

Optical and ESR studies of U^{5+} luminescent molecular centers in x- and γ -irradiated $LiF-U_3O_8$ crystals

R. Parrot and C. Naud

Université P. et M. Curie, Laboratoire de Luminescence, 4, place Jussieu - 75230 Paris Cedex 05, France*

C. J. Delbecq and P. H. Yuster

Argonne National Laboratory, Argonne, Illinois 60439

(Received 9 February 1976)

Optical spectra are reported of several new U^{5+} centers of noncubic symmetry appearing after x or γ irradiation of LiF crystals doped with uranium oxides. Two of these centers are studied in detail. First, all of their seven energy levels are determined by absorption, emission, and excitation experiments. Second, optical and ESR studies of the growing rates of these centers under irradiation show that one of them can most likely be associated to a $(U^{5+}O_3F)^{6-}$ center of C_{4v} symmetry already known in ESR. Finally, the energy levels and g factors of the U^{5+} ions in C_{4v} symmetry are calculated in a crystal-field model by using a best-fit procedure whose validity is discussed.

I. INTRODUCTION

The optical and paramagnetic properties of transuranium elements have been extensively studied experimentally as well as theoretically over the last three decades¹ so that many detailed results concerning the $5f^n$ shells are now available.

In the case of uranium ions, many ionization states have been studied in various compounds. The most studied ion has been U^{4+} ($5f^2$) for which many optical results as well as electron and ultrasonic paramagnetic resonance studies have been published.²⁻¹⁰ Since its identification by Bleaney *et al.*¹¹ in CaF_2 and BaF_2 few optical studies of U^{3+} have been reported although some recent works on this ion were concerned with the spin-lattice relaxation¹² and the electric field effect on EPR spectra.¹³ Only optical-absorption spectra⁴ and gyromagnetic factors¹⁴ of presumed U^{2+} ions in CaF_2 have been recently published.

Early detailed results on $5f^1$ configurations with which we will be mainly concerned here were obtained on neptunium hexafluoride by Eisenstein *et al.*¹⁵ and Hutchinson *et al.*^{16,17} and on tetravalent protactinium in Cs_2ZrCl_6 by Axe *et al.*¹⁸ In the case of uranium, many complexes of pentavalent uranium were grown by Penneman *et al.*¹⁹ and the absorption spectrum of $CsUF_6$ was studied in detail by Reisfeld.²⁰ EPR studies were performed recently on $LiUF_6$, $NaUF_6$, $NOUF_6$ and $CsUF_6$ by Rigny *et al.*^{21,22} and Drifford *et al.*²³ Recently, a study of presumed U^{5+} ions in zircon²⁴ was reported, however no detailed interpretation of the optical results was made to reinforce the experimental observations.

In the case of alkali halides doped with uranyl acetate, nitrate, and sulfate, emission spectra

of uranium have been recorded for a long time²⁵ but it is only recently that experiments on the emission as well as the absorption spectra have been performed to understand the origin of the numerous lines appearing in these spectra. In particular, many detailed investigations on the piezospectroscopic effect,²⁶ the temperature shifts,²⁷ and the linear Stark effect^{28,29} have been made on the lines appearing in LiF and NaF crystals doped with uranyl salts. However, the origin of the very complex spectra appearing in these compounds is not yet understood; most of the authors working on this subject consider the observed spectra as being due to U^{6+} ions whose electronic configuration is that of radon so that the observed spectra could be due to excited configurations of U^{6+} .

A recent study by Lupei and Yuster³⁰ of new paramagnetic uranium centers created under γ or x irradiation in alkali halides doped with uranium oxides, and an analysis by Lupei and Ursu³¹ of a magnetic center associated to U^{5+} in C_{4v} symmetry led us to study the optical spectra of these ions and elaborate a coherent interpretation of both their optical and ESR spectra.

In Sec. II we will present typical optical spectra of LiF-U in nonirradiated and γ - or x-irradiated crystals and two sets of seven energy levels for U^{5+} centers in low symmetry. Section III will be concerned with the theoretical analysis of optical and magnetic properties of U^{5+} in C_{4v} symmetry and a discussion of the results.

II. EXPERIMENTS

A. Samples and experimental procedure

The crystals were grown by the Kyropoulos method. Three concentrations of uranium were

obtained by starting from the following quantities: 80-g LiF + 0.2-g U_3O_8 , 80-g LiF + 0.08-g U_3O_8 , 80-g LiF + 0.04-g U_3O_8 . Either natural uranium or uranium enriched in ^{235}U was used. Pure LiF crystals grown by Eagle-Picher were used as reference crystals in experiments under irradiation.

Optical-absorption experiments reported here were performed with a Cary 14 spectrometer and with Jobyn-Yvon HRS-2 spectrometers. Several preliminary analyses in the infrared region (1.5–3.5 μm) of the emission spectrum of x- and γ -irradiated LiF-U crystals were performed with a spectrometer manufactured by Huet (model GIRARD); further analysis in the 2–4- μm region was made with a HRS-2 spectrometer equipped with a 300-lines/mm grating blazed at 3 μm . The excitation light came from a 450-W xenon lamp and was filtered by a prism monochromator (Zeiss SPM 1). In excitation experiments, the exciting light (3500 \AA to 1.8 μm) was filtered by HRS-2 spectrometers equipped with different gratings, the fluorescent light passed through a germanium filter (thickness 0.5 mm, transparent for $\lambda > 1.8 \mu\text{m}$) and was detected by a PbS cell cooled at 195 K. These experiments were performed either at room temperature or at liquid-nitrogen temperature in cryostats with quartz windows.

The EPR experiments were made with a Varian 4502 spectrometer operating in the X band (9.2 GHz). A temperature regulated gas flow of cooled nitrogen permitted obtaining any temperature between 93 and 300 K.

The x irradiation was performed with 50-keV x rays. The γ irradiation was performed with a Co source.

B. Optical experiments, energy levels

Figures 1(b) and 2(b) show clearly the complexity of the absorption spectrum of nonirradiated LiF-U crystals appearing at liquid-nitrogen temperature in the region 3300–5300 \AA and the absence of any absorption line in the region 5300–25 000 \AA .

As usually recognized, the absence of either an absorption line or emission line in the near infrared region is an indication that no U^{2+} , U^{3+} , and U^{4+} centers exist in nonirradiated LiF-U crystals since their spectra should extend from the ir region to the uv region as demonstrated for example by Conway² for U^{4+} and more recently by Hargreaves⁴ for U^{2+} , U^{3+} , and U^{4+} ; furthermore U^{5+} centers are not expected since both the high value of the spin-orbit coupling constant ($\lambda \sim 1800 \text{ cm}^{-1}$) and experiments in other compounds indicate that emission and several absorption lines should appear in the ir region. This remark led us to consider the possibility of obtaining and clearly recognizing strongly ionized uranium centers by irradiating LiF-U crystals. After unsuccessful attempts to create new uranium centers by uv irradiation either at room or liquid-nitrogen temperature, γ - and x-irradiation experiments were performed.

Figures 1(a) and 2(a) represent absorption spec-

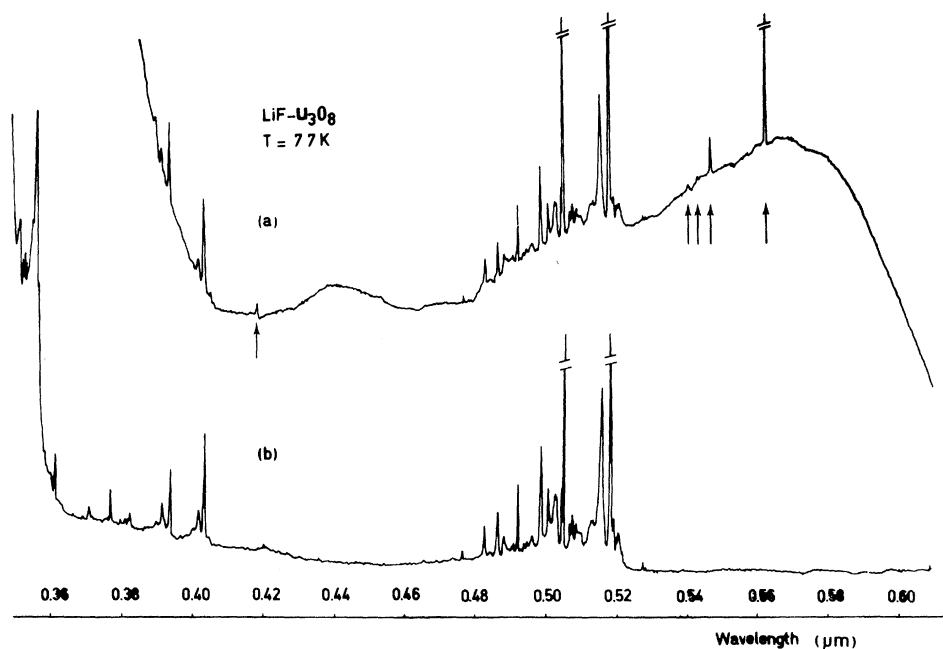


FIG. 1. Absorption spectra of (a) γ -irradiated and (b) nonirradiated LiF- U_3O_8 crystals. The new lines appearing in γ -irradiated crystals are indicated by arrows.

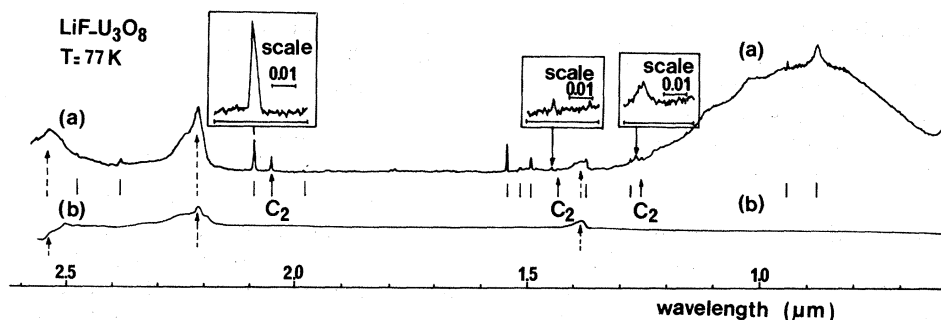


FIG. 2. (a) Infrared absorption spectra of γ -irradiated $LiF-U_3O_8$ crystals. The vertical bars give the positions of the observed absorption lines. The inserts represent the absorption lines of the center C_1 studied in this paper. The arrows give the positions of another uranium center (center C_2). The spurious absorption bands of the Cary 14 spectrometer are indicated by broken arrows. (b) No absorption line is observed in the infrared region in nonirradiated crystals.

tra obtained at liquid-nitrogen temperature after γ irradiation at room temperature. The band centered at 4400 \AA can be one of the absorption bands of the M centers in $LiF-U$. These bands appear in pure LiF crystals irradiated under like conditions of irradiation. Two other bands centered at 5700 and 9500 \AA appear in $LiF-U$ but did not in pure LiF . In addition to these bands many new narrow lines can be distinguished on these spectra in the visible region as well as in the ir region. [Several very small lines indexed in Fig. 2(a) appear clearly after a very long period of irradiation.] In order to refute the objection that these lines or several of them could be due to the formation on the surface of the crystals of uranium oxides or nitrates during the irradiation in presence of air, absorption experiments were carried out on irradiated samples and on the core of these samples. No difference in the spectra was observed. In an attempt to simplify the absorption spectra, we tried to avoid electron trapping and therefore the creation of color centers such as F , M centers and F_2^- molecular centers. Absorption experiments were therefore performed by irradiating briefly the crystals at liquid-nitrogen temperature and maintaining this temperature during the optical experiments. A spectrum showing only the three new lines given in the inserts in Fig. 2(a) and one new line at 5628 \AA [see Fig. 1(a)] was observed under these conditions. This experiment indicates that electron trapping in the neighborhood of the uranium ions could be the origin of the appearance of many different centers in low symmetry. We will demonstrate below by means of emission and excitation experiments that the three lines given in the inserts in Fig. 2(a) are three absorption lines of one U^{5+} center which will be denoted C_1 center and that the three lines marked by an arrow in Fig. 2(a) are three

absorption lines of another U^{5+} center (denoted C_2 center in the following). We will also demonstrate that none of the new absorption lines appearing in Fig. 1 can be associated to centers C_1 or C_2 .

For convenience, the experiments in emission and excitation were performed under x irradiation. In order to get an adequate signal to noise ratio, we had to irradiate the crystals so heavily that

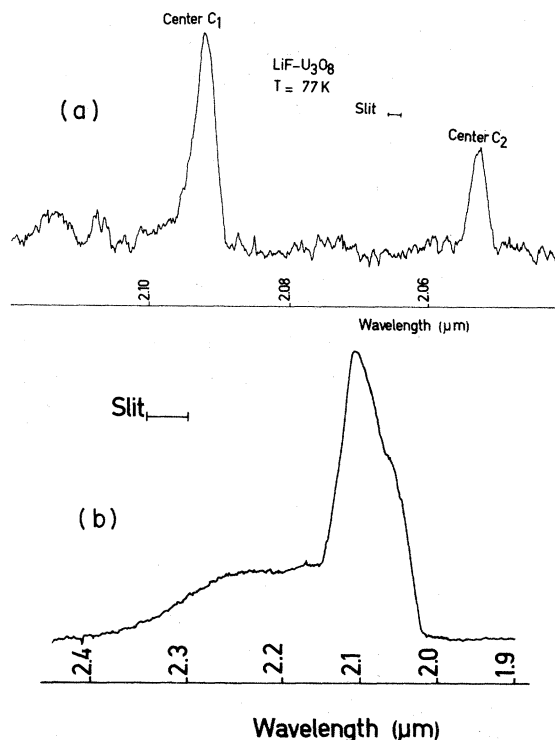


FIG. 3. Emission spectra of the centers C_1 and C_2 . (a) The zero-phonon lines. (b) The zero-phonon emission lines and emission bands of the centers C_1 and C_2 .

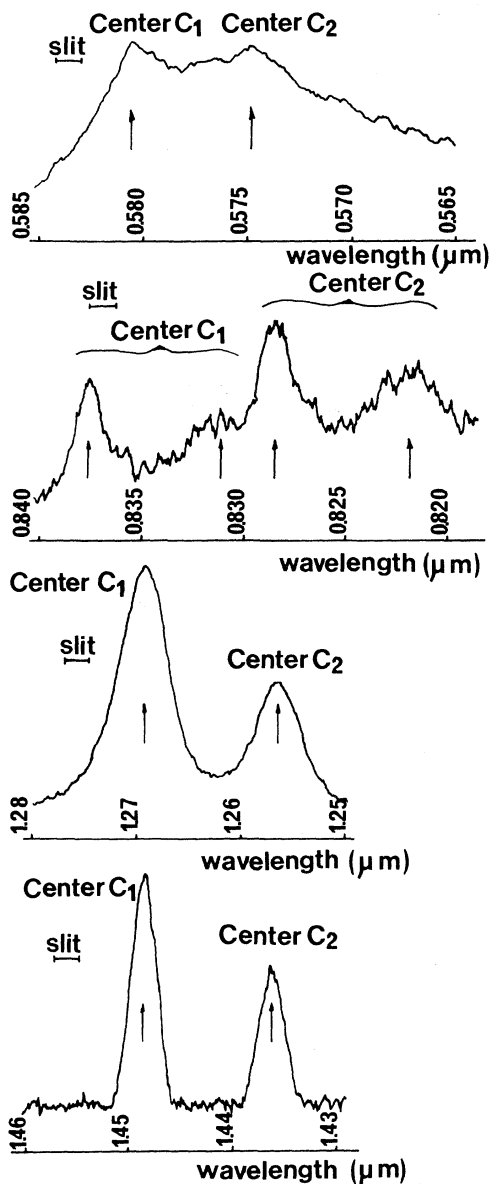


FIG. 4. Excitation spectra of the centers C_1 and C_2 . Owing to the smallness of the signal-to-noise ratio and the presence of strong emission lines of the xenon lamp in the region 0.82–0.84 μm , the indexation of the excitation lines is somewhat dubious in this region.

two U^{5+} centers (C_1 and C_2 centers) were observed simultaneously. Figure 3 represents the emission lines of the centers C_1 and C_2 . No other emission was observed in the range 2–4 μm . Figure 4 represents the excitation spectra of the centers C_1 and C_2 . Five energy levels were determined for each U^{5+} center by these spectra, two of them were already found in absorption experiments (levels at 6903 and 7878 cm^{-1} for the center C_1 , and at 6962 and 7958 cm^{-1} for the

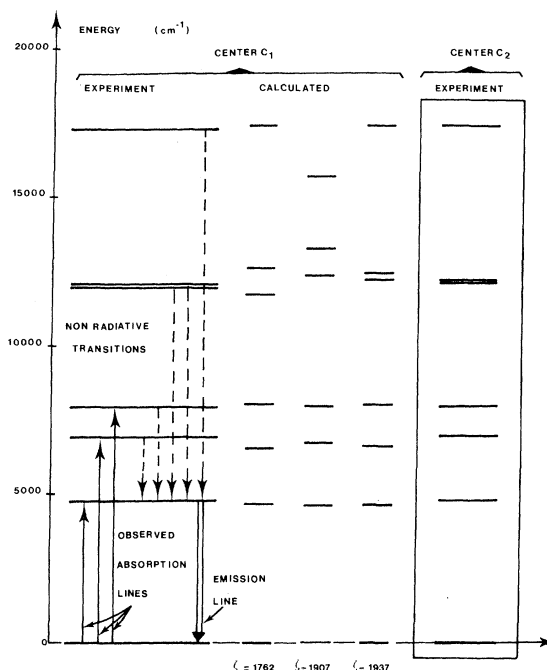


FIG. 5. Representation of the observed and calculated energy levels of center C_1 and observed energy levels of center C_2 . The broken arrows represent nonradiative transitions to the fluorescent level. The three upper levels at higher energy were observed in excitation spectra only. The calculated energy levels are also given in Table I.

center C_2); none of the three other energy levels was observed in absorption experiments. It must be noted that no other excitation line was observed in the range 3500–18000 \AA . The results of these optical experiments are summarized in Fig. 5 and Table I.

C. Growing rates

Although the paramagnetic resonance of U^{5+} centers had been previously reported in irradiated LiF crystals,^{30,31} experiments were needed to identify unambiguously the fundamental levels of the centers C_1 and C_2 . The method used for this purpose was to study simultaneously the growing rates of the centers C_1 and C_2 in terms of the x irradiation and the growing rate of a predominant U^{5+} center appearing in EPR spectra and interpreted by Lupei and Ursu as being due to U^{5+} centers in C_{4v} symmetry.³¹

Figure 6(a) represents the optical-absorption coefficients for centers C_1 and C_2 in terms of the x irradiation. (The x irradiation was performed at room temperature and the absorption coefficients were measured at 77 K on the lines at 4778 and 4867 cm^{-1} .) This figure shows that the

TABLE I. Experimental energy levels of centers C_1 and C_2 and calculated energy levels of center C_1 (in cm^{-1}).

Experimental energy levels	Center C_1 Calculated energy levels			Center C_2 Experimental energy levels
	False minimum 1	Best fit	False minimum 2	
17 240	17 428	17 421	15 684	17 395
12 030	12 424	12 577	13 258	12 167
11 939	12 191	11 696	12 320	12 070
7878	7970	8017	7922	7958
6903	6586	6620	6672	6962
4778	4607	4696	4596	4867

absorption coefficient of the center C_2 increases continuously, while the absorption coefficient of the center C_1 reaches a maximum for an irradiation time of approximately 20 min and then decreases. (The same behavior of centers C_1 and C_2 was also observed under γ irradiation.)

The predominant U^{5+} center appearing in ESR spectra in x-irradiated LiF crystals has been described by the following Hamiltonian by Lupei

and Ursu³¹:

$$\mathcal{H} = g_{\parallel} \mu_B H_Z S_Z + g_{\perp} \mu_B (H_x S_x + H_y S_y) + A_F S_x I_{F_x} + B_F (S_x I_{F_x} + S_y I_{F_y}).$$

S is the spin of the U^{5+} ion. I_F is the nuclear spin of fluorine ions ($I_F = \frac{1}{2}$). The numerical values of the constants are: $|g_{\parallel}| = 0.2523$, $|g_{\perp}| = 0.4708$, $|A_F| = 11.8 \times 10^{-4} cm^{-1}$, and $|B_F| = 7.5 \times 10^{-4} cm^{-1}$.³¹ The ESR experiments led these authors to adopt the model given in Fig. 7 for the U^{5+} center of C_{4v} symmetry. The growing rate of this center [see Fig. 6(b)] was studied in ESR experiments by measuring, at 93 K, the peak-to-peak amplitude of the derivative of the absorption lines. The magnetic field was oriented along a [100] crystallographic axis. It must be noted that several weak

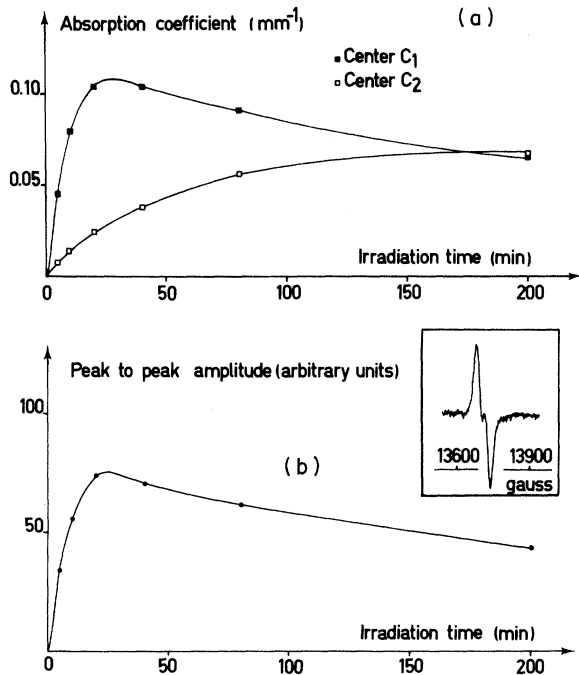


FIG. 6. (a) Absorption coefficients of the centers C_1 and C_2 in terms of the x irradiation. The measurements were performed on the lines at $4778 cm^{-1}$ (center C_1) and $4867 cm^{-1}$ (center C_2). (b) Peak-to-peak amplitude of the derivative of the absorption lines of the U^{5+} centers in C_{4v} symmetry, in terms of the x irradiation. The insert represents the line appearing at lower magnetic field ($\vec{H} \parallel [100]$). The splitting of this line is due to a superhyperfine interaction with one fluorine ion.

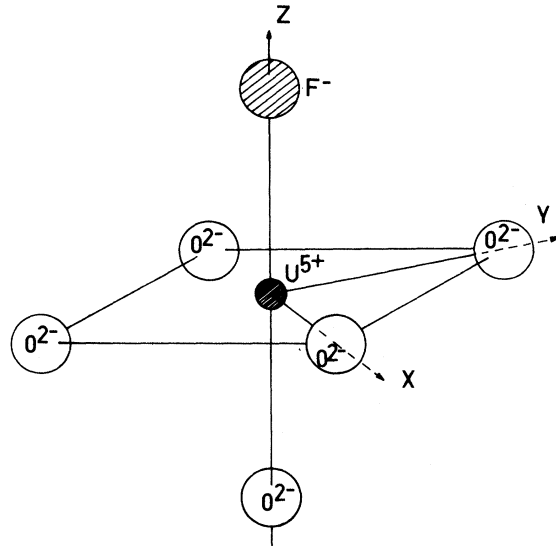


FIG. 7. Adopted structure for the center C_1 and axis system used in the calculations. Of course the F^- ion can replace any one of the six oxygen ions, so that three differently oriented centers are observed in ESR experiments.

absorption lines of other centers appeared in the region 6–18 kG after the x irradiation, however, the ESR spectrum of the center C_2 was not unambiguously identified in these experiments.

A comparison of Figs. 6(a) and 6(b) clearly shows that the growing rates of the center C_1 and of the U^{5+} center of C_{4v} symmetry are identical so that the center C_1 can most likely be attributed to the molecular center given in Fig. 7.

III. INTERPRETATION

The crystal-field calculations were performed for U^{5+} ions in C_{4v} symmetry. In a first step we determined all sets of parameters (five crystal-field parameters and the spin-orbit coupling constant ζ_{5f}) giving an exact fitting for all energy levels. Next the g factors of the fundamental level were deduced from the calculated wave functions. The calculated g_{\perp} factors not being in good agreement with the experimental values, the fitting procedure was extended to the g factors of the fundamental level.

The crystal-field parameters B_k^q for a $5f_1$ electron in C_{4v} symmetry can be defined, in the axis system given in Fig. 7, by the crystal-field Hamiltonian

$$\mathcal{H}_C = B_2^0 C_0^2 + B_4^0 C_0^4 + B_4^4 (C_4^4 + C_{-4}^4) \\ + B_6^0 C_0^6 + B_6^4 (C_4^6 + C_{-4}^6).$$

The C^k 's are electronic tensor operators related to the spherical harmonics Y^k by

$$C^k = [4\pi/(2k+1)]^{1/2} Y^k.$$

The chosen basis $\{t\tau j\}$ is defined in Table II. The matrix elements of the spin-orbit interaction \mathcal{H}_{SO} (diagonal in j) are $\langle \frac{5}{2} | \mathcal{H}_{SO} | \frac{5}{2} \rangle = -2\zeta_{5f}$ and $\langle \frac{7}{2} | \mathcal{H}_{SO} | \frac{7}{2} \rangle = \frac{3}{2}\zeta_{5f}$. The matrix elements of \mathcal{H}_C (diagonal in $t\tau$) were calculated with the following

formula:

$$\langle t\tau j | C_q^k | t\tau j' \rangle \\ = (-1)^{j+1/2} ([j][j'])^{1/2} \begin{Bmatrix} j & k & j' \\ 3 & \frac{1}{2} & 3 \end{Bmatrix} \langle 3_{\parallel} C^k_{\parallel} 3 \rangle \\ \times \sum_{m_l, m_l'} (-1)^{m_l} (t\tau j | 3m_l) (t\tau j' | 3m_l') \\ \times \begin{pmatrix} 3 & k & 3 \\ -m_l & q & m_l' \end{pmatrix} ([j] = 2j+1).$$

The needed g tensors were easily calculated by writing the Zeeman Hamiltonian in terms of tensor operators of rank 1 for the orbital momentum and for spin. Since no plausible solution was obtained giving a lower Γ_6 doublet (anticipating the results of the fitting procedures), we will only give the general form of the tensor for the four perturbed Γ_7 doublets. Defining the two components of a perturbed Γ_7 doublet by

$$| \Gamma_7 \pm \rangle = \alpha | \Gamma_7(\frac{5}{2}) \pm \frac{1}{2} \rangle + \beta | \Gamma_7'(\frac{5}{2}) \pm \frac{1}{2} \rangle \\ + \gamma | \Gamma_7(\frac{7}{2}) \pm \frac{1}{2} \rangle + \delta | \Gamma_7'(\frac{7}{2}) \pm \frac{1}{2} \rangle,$$

the two components of the g -tensors are given by

$$g_{\parallel} = \frac{2}{7} \{ -5\alpha^2 + 8(5)^{1/2} \alpha \beta + (8/\sqrt{3}) \alpha \gamma - 4\alpha \delta \\ + 11\beta^2 + [2(5)^{1/2}/\sqrt{3}] \beta \gamma + 2(5)^{1/2} \beta \delta \\ + 12\gamma^2 + 16\sqrt{3} \gamma \delta - 4\delta^2 \}$$

and

$$g_{\perp} = \frac{2}{7} [-5\alpha^2 + 8/\sqrt{3} \alpha \gamma + 5\beta^2 - 4\sqrt{5} \alpha \beta + 2\alpha \delta \\ - (\sqrt{5}/\sqrt{3}) \beta \gamma - 8\sqrt{3} \gamma \delta - (5)^{1/2} \beta \delta + 12\gamma^2 - 12\delta^2].$$

Owing to the relative complexity of the $(UO_5F)^{6-}$ molecular centers with respect to known U^{5+} centers, we did not try to use as a guide for the fitting procedures, the previously determined values of the crystal-field parameters in known cubic

TABLE II. Chosen basis for a $5f$ electron in a crystal field of C_{4v} symmetry.

States	Wave functions
$j = \frac{5}{2} \quad \Gamma_7 \pm \frac{1}{2}$	$[1/(6)^{1/2}] \frac{5}{2} \pm \frac{5}{2} \rangle - [(5)^{1/2}/(6)^{1/2}] \frac{5}{2} \mp \frac{3}{2} \rangle$
$\Gamma_6 \pm \frac{1}{2}$	$ \frac{5}{2} \pm \frac{1}{2} \rangle$
$\Gamma_7' \pm \frac{1}{2}$	$[(5)^{1/2}/(6)^{1/2}] \frac{5}{2} \pm \frac{5}{2} \rangle + [1/(6)^{1/2}] \frac{5}{2} \mp \frac{3}{2} \rangle$
$j = \frac{7}{2} \quad \Gamma_6 \pm \frac{1}{2}$	$\pm [(5)^{1/2}/(12)^{1/2}] \frac{7}{2} \mp \frac{7}{2} \rangle \pm [(7)^{1/2}/(12)^{1/2}] \frac{7}{2} \pm \frac{1}{2} \rangle$
$\Gamma_7 \pm \frac{1}{2}$	$\pm \frac{1}{2} \sqrt{3} \frac{7}{2} \pm \frac{5}{2} \rangle \mp \frac{1}{2} \frac{7}{2} \mp \frac{3}{2} \rangle$
$\Gamma_6' \pm \frac{1}{2}$	$\pm [(7)^{1/2}/(12)^{1/2}] \frac{7}{2} \mp \frac{7}{2} \rangle \mp [(5)^{1/2}/(12)^{1/2}] \frac{7}{2} \pm \frac{1}{2} \rangle$
$\Gamma_7' \pm \frac{1}{2}$	$\pm \frac{1}{2} \frac{7}{2} \pm \frac{5}{2} \rangle \pm \frac{1}{2} \sqrt{3} \frac{7}{2} \mp \frac{3}{2} \rangle$

TABLE III. Values (in cm⁻¹) of the spin-orbit coupling constants ζ_{5f} and of the crystal-field parameters B_k^q giving an exact fitting for the optical levels of the C_{4v} center of U⁵⁺ in LiF. The calculated (but not fitted) components of the g tensor are also given except when the fundamental level is a Γ_6 level.

ζ_{5f}	721	1027	1612	1624	1819
B_2^0	7571	6968	- 7966	- 8138	5897
B_4^0	30 085	29 285	-25 160	-24 835	23 535
B_4^4	9847	-9559	8518	- 8606	9039
B_6^0	3566	3930	- 2734	- 2664	6463
B_6^4	-773	772	949	- 1080	1134
g_{\parallel}	0.7756	0.2985	Γ_6	Γ_6	0.2320
g_{\perp}	1.1291	0.7266	Γ_6	Γ_6	0.2186

or nearly cubic compounds. Instead, we first tried to systematically find all mathematical solutions (even if physically implausible) for the spin-orbit parameter and the crystal-field parameters by fitting only the energy levels. Five different solutions for ζ_{5f} and the B_k^q 's giving an exact fitting for the optical transitions were found (see Table III). Two solutions giving very low values for ζ_{5f} ($\zeta_{5f} = 721$ cm⁻¹ and $\zeta_{5f} = 1027$ cm⁻¹) can be safely rejected. Two solutions corresponding to $\zeta_{5f} = 1612$ and 1624 cm⁻¹ give a lower Γ_6 level and one solution corresponding to $\zeta_{5f} = 1819$ cm⁻¹ gives a fundamental level Γ_7 whose

g_{\parallel} factor is in relatively good agreement with experiment ($g_{\parallel \text{expt}} = 0.2523$; $g_{\parallel \text{calc}} = 0.2320$), but g_{\perp} factor is in poor agreement with experiment ($g_{\perp \text{expt}} = 0.4708$; $g_{\perp \text{calc}} = 0.2186$).

We will now present the results obtained by fitting simultaneously the energy levels and the g factors of the fundamental level assumed to be a perturbed Γ_7 level. Of course, an exact fitting is no longer expected since eight experimental values (six for the optical transitions and two for the g factors) are to be fitted with six parameters. The parameters were computed by solving the following system of eight equations:

$$\frac{V_{\text{expt } i} - V_i}{V_{\text{expt } i}} = \frac{1}{V_{\text{expt } i}} \sum_{j=1}^6 \frac{\delta V_i}{\delta P_j} dP_j \quad (i=1-8), \quad (1)$$

and minimizing the quantity:

$$S = \sum_{i=1}^8 \left(\frac{V_{\text{expt } i} - V_i}{V_{\text{expt } i}} \right)^2. \quad (2)$$

$V_{\text{expt } i}$ is the i th experimental value. V_i is the value computed from a set of six parameters P_j . The introduction of $V_{\text{expt } i}$ in the denominators of formulas (1) and (2) is a coherent way to obtain a correct least-mean-squares fitting for both the energy levels (expressed in cm⁻¹) and the g factors. The best fit was obtained for a physically implausible value for ζ_{5f} ($\zeta_{5f} = 1210$ cm⁻¹, $s_{\text{min}} = 2.7 \times 10^{-3}$). However, ten false minima in the sense of Mackey *et al.*⁷ have been obtained during the calculation. Four physically implaus-

TABLE IV. Values of ζ_{5f} and of the B_k^q 's (in cm⁻¹) given by the best fit and by two "false" minima when fitting both the optical energy levels and the g factors for the C_{4v} center of U⁵⁺ in LiF. The mixing parameters $\alpha, \beta, \gamma, \delta$ are defined in Sec. III.

ζ_{5f}	False minimum 1 ($s = 5.3 \times 10^{-3}$)	Best fit ($s = 4.9 \times 10^{-3}$)	False minimum 2 ($s = 2.2 \times 10^{-2}$)
	1937	1762	1907
B_2^0	6069	7549	- 3818
B_4^0	22 826	21 418	17 196
B_4^4	9928	11 761	14 028
B_6^0	6674	6946	1798
B_6^4	102	586	- 885
g_{\parallel}	0.2496	0.2497	0.2503
$g_{\parallel \text{expt}} = 0.2523$			
g_{\perp}	0.4654	0.4667	0.4645
$g_{\perp \text{expt}} = 0.4708$			
α	0.935 61	0.919 58	0.934 53
β	0.034 24	0.093 00	0.011 00
γ	0.350 93	0.381 73	0.352 43
δ	- 0.017 44	0.002 11	0.048 19

ible solutions corresponding to $\zeta_{sf} = 1266; 1268, 1270, \text{ and } 1284 \text{ cm}^{-1}$ have been rejected. Amongst the six remaining physically plausible solutions corresponding to $\zeta_{sf} = 1708 \text{ cm}^{-1}$ ($s_{\min} = 3.7 \times 10^{-2}$); 1762 cm^{-1} ($s_{\min} = 4.9 \times 10^{-3}$); 1834 cm^{-1} ($s_{\min} = 3.0 \times 10^{-2}$); 1907 cm^{-1} ($s_{\min} = 2.2 \times 10^{-2}$); 1922 cm^{-1} ($s_{\min} = 2.5 \times 10^{-2}$); 1937 cm^{-1} ($s_{\min} = 5.3 \times 10^{-3}$); we selected the three solutions corresponding to the three lowest values for s . These three solutions are given in Table IV (in this table the best fit is that obtained for the plausible solutions). The calculated energy levels corresponding to the best fit and to the two "false" minima are given in Table I.

The computed values given in the last column of Table III, and in Table IV necessitate several comments.

First, during the calculations, it appeared that the g factors (Table IV) depend on all the mixing parameters. In particular, the contribution to the g factors of the relatively small β and γ mixing parameters is as important as the contribution of the other parameters.

Second, the values reported in Table IV show that the sign of B_2^0 (and B_6^4) is not the same for all the plausible solutions. It is thus necessary to discuss the physical validity of the B_k^q 's

The crystal-field parameters $B_k^q/\langle r^k \rangle$ were calculated in a point-charge model by adapting the results obtained by Barthou in octahedral symmetry to our problem.³² The calculation was performed by assuming that no deformation of the LiF structure occurs when introducing the $(\text{UO}_5\text{F})^{6-}$ center in the lattice. (This hypothesis is justified by the closeness of the ionic or covalent radii of Li^+ and U^{5+} , and O^{2-} and F^- ions.) 1331 cells were taken into account, each cell containing eight ions. The calculated $B_k^q/\langle r^k \rangle$'s were found to be $B_2^0/\langle r^2 \rangle = -4010 \text{ cm}^{-1}/a_0^2$, $B_4^0/\langle r^4 \rangle = 1690 \text{ cm}^{-1}/a_0^4$, $B_4^4/\langle r^4 \rangle = 1180 \text{ cm}^{-1}/a_0^4$, $B_6^0/\langle r^6 \rangle = 14 \text{ cm}^{-1}/a_0^6$, and $B_6^4/\langle r^6 \rangle = -63 \text{ cm}^{-1}/a_0^6$ (a_0 is the first Bohr radius). Thus, the crystal-field model justifies the signs of the B_k^q 's as given by the false minimum 2 (see Table IV). However, a detailed analysis shows that the value and even the sign of B_2^0 (and also B_6^0) depend upon the electric charges of the nearest neighbors so that it could be misleading to eliminate the set of parameters corresponding to the false minimum 1 or to the best fit or both (see Table IV).

Finally, we must remark that none of the so-

lutions given in Table III is in agreement with the crystal-field model. In particular, two solutions giving a fundamental Γ_6 level can be safely rejected.

IV. CONCLUSION

Amongst the numerous new centers created by x and γ irradiation of LiF doped with uranium oxides, two have been clearly identified as being due to U^{5+} ions. All seven energy levels of these ions in low symmetry have been determined by absorption, emission, and excitation experiments. One of these centers has been attributed to U^{5+} centers in C_{4v} symmetry whose g tensor for the fundamental state was already known. Unfortunately, the small number of U^{5+} centers created under irradiation did not allow us to perform Zeeman experiments on the optical levels nor double-resonance experiments which could have permitted us to relate directly the fundamental level to the excited levels.

In the interpretation of the experimental results, the difficulties often encountered in the studies of uranide ions were strongly enhanced due to the low symmetry and the expected effects of covalency of the surrounding oxygen ions. A parametrization procedure performed by fitting exactly all energy levels has shown that one set of parameters (five crystal-field parameters and the spin-orbit coupling constant) gives a correct value for the g_{\parallel} factor but a g_{\perp} factor which is in poor agreement with experiment. Another set of parameters was obtained from the best fit for both the g tensor of the fundamental level and the optical energy levels. This last set of parameters permitted us to calculate all the energy levels with an error less than 550 cm^{-1} and the g factors with an error less than 0.01. However, the presence of two "false" minima appearing during the computation indicates that one must be very careful in using this set of parameters for further calculations.

ACKNOWLEDGMENTS

One of us (R.P.) would like to thank Dr. O. C. Simpson for the opportunity to do the preliminary experiments at Argonne National Laboratory. Thanks are due to Professor W. A. Runciman and to Professor B. R. Judd for very helpful discussions concerning the spectroscopy of uranide ions. We are also indebted to Dr. J. Vincent, J. Cartigny, and Y. Delaval for use of the Huet spectrometer.

- *Equipe de recherche associée au Centre National de la Recherche Scientifique.
- ¹G. H. Dieke, and A. B. F. Duncan, *Spectroscopic Properties of Uranium Compounds* (McGraw-Hill, New York, 1949).
- ²J. G. Conway, *J. Chem. Phys.* **31**, 1002 (1959).
- ³R. S. Title, P. P. Sorokin, M. J. Stevenson, G. D. Pettit, J. E. Scardefield, and J. R. Lankard, *Phys. Rev.* **128**, 1 (1962).
- ⁴W. A. Hargreaves, *Phys. Rev. B* **2**, 2273 (1970).
- ⁵S. D. McLaughlan, *Phys. Rev.* **150**, 118 (1966).
- ⁶I. Richman, P. Kisliuk, and E. Y. Wong, *Phys. Rev.* **155**, 2 (1967).
- ⁷D. J. Mackey, W. A. Runciman, and E. R. Vance, *Phys. Rev. B* **11**, 211 (1975).
- ⁸H. C. Meyer, P. F. Mc Donald, and J. D. Stettler, *Phys. Lett. A* **24**, 569 (1967).
- ⁹G. C. Wetsel, Jr., *J. Appl. Phys.* **39**, 692 (1968).
- ¹⁰D. R. Johnston, R. A. Satten, C. L. Schreiber, and E. Y. Wong, *J. Chem. Phys.* **44**, 3141 (1966).
- ¹¹B. Bleaney, P. M. Llewellyn, and D. A. Jones, *Proc. Phys. Soc. Lond. B* **69**, 858 (1956).
- ¹²R. Furrer, F. Seiff, and J. Pelzl, *Phys. Status Solidi* **63**, 549 (1974).
- ¹³A. Kiel, and W. B. Mims, *Phys. Rev. B* **7**, 2917 (1973).
- ¹⁴P. F. Mc Donald, E. L. Wilkinson, and R. A. Jensen, *J. Phys. Chem. Solids* **28**, 1629 (1967).
- ¹⁵J. C. Eisenstein, and M. H. L. Pryce, *Proc. Soc. A* **255**, 181 (1959).
- ¹⁶C. A. Hutchinson, Jr., and B. Weinstock, *J. Chem. Phys.* **32**, 56 (1960).
- ¹⁷C. A. Hutchinson, Jr., T. Tsang, and B. Weinstock, *J. Chem. Phys.* **37**, 555 (1962).
- ¹⁸J. D. Axe, H. J. Stapleton, and C. D. Jeffries, *Phys. Rev.* **121**, 1630 (1961).
- ¹⁹R. A. Penneman, G. D. Sturgeon, and L. B. Asprey, *Inorg. Chem.* **3**, 126 (1964).
- ²⁰M. J. Reissfeld and G. A. Crosby, *Inorg. Chem.* **4**, 65 (1965).
- ²¹P. Rigny, and P. Plurien, *J. Phys. Chem. Solids* **28**, 2589 (1967).
- ²²P. Rigny, A. J. Dianoux, and P. Plurien, *J. Phys. Chem. Solids* **32**, 1175 (1971).
- ²³M. Drifford, P. Rigny, and P. Plurien, *Phys. Lett. A* **27**, 620 (1968).
- ²⁴E. R. Vance and D. J. Mackey, *J. Phys. C* **7**, 1898 (1974).
- ²⁵M. K. Slattery, *J. Opt. Soc. Am.* **19**, 175 (1929).
- ²⁶A. A. Kaplyanskii and N. A. Moskvin, *Opt. Spectrosc.* **14**, 357 (1963).
- ²⁷A. A. Kaplyanskii, N. A. Moskvin, and P. P. Feofilov, *Opt. Spectrosc.* **16**, 339 (1964).
- ²⁸O. D. Gavrilov, A. A. Kaplyanskii, V. N. Medvedev, and N. A. Moskvin, *Opt. Spectrosc.* **27**, 521 (1969).
- ²⁹A. A. Kaplyanskii, V. N. Medvedev, N. A. Moskvin, and O. D. Gavrilov, *J. Lumin.* **1**, 923 (1970).
- ³⁰V. Lupei and P. H. Yuster, in *Proceedings of the Seventeenth Ampere Congress, Turku, 1972* (Wikuri Physical Laboratory, Turku, Finland, 1972), p. 93.
- ³¹V. Lupei and I. Ursu, 18th Ampere Congress, Nottingham, 1974 (unpublished).
- ³²C. Barthou, *C. R. Acad. Sci. (Paris)* **271**, 1104 (1970).