

Electron paramagnetic resonance studies in photorefractive crystals I: Hyperfine interaction and photoinduced charge transfer in $^{233}\text{U}^{5+}$ and $^{238}\text{U}^{5+}$ doped LiNbO_3

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Abstract. Electron paramagnetic resonance studies were conducted on the photoinduced charge transfer and also hyperfine interaction of U^{5+} stabilized in photorefractive matrix LiNbO_3 . This work deals with: (i) first observation of hyperfine structure due to ^{233}U ($I = 5/2$) in its pentavalent state at octahedral sites and comparison with other possible site symmetries, (ii) photoinduced charge transfer as observable by EPR and its relevance to photorefractive behaviour of LiNbO_3 . The effect of chemical bonding on the hyperfine interaction of $5f^1$ configuration was also studied by converting the existing literature data on $^{235}\text{U}^{5+}$ to that of $^{233}\text{U}^{5+}$ by standard methods. This suggests that progressive substitution of oxygen by F^- , in the series UO_6^{7-} , $(\text{UO}_5\text{F})^{6-}$ and $(\text{UO}_4\text{F}_2)^{5-}$ drastically decreases the hyperfine coupling constant A_{\parallel} , along the local distortion axis. This trend is explained as being due to the absence of ligand ion along the distortion axis at U^{5+} site in trigonal LiNbO_3 . The effects of illumination by copper vapor laser (CVL) on the intensity of the U^{5+} signal was studied in the 10–300 K region. The kinetics of decay and restoration of U^{5+} was also studied between 10–100 K range. The decay kinetics was found to obey double exponential. The reduction of concentration of U^{5+} with CVL-illumination and its restoration in the absence of light show that pentavalent uranium takes part in the photorefractive effects in LiNbO_3 .

Keywords. Electron paramagnetic resonance; photorefraction; LiNbO_3 ; uranium; hyperfine interaction.

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1. Introduction

Lithium niobate is ferroelectric at room temperature [1] and it has exhibited many interesting properties. Notable among them is the first observation of photorefractive effect and the associated possibility of storing information in terms of holograms [2–4]. Mechanism of this process has been identified as due to the photoinduced charge transfer involving Fe^{3+} impurity. In the early years of the discovery of photorefractive effects in LiNbO_3 , the effect of impurities, particularly those of 3d-group, on photorefractive properties has been investigated [3]. The possibility of stabilizing Fe and Mn in different valence states facilitating the photoinduced charge transfer appears to be important for photorefraction. As multivalence is important, the trivalent lanthanides may not be good candidates for this process. On the other hand, uranium

exhibiting multivalence is potentially a good candidate to enhance photorefractive behaviour of LiNbO₃. Work of Okamoto *et al* [5] suggests that the uranium dopant enhances photorefractive sensitivity in U:LiNbO₃, however, the hologram is nearly permanent. It may be noted that in the sample of Okamoto *et al*, uranium may be in tetravalent/hexavalent states.

Burton Lewis *et al* [6] have shown that U⁵⁺ gets stabilized at Nb⁵⁺ sites in LiNbO₃, with six-fold oxygen coordination, on doping with U₃O₈. They have shown that the symmetry of site is almost perfectly octahedral. Among all the oxidation states of uranium the pentavalent ion, U⁵⁺, with outer electronic configuration, 5f¹, is an interesting candidate for electron paramagnetic resonance (EPR) investigations. In the case of U⁵⁺ ion in perfectly octahedral coordination, the 7-fold degenerate 5f-orbitals split into a_{2u}(Γ₂), t_{2u}(Γ₄) and t_{1u}(Γ₅) (Γ's are Bethe's notation) with the orbital singlets a_{2u} as the ground state [7,8]. The quenching of orbital angular momentum increases the spin-lattice relaxation time making its EPR observable at easily accessible temperatures. When spin orbit interaction is taken into account the symmetry classification of these levels would change, the lowest state being Γ₇. In the present work we have carried out a similar investigation with ²³⁸U⁵⁺/²³³U⁵⁺ doped LiNbO₃ directed at getting information on the hyperfine interaction between I = 5/2 of ²³³U and 5f¹ electron having a_{2u} character under octahedral symmetry and also to investigate the possible role of uranium ion in photoinduced charge transfer processes. The only published report on the hyperfine structure of ²³³U in EPR is of trivalent uranium in LaCl₃ by Dorain *et al* [9]. In this paper we present the results of three important aspects of U⁵⁺ in LiNbO₃: (i) The first report of hyperfine structure of ²³³U in its pentavalent form and in octahedral symmetry. (ii) The systematics of the hyperfine coupling constant of ²³³U⁵⁺ in (UO₆)⁷⁻ with progressive substitution of O²⁻ by the more ionic ligand F⁻. This was made possible by using the h.f.s. data available on ²³⁵U⁵⁺ in (UO₅F)⁶⁻ and (UO₄F₂)⁵⁻ sites stabilized in alkali fluorides [7, 10, 11]. (iii) The first report of the valence change of pentavalent uranium on illumination with copper vapor laser between 10–100 K.

2. Experimental

The sample of ²³³U⁵⁺ : LiNbO₃ was prepared by the flux method described by Lewis *et al* [6]. Appropriate quantities of Li₂CO₃, Nb₂O₅ and U₃O₈ (8% by weight) were mixed and the mixture was slowly added to the molten LiCl. After cooling the melt, the LiCl was easily leached out by dissolving in pure water leaving behind insoluble uranium doped in LiNbO₃. Further, the residue was washed with alcohol and dried under I.R. lamp. The XRD patterns of the sample showed that the LiNbO₃ formation was complete. Finally, the sample was sealed in quartz tubes for recording EPR spectra. This work was done in glove-box specially made for handling radioactive materials. The outer surface of the quartz tube was decontaminated by nitric acid, teepol and water before recording the spectra, which were measured at 77 K using a Bruker ESP-300 EPR spectrometer operating at the X-band frequency.

The effect of laser illumination on the EPR spectrum was studied using an optical transmission cavity. The sample LiNbO₃ in single crystal form doped with ²³⁸U was

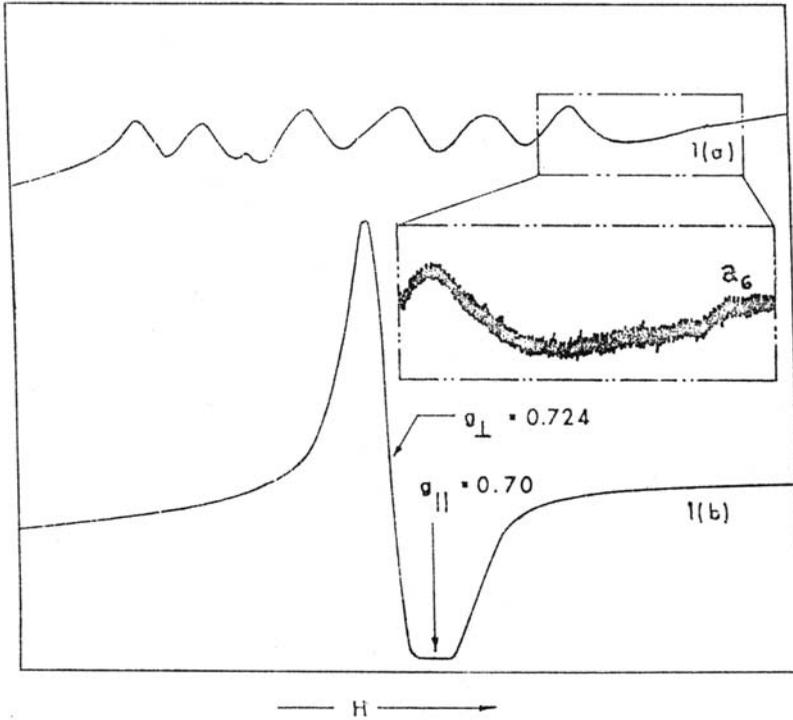


Figure 1. EPR spectrum of U^{5+} in $LiNbO_3$ powder at 77 K: (a) doped with $^{233}U_3O_8$; (b) doped with natural U_3O_8 . As expected the perpendicular spectrum is more intense than the parallel one. The g_{\parallel} value was calculated from $^{238}U^{5+}$ spectrum. The separation between field corresponding to g_{\parallel} , and high field hyperfine components of the parallel spectrum (a_6 in the inset) were used for calculating A_{\parallel} .

illuminated *in situ* using a 10 W copper vapor laser. The temperature of the sample was varied between 10 and 300 K using a closed cycle helium refrigerator supplied by M/S APD Cryogenics.

3. Experimental results

3.1 EPR spectra of $^{233}U^{5+}$

The EPR spectra obtained on $^{233}U^{5+}$ doped $LiNbO_3$ at 77 K is shown in figure 1(a). The EPR spectra obtained under identical condition for natural U^{5+} in $LiNbO_3$ are also shown in figure 1(b) for comparison. The spectrum of $^{233}U^{5+}$ consists predominantly of a sextet arising from hyperfine interaction with $I = 5/2$ of ^{233}U . In view of the powder nature of the sample it is attributed to the perpendicular components. From the natural uranium (V) spectrum it can be unambiguously seen that there is a slight g -anisotropy with $g_{\parallel} = 0.70$ and $g_{\perp} = 0.724$. These values are slightly different from the isotropic g reported by Lewis *et al* [6]. The g anisotropy as defined by Ursu and Lupei [7] is

$$\delta g = 3|(g_{\parallel} - g_{\perp})/(g_{\parallel} + 2g_{\perp})| \approx 0.02$$

Table 1. g -values of U^{5+} centre in $LiNbO_3$ and other reported U^{5+} complexes with oxygen coordination.

Nature of the complex	g_{\parallel}	g_{\perp}	Reference
$^{233}UO_6 : LiNbO_3$	0.710 ± 0.001	0.724 ± 0.001	Present work
$UO_5 V_F : LiF$ (Tg3)	0.13	0.595	10
$UO_6 : LiF$ (Tg4)	0.326	0.362	10

Table 2. Systematization of ^{233}U hyperfine coupling constant in $[UO_6]^{7-}$ with progressive fluoride substitution. The ^{233}U data on UO_5F and UO_4F_2 were calculated from the ^{235}U -h.f.s. data available.

Complex	A_{\parallel} (in 10^{-4} cm^{-1})	A_{\perp} (in 10^{-4} cm^{-1})	A_{iso} (in 10^{-4} cm^{-1})
$UO_6 : LiNbO_3$	145 ± 10	128 ± 2	134
$UO_5F : NaF$	119.6	146.9	137.8
<i>trans</i> $UO_4F_2 : NaF$	88.4	150.8	130.0
<i>trans</i> $UO_4F_2 : KF$	93.6	153.5	133.5

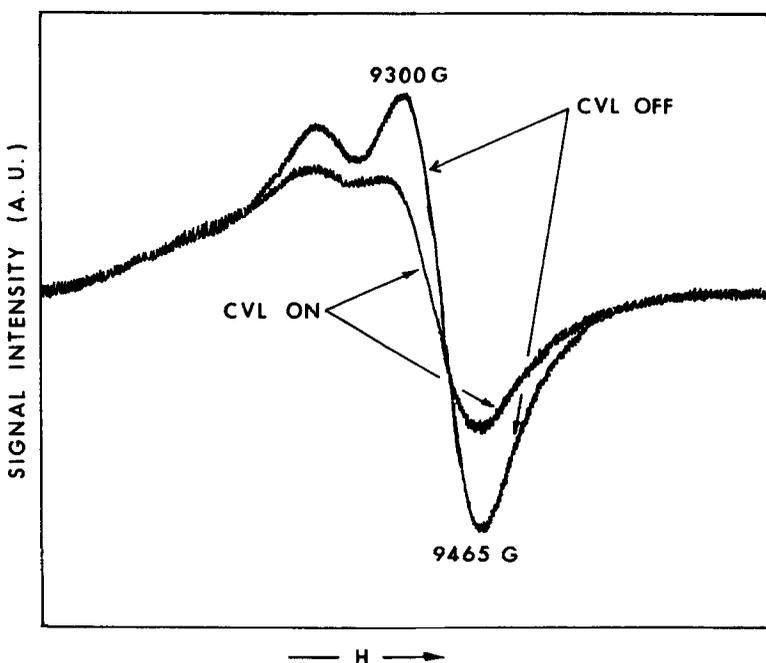


Figure 2. The effects of laser illumination on the EPR spectrum of U^{5+} in $LiNbO_3$ at 10 K. (a) Without laser, (b) with CVL illumination.

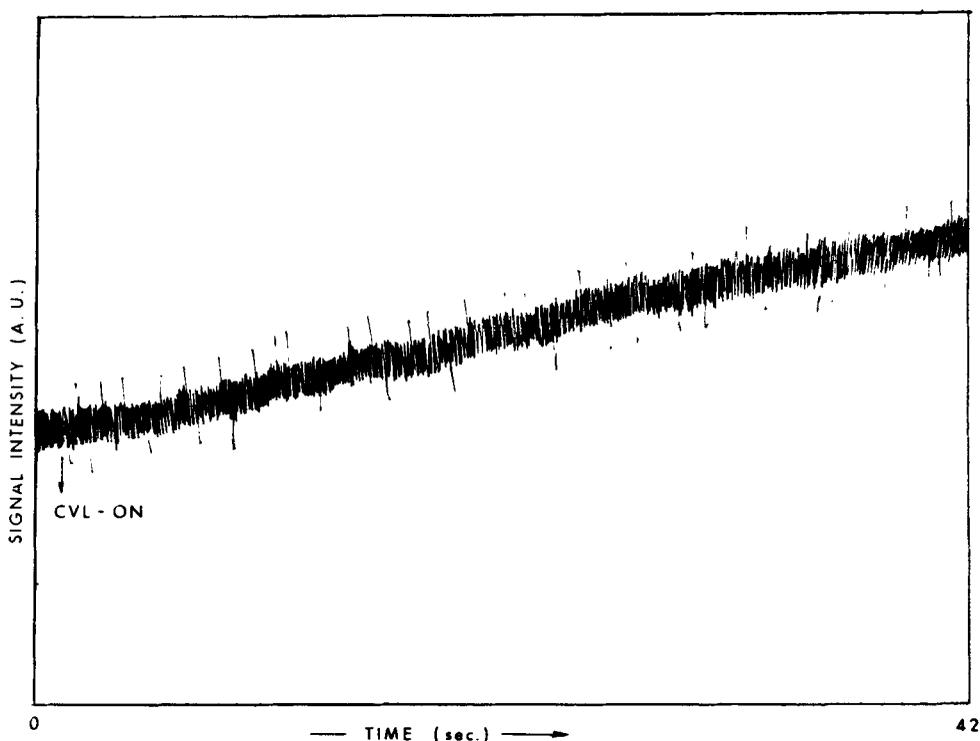


Figure 3a. The decay of EPR of U^{5+} signal on laser illumination. The apparent rise in the signal is due to locking of the field on the lower inflection point of the derivative signal.

which is considerably less than the corresponding values for U^{5+} in other octahedral oxy-fluoro coordinations. This point is of relevance in analyzing the hyperfine spectrum of $^{233}U^{5+} : LiNbO_3$ powder, in which the perpendicular component is most intense. In the EPR spectra of $^{235}U^{5+}$ in oxyfluoro coordinations in NaF and LiF, the quadrupole interaction has been reported [7] to be of the order of or stronger than the electron-nuclear (magnetic) interaction. The interaction term contains the product of z-component of electric field gradient (e.f.g.) produced by fluoride substitution in the first coordination and the quadrupole moment of ^{233}U nucleus. This gave rise to unusual hyperfine structure in the 'perpendicular' spectrum of $^{235}U^{5+} : LiF$ and it has been analyzed by a new perturbation scheme developed by Lupei *et al* [12]. This predicted a number of intense forbidden transitions ($\Delta m_I > 1$) and more interestingly, that the splitting of $m_I = +5/2$ and $+7/2$ ($I(^{235}U) = 7/2$) transitions should vanish at $\theta = 90^\circ$ resulting in an intense line at the centre (i.e. the field position corresponding to A.I.S = 0). It can be seen in figure 1(a) that these features are completely absent for $^{233}U^{5+} : LiNbO_3$ ($\theta = 90^\circ$) suggesting that quadrupole terms can be neglected, despite small anisotropy seen in the g-tensor. Therefore the hyperfine sextet was analyzed by standard methods and the spin Hamiltonian constants along with reported ones for other U^{5+} ions in oxy-fluoro coordinations are given in tables 1 and 2. As mentioned earlier this is the first report of hyperfine coupling constants for ^{233}U in pentavalent form. The only other report of

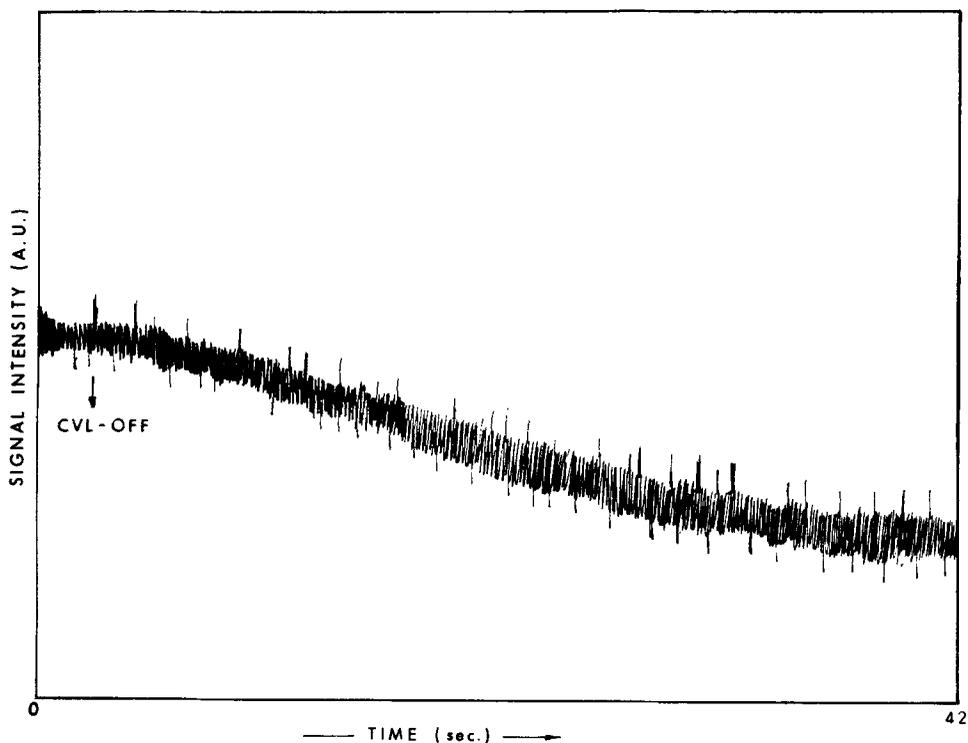


Figure 3b. The recovery of EPR signal of U^{5+} on switching off the laser.

similar data for ^{233}U was in trivalent form reported by Dorain *et al* [9] for $^{233}U^{3+}$ in $LaCl_3$.

3.2 Effects of illumination with copper vapour laser

As mentioned earlier $LiNbO_3$ single crystals doped with ^{238}U were used for these studies. U^{5+} was stabilized by gamma irradiation. The single crystal loaded in an optical transmission cavity (Bruker ER4104 OR) was illuminated using light from CVL (510 and 578 nm). Figure 2 shows the effect of laser illumination on the intensity of U^{5+} signal at 10 K. By locking the magnetic field on the EPR derivative peak (on the lower inflection point) the decay of the signal with laser illumination and recovery after CVL was put off and were recorded as a function of time. Figures 3(a) and (b) show the decay and recovery of the signal. (The apparent increase and decrease occurred respectively, for decay and growth as the field was locked on the lower inflection point of EPR signal.)

4. Discussion

4.1 Structure of pentavalent U-complex

EPR of U^{5+} was reviewed by Ursu and Lupei [7] and also more recently by Miyake [13]. Miyake discussed the dependence of g -value as a function of axial and orthorhombic

distortions and presented curves which can effectively be used for the estimation of axial and orthorhombic distortions. By analysis it may be concluded that for a perfect octahedral symmetry the g -value of U^{5+} is expected to be around 1.1 and under C_{2v} distortion the $|g|$ value decreases from this value. Further it was seen that the position of ground Γ_7 and excited Γ'_7 states were found to be independent of ϵ (axial distortion parameter) for small distortion and hence g -value is not expected to be highly anisotropic despite the lower site symmetry. From the g -value in the present case which is nearly isotropic, the axial distortion ϵ is estimated to be (from figure 6 of Miyake) 1100 cm^{-1} and orthorhombic distortion $|\epsilon r| = 270 \text{ cm}^{-1}$. U^{5+} ion in LiNbO_3 takes the position of Nb^{5+} site, having three long (2.113 Å) and three short (1.889 Å) Nb–O bonds in LiNbO_3 [3]. Therefore the g -value obtained is consistent with that expected at this site symmetry. The deviation from the expected g -value of $|J = 5/2, \Gamma_7\rangle$ state is also attributed for the crystal field admixing of upper $|J = 7/2, \Gamma_7\rangle$ state [8]. The expected g -value is

$$g = (-10/7) \cos^2 \alpha + (16/7\sqrt{3}) \cos \alpha \sin \alpha + (24/7) \sin^2 \alpha,$$

where $\cos \alpha$ and $\sin \alpha$ give the admixture of $|J = 5/2, \Gamma_7\rangle$ and $|J = 7/2, \Gamma_7\rangle$ states in the ground doublet. Using the g_{iso} value $\{g_{\parallel} + 2g_{\perp}\}/3$, the ground state doublet is found to have the form

$$|\pm\rangle = 0.905|J = 5/2, \Gamma_7\rangle + 0.308|J = 7/2, \Gamma_7\rangle.$$

The hyperfine constant for $^{233}\text{U}^{5+}$ ($5f^1$) depends upon the nature of ground state and it is given in terms of $\cos \alpha$ and $\sin \alpha$ by the expression [8]

$$A = 2g_n\beta\beta_n \langle r^{-3} \rangle [(-16/7) \cos^2 \alpha - (8/7\sqrt{3}) \cos \alpha \sin \alpha + (16/7) \sin^2 \alpha - k\{(5/21) \cos^2 \alpha + (16/7\sqrt{3}) \cos \alpha \sin \alpha + (3/7) \sin^2 \alpha\}],$$

where k is the constant related contribution from core polarization, $\langle r^{-3} \rangle$ is the expectation value for the radial distribution of the $5f$ electron and other symbols have their usual meaning. By taking A_{iso} as $134 \times 10^{-4} \text{ cm}^{-1}$, $\langle r^{-3} \rangle = 5.6 \text{ a.u.}$ and the values of $\cos^2 \alpha$ and $\sin^2 \alpha$, the hyperfine coupling constant takes the expression

$$A_{\text{iso}} = -2g_n\beta\beta_n \langle r^{-3} \rangle \{2.045 + k 0.643\},$$

the value of k for $^{233}\text{U}^{5+}$ being -3.18 .

4.2 Comparison with perturbed $(\text{UO}_6)^{7-}$ centres

Extensive EPR work has been reported on $^{238}\text{U}^{5+}$ and $^{235}\text{U}^{5+}$ in $(\text{U}(\text{O}_{6-x}\text{F}_x)_{x=1,2})^{7-}$ and $\text{UO}_5 \cdot \text{V}_F$ centres stabilized in LiF and NaF matrices [10, 12]. Among these, two centres with no fluorides in the immediate coordination were reported by Lupei and Lupei [10] on the basis of the absence of ^{19}F -s.h.f.s. These were designated as Tg3 and Tg4. The Tg3 centre was assumed to correspond to an $\text{U}^{5+}-\text{O}_5$ associated with an F-vacancy taking the place of $\text{Li}-\text{F}_6$ octahedron. Therefore Tg3 takes the form of $(\text{U}^{5+}\text{O}_5\text{V}_F)$. This centre was reported to have the following g -values: $g_{\parallel} = 0.13$ and $g_{\perp} = 0.595$. The Tg4 centre was assumed to correspond to $(\text{UO}_6)^{7-}$ octahedron at a $(\text{LiF}_6)^{5-}$ site slightly perturbed by a

cation impurity such as Cu, Ag or Au. This centre was reported to have the g -values: $g_{\parallel} = 0.326$ and $g_{\perp} = 0.362$. The Tg4 centre is closest to the U^{5+} centre in $LiNbO_3$ and next comes the Tg3 centre. In view of the apparent high symmetry of $(UO_6)^{7-}$ in $LiNbO_3$, as well as in cubic LiF , it is rather intriguing that the g -values of Tg4 are widely different from those in $LiNbO_3$. This is probably due to lower symmetry components of the crystalline field arising from associated lattice defects in alkali fluoride lattices.

4.3 Systematics of $(^{233}UO_{6-x}F_x)$ hyperfine coupling constants with F^- -substitutions

To understand the systematics of the effect of F-substitution in $(^{233}UO_6)^{7-}$, on the hyperfine coupling constant, the hyperfine data for $^{235}U^{5+}$ in oxyfluoro coordinations is used. The ratio of magnetic moments of two isotopic species of the same paramagnetic ion will be the ratio of the respective products AI [13]. Therefore $(AI)^{233}/(AI)^{235} = 0.65/-0.361$ [14]. This gives the value of $|(A)^{233}| = 2.6 (A)^{235}$. Using this, the values of A^{233} were calculated for $(UO_4F_2)^{5-}$ and $(UO_5F)^{6-}$ complexes from the data published by Lupei *et al* [12]. These values are summarized in table 2. It can be seen that the value of A_{\parallel} decreased drastically with fluoride ion substitution, with an associated increase in the value of A_{\perp} . The value of A_{iso} was found to be essentially unaltered.

The systematic decrease of A_{\parallel} , with fluoride substitution looks rather surprising in the first instance as substitution with a more ionic ligand is expected to increase the hyperfine coupling constant. It can be understood by considering the site symmetry of the U^{5+} complex, the shape of $5f$ orbitals and their relative energies at the respective sites. In perfectly octahedral symmetry the ground a_{2u} orbital is directed away from the ligands and therefore no direct overlap is expected. However, lowering of symmetry together with spin-orbit interaction brings in Γ_7 character to the upper sigma antibonding t_{1u} orbital set. As the ground state a_{1u} orbital transforms as Γ_7 , the lowering of symmetry admixes the antibonding t_{1u} into the ground state. This enhances the electron density in the direction of distortion (z-axis). The $[UO_4F_2]^{5-}$ and $[UO_5F]^{6-}$ complexes in alkali fluorides have D_{4h} and C_{4v} symmetries respectively, whereas the symmetry axis of U^{5+} site in $LiNbO_3$ is a three-fold axis coincident with the centre of an octahedral face. Therefore for the oxyfluoro complexes in alkali halide matrices, there is an increased covalency in the axial direction thereby decreasing the A value. For U^{5+} in $LiNbO_3$ there is no bond in the direction of z-axis and hence a larger value is found for the magnitude of the parallel component of the hyperfine coupling constant.

4.4 Effects of laser illumination

Okamoto *et al* [5] investigated the effect of uranium dopant on the photorefractive sensitivity for $LiNbO_3$. They have reported that the hologram is stable for an unusually long time. The main aspect where our work differs from that of Okamoto *et al* is that we have stabilized U^{5+} in $LiNbO_3$, and that we have focussed our attention only on the role of U^{5+} in photoinduced charge transfer thereby formation of phase grating. The results shown in figure 2 give evidence for photoinduced reduction in U^{5+} concentration. The uranium dopant exists in tetravalent and/or probably hexavalent form in $LiNbO_3$ crystal. It may be noted that U^{4+} in octahedral symmetry does not give EPR signal. The decay of

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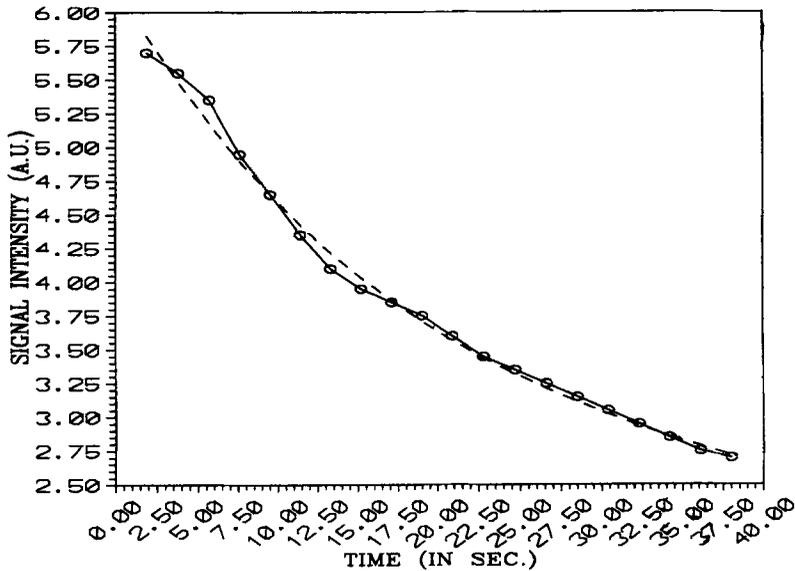


Figure 4. The fitting of the decay of EPR signal of U^{5+} to a double exponential ($\tau_1 = 16$ s, $\tau_2 = 146$ s at 10 K). The dashed curve is the theoretical fit.

the signal was fit to both single and double exponential forms. The double exponential decay gave a very satisfactory fit. A typical calculated decay curve along with experimental points is shown in figure 4. The two decay constants τ_1 and τ_2 corresponding to various temperatures are given in table 3. It may be seen that the decay consists of one faster component which is temperature independent and another one which is slower but temperature dependent. The logarithmic temperature dependent decay constant vs. $1/T$ yielded a straight line with slope of 2.9. Fitting with two exponentials suggests the possibility of two types of trapping centres/mechanisms due to the photoinduced charge transfer process. Temperature independent process might imply a direct electron transfer photoexcitation between two trapping centres without involving mobility of charge carriers through conduction band. The temperature dependent process on the other hand would involve temperature dependence of mobility, dielectric relaxation time, number of charge carriers, etc. [13]. The temperature dependence of τ_2 can fit to an Arrhenius kind of equation with associated activation energy 0.25×10^{-3} eV. This shows the trap is extremely shallow and that probably was the reason for observing these effects in 10–80 K region. The band gap of $LiNbO_3$ is 3.8 eV. Therefore excitation with CVL is not expected to give inter-band transition. The reduction in U^{5+} signal, on CVL illumination and its restoration suggest that the photoinduced processes may be electron transfer between defect centers. If it is between U^{5+} and U^{4+} it can be of the form

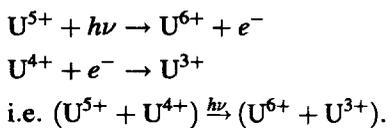
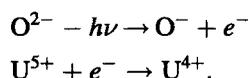


Table 3. Time constants for the double exponential decay of U^{5+} on CVL illumination.

Temperature (K)	τ_1 (s)	τ_2 (s)
10	16	146
40	16	178
80	16	183
100	16	210

The reverse electron transfer would restore the U^{5+} signal on putting off the laser illumination. This transition between two different valence states of uranium, may be identified with the temperature independent process with time constant of ~ 16 s. The intrinsic instability of the lower valence states of uranium at Nb^{5+} site could be responsible for this.

Another possible pathway may be



In this process the recovery of the signal may be very slow as U^{4+} is stable in this lattice. Further O^- should be detectable by EPR. As O^- was not detected, this pathway is considered less probable.

5. Conclusion

The hyperfine interaction data of $^{233}U(V)$ in octahedral $(UO_6):LiNbO_3$ is presented. The systematics of variation of hyperfine coupling with F^- -substitution can be explained using a simple crystal field approach. It is observed that uranium in pentavalent state takes part in photoinduced valence change which is the basic mechanism for photorefraction.

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