm, which was not present before the irradiation, together with other lines given in Table 1. The energy separation of this 547·2 nm line from the 505·2 nm line is 1518 cm$^{-1}$, which is identical with the energy separation between the 562·8 nm line and the 518·5 nm line, although this could be fortuitous.

## 4. Results for X-irradiated NaF:U, O

NaF:U, O crystals, when X-irradiated, showed the presence of a strong absorption line at 580·6 nm and a weak absorption line at 627·6 nm (see Fig. 7). MCD experiments on the X-irradiated sample showed both these lines giving temperature-independent derivative shaped MCD signals, with the 627·6 nm line giving a much stronger MCD signal than the 580·6 nm line. No fluorescence was observed.

Uniaxial stress experiments were tried on an X-irradiated NaF:U, O sample at 10 K, up to a sample pressure of 10 kg mm$^{-2}$. The procedure was analogous to that for LiF:U, O. No splitting of the 580·6 nm line was observed. The 627·6 nm line was too weak to look for stress effects. Using the same experimental set-up as before, the growth curve of the 580·6 nm line was obtained (see Fig. 8).

## 5. Discussion of the Results

Although the 562·8 nm absorption line in X-irradiated LiF:U, O crystals has been reported earlier (Parrot *et al.* 1977), this is the first time an absorption line due to irradiation of NaF:U, O around the same region, 580·6 nm, has been found. These centres have been shown to be associated with uranium and are formed on irradiation. The temperature-independent MCD of these centres clearly proves that these are not paramagnetic centres like the $C_1$ centre in LiF:U, O (Parrot *et al.* 1977). The enhancement of the signals when X-irradiation is stopped and the sample is warmed (see Figs 6 and 8) may indicate that these centres are connected with the mobility of some defects in the crystal.

It is very difficult at this stage to ascribe these lines to centres of a particular defect complex with any certainty. One of the possible models is shown in Fig. 9. During X-irradiation the fluorine ion in the UO$_5$F complex can be removed from the normal

lattice site, thereby creating a vacancy and giving rise to the complex shown in Fig. 9. This would give a singlet ground state as expected from the temperature-independent MCD results and retain the tetragonal symmetry. The absorptions at $562 \cdot 8$ nm in LiF : U, O and $580 \cdot 6$ nm in NaF : U, O could arise from a transfer of an electron from the 2p orbital of an oxygen ion to either the vacancy or the uranium ion.

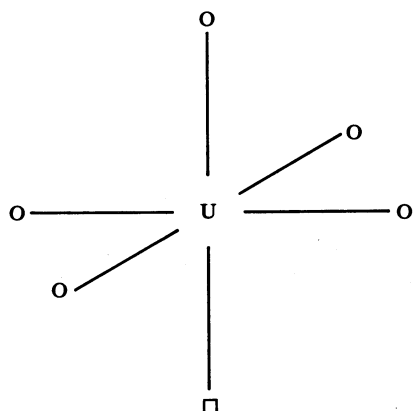Fig. 9.   A possible model for the $562 \cdot 8$ nm centre in LiF : U, O and the $580 \cdot 6$ nm centre in NaF : U, O. The square symbol denotes a fluorine vacancy.

When the irradiation is stopped, there will be diffusion of vacancies through the crystal by the jump of an adjacent ion of the appropriate sign into the vacancy, the vacant lattice site thus moving to a new position in the crystal. This would result in more $UO_5F$ centres trapping a vacancy and hence a growth in the $562 \cdot 8$ nm line. For a jump of a normal ion into a vacancy a potential barrier must be overcome, hence this process requires an activation energy and is temperature-dependent. This explains why there was no appreciable change in the $562 \cdot 8$ nm line when the radiation was stopped and the sample was maintained at low temperatures.

Although increasing the temperature caused an increase in the new absorption lines (see Figs 6 and 8) it did not give a very dramatic effect. This could be due to the vacancies getting trapped at other impurity centres in the solid or at dislocations. One could also expect that the complex shown in Fig. 9 would tend to dissociate when the sample is warmed (Schulman and Compton 1962). But even in this simple model, it is difficult to predict the charge transfer responsible for the absorption lines. If it is the transfer of an electron from the 2p orbital of the oxygen to the uranium 5f orbital, in analogy with the principal centres (Runciman et al. 1986) we would expect $A_2$, $A_1$ states and an E state with a small g-value to be the lowest excited states, although not necessarily in the same order. The $562 \cdot 8$ nm line in LiF : U, O and the $580 \cdot 6$ nm line in NaF : U, O are due to excited E states with small g-values, but there is no suggestion of an allowed transition from the ground state to an $A_1$ state close to the E state. The transfer of an electron from the 2p orbital of an oxygen ion to the vacancy will require the electron to be from a $\pi$ bond of the 2p orbital (having $m_l = \pm 1$) to give a degenerate excited state, but this would result in a g-value closer to one than to zero. Hence, more experiments are required to find the nature of these centres and of the transition giving rise to the observed absorption. Since the new absorption lines are at lower energies than the fluorescent lines, the new centres are well placed to quench the fluorescence that was present in the unirradiated crystals.

Although the data given in Table 1 indicate the possibility for the new absorption lines created by X-irradiation in LiF : U, O in the blue and ultraviolet regions to be connected with the centre responsible for the $562 \cdot 8$ nm line, it can be concluded from the temperature dependence of the MCD signals that at least the $418 \cdot 4$ nm line and the $384 \cdot 5$ nm line are due to a different centre or centres from the $562 \cdot 8$ nm line. These two lines are due to transitions from a degenerate ground state, while the centre responsible for the $562 \cdot 8$ nm line has a singlet ground state. The $547 \cdot 2$ nm line in X-irradiated LiF : U, O is possibly associated with a change of some form by irradiation of the centres giving the $505 \cdot 2$ nm absorption line, which is associated with a tetragonal impurity centre, possibly containing the hydroxyl ion.

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