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Spectroscopic Investigation of U(DBM)₄, U(TFBA)₄, Th(DBM)₄:U(IV), Th(TFBA)₄:U(IV) Single Crystals (DBM = 1,4-Dibenzoyl-1,3-butane dione, TFBA = 4,4,4-Trifluoro-1-phenyl-1,3-butane dione)

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Single crystals of U or Th(DBM)₄-solvate, U or Th(TFBA)₄ and Th(DBM)₄-solvate or Th(TFBA)₄ doped with U(IV), few tenths of cubic millimeters in size, have been grown at low temperature from benzene (DBM) or toluene (TFBA) solutions. Other conditions do not lead to so large single crystals.

All tetrakis-dibenzoylmethanato crystals exchange benzene molecules giving solvate crystals. They only can be kept unchanged in benzene saturated atmosphere. The yet unknown structure of these solvates are slightly different from the known 'dry' orthorhombic U(DBM)₄ (Pccn) [1, 2]. First investigation on U(DBM)₄ solvate essentially shows a 15% increasing of the *b* parameter and a 20% increasing of the orthorhombic volume cell. Space group is Pccb. This probably means that benzene molecules insert themselves between the U(DBM)₄ layers of the dry crystals. In both structures, U lies on a C₂ crystallographic axis parallel to *z*. The structure of the tetrakis-trifluorobenzoylmethanato crystals is known to be tetragonal (I4₁/a) [3].

Polarized high resolution spectra of all these single crystals have been obtained between 4000 and 20000 Å in the temperature range 4–300 K. Some common features appear on these spectra. The thorium chelates show two bands. The Th(DBM)₄:U(IV) and Th(TFBA)₄:U(IV) which are the best resolved spectra among all the recorded ones, show about thirty vibronic bands, some of them having a width of 10 Å at 4 K.

A quite good polarization of Th(DBM)₄:U(IV) spectra is surprising for such an orthorhombic lattice. This means that probably the two optical axes are so close together that the crystal appears at 4 K as uniaxial. The 4 K polarized spectra look like very accurately the σ and π U⁴⁺ spectra in β -ThBr₄ and β -ThCl₄ matrix or UCl₄, all of them being uniaxial tetragonal crystals [4, 5] where point group symmetry of U⁴⁺ in D_{2d}. So, point group symmetry of

U(IV) is close to D_{2d} or another group whose characteristic table is the same.

These observations cannot be explained according to the above mentioned insertion of benzene molecules without any other changes in the positions of U in the lattice. In dry U(DBM)₄, point group symmetry of U(IV) is D_{4d} or C₂ depending on whether the considered environment is a square antiprism of oxygen or the whole molecule. Spectra of Th(DBM)₄:U(IV) have been temporarily assigned on the D_{2d} basis point group symmetry. Broadness of the lines leads to poorly significant values of the F_k and B_q^k parameters.

As expected for a tetragonal crystal and a S₄ point group symmetry for U(IV), polarization of Th(TFBA)₄:U(IV) is found and spectra of U(IV) are very different from those of D_{2d} symmetry. σ lines are more numerous than π lines and this could indicate according to dipole selection rules for S₄, that ground state is two fold degenerate. Unfortunately no spectra of U(IV) have today been assigned in a such symmetry. The spectra we have recorded could be a basis for calculations.

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Spectra of U⁴⁺ Ion at a Site of D_{2d} Symmetry

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The optical spectra of U⁴⁺ ion (5 f²) at a site of D_{2d} symmetry were studied by different authors in various matrices as UCl₄ [1–5], ZrSiO₄ [6, 7], HfSiO₄ [8], ThSiO₄ [8] and ThBr₄ [9, 4]. There also exist data on magnetic susceptibility of UCl₄ [10–13] and USiO₄ [14] but most results do not agree with those obtained from optical spectra. At this point, one can note the disparity between the previous results concerning UCl₄, which was the most studied of all these crystals and mention the necessity of performing both optical and magnetic studies on single crystals of the same origin. A recent study of these issues leads to a better agreement [5, 15].

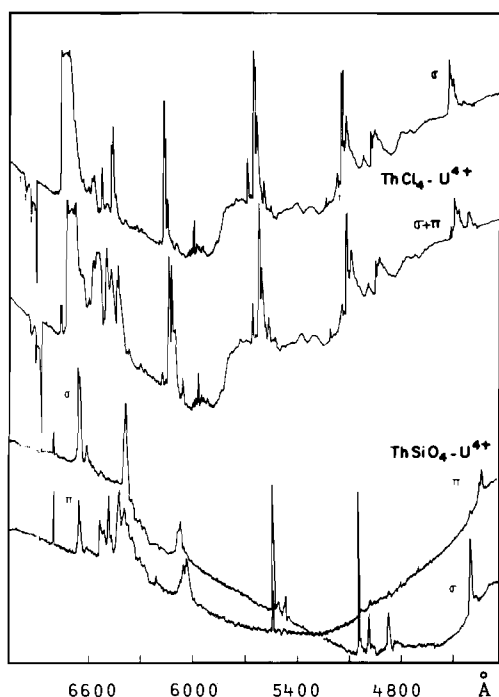


Fig. 1. Optical absorption spectra of $\text{ThSiO}_4\text{-U}^{4+}$ in comparison with those of $\text{ThCl}_4\text{-U}^{4+}$ at 4.2 K.

Therefore, it seems of interest to grow some of these crystals as single crystals and study again the optical spectra of U^{4+} in the D_{2d} symmetry. This way we could compare the spectra to one another in order to assign the absorption and emission lines more accurately.

So we grew single crystals of UCl_4 and $\text{ThCl}_4\text{:U}^{4+}$ by the Bridgman method [16] and $\text{ThSiO}_4\text{:U}^{4+}$ by the flux method following Chase and Osmer [17]. Then we recorded polarized spectra of U^{4+} in ThCl_4 and ThSiO_4 (Fig. 1) and unpolarized spectra for UCl_4 (Fig. 2). In all these spectra the main features are quite similar but the more clear ones are obtained with $\text{ThSiO}_4\text{:U}^{4+}$. In fact, the U^{4+} absorption bands in UCl_4 are very broad, probably due to the interaction between the U^{4+} ions and in $\text{ThCl}_4\text{:U}^{4+}$ they are affected by the incommensurate and modulated structure of the low temperature phase of ThCl_4 .

This interesting last point needs more explanations. In ThCl_4 a phase transition occurs at 70 K and the dynamic of the structure alteration was studied in the isomorphous crystal ThBr_4 , mainly by neutron diffraction [18]. It was shown that the matrix loses its periodic structure in one direction (the z axis corresponding to the S_4 optical axis). The halide displacements are different in each unit cell and can be described by a sinus function of the distance to the origin of the unic cell. This results in having the Th^{4+} ion and therefore its substitute U^{4+}

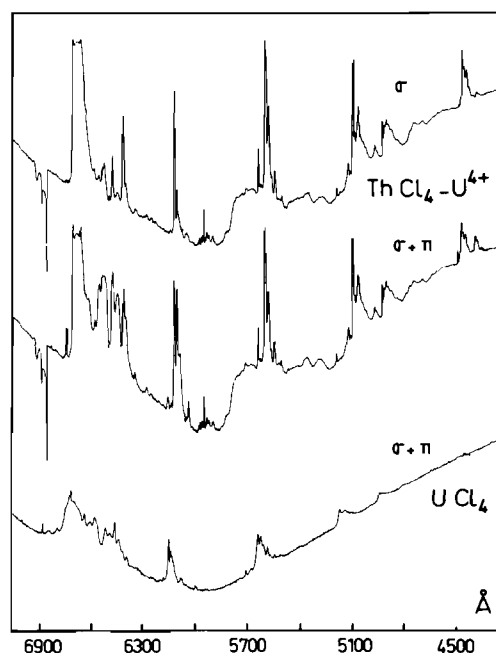


Fig. 2. Optical absorption spectra of UCl_4 in comparison with those of $\text{ThCl}_4\text{-U}^{4+}$ at 4.2 K.

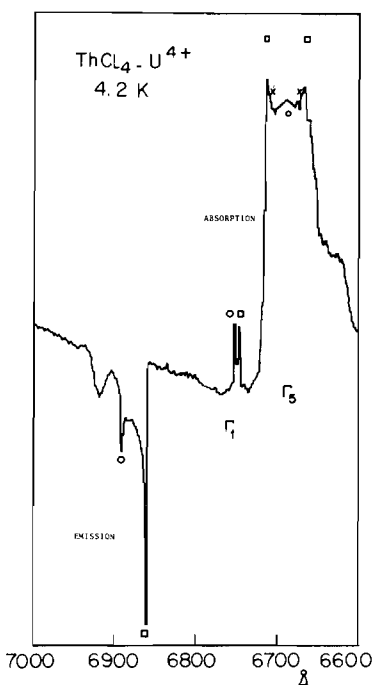


Fig. 3. Special features in the optical spectra of $\text{ThCl}_4\text{-U}^{4+}$ due to the incommensurate structure of ThCl_4 . \square : D_2 extreme symmetry. \times : D_2 intermediate symmetry. \circ : D_{2d} symmetry.

in an infinity of D_2 symmetry sites and some of D_{2d} symmetry (each D_2 site being very close to the D_{2d} symmetry). This continuous modulation of the

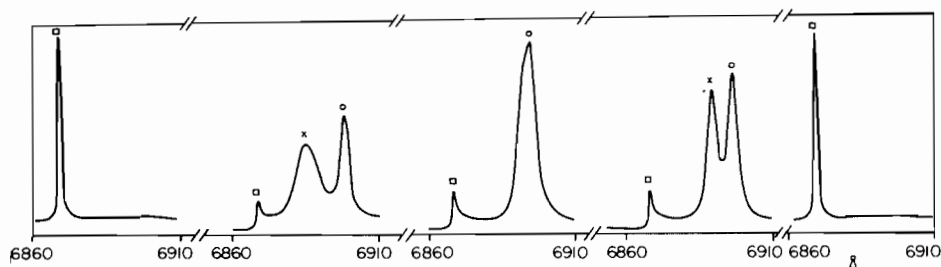


Fig. 4. Fluorescence spectra of $\text{ThCl}_4\text{-U}^{4+}$ recorded when the wavelength λ_{ex} is selectively scanned through the absorption band (Fig. 3). From left to right: $\square \lambda_{\text{exc}}: 6676 \text{ \AA}$; $\times \lambda_{\text{exc}}: 6690 \text{ \AA}$; $\circ \lambda_{\text{exc}}: 6698 \text{ \AA}$; $\times \lambda_{\text{exc}}: 6714 \text{ \AA}$; $\square \lambda_{\text{exc}}: 6722 \text{ \AA}$.

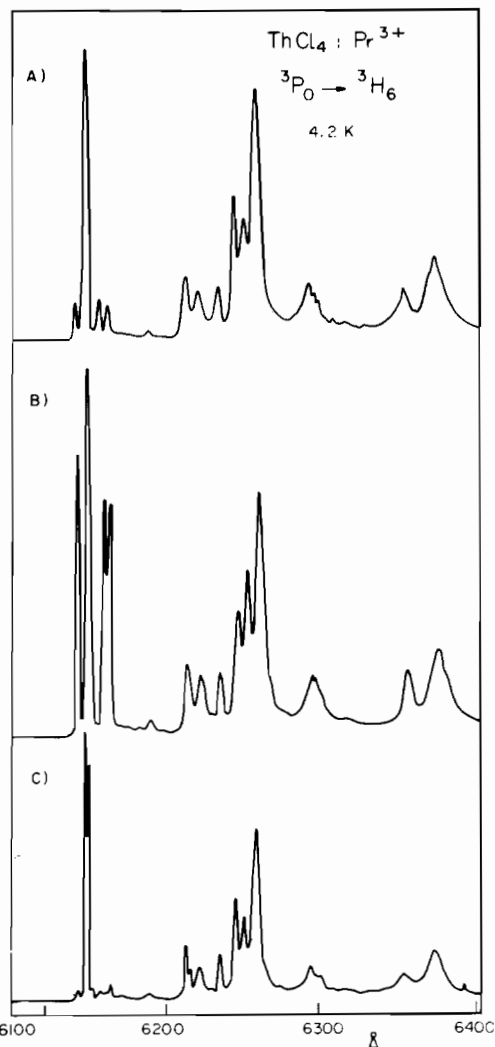


Fig. 5. ${}^3\text{H}_4 \rightarrow {}^3\text{P}_0$ absorption line in $\text{ThCl}_4\text{-Pr}^{3+}$.

D_2 symmetry between two maximum distortions gives rise to special features which have not been seen up to now in any other optical spectra. The absorption and emission lines of U^{4+} in ThCl_4 , rise and fall very steeply due to edge singularities which

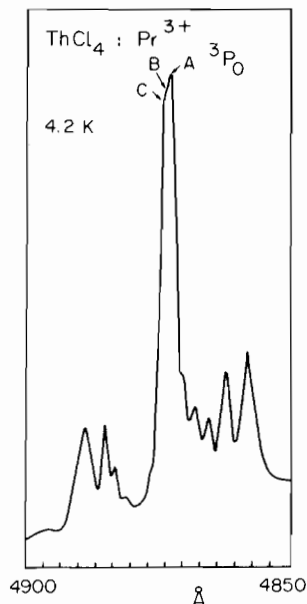


Fig. 6. Fluorescence spectra when the ${}^3\text{P}_0$ is scanned selectively: A: $\lambda_{\text{exc}} = 4872 \text{ \AA}$. B: $\lambda_{\text{exc}} = 4873 \text{ \AA}$. C: $\lambda_{\text{exc}} = 4874 \text{ \AA}$.

are connected by a continuum of lines corresponding to U^{4+} in the intermediate D_2 symmetries [19–21] (Fig. 3). Selective excitation of the different sites produces fluorescence lines whose energy varies continuously between the system singularities (Fig. 4).

Thus in ThCl_4 , The U^{4+} doping ion acts as an indicator of the incommensurate structure of the low temperature phase. One question that arises then is: would a lanthanide give the same type of information? Though the phenomenon seems much smaller as one would expect with the 4f electrons which are more protected against the crystal field interaction, some special features were recorded in the spectra of Pr^{3+} ($4f^2$) in ThCl_4 (Figs. 5, 6) and are under study [22].

In conclusion, $\text{ThSiO}_4\text{:U}^{4+}$ spectra give the clearest set of data concerning U^{4+} in the D_{2d} site symmetry. The spectra are well polarized with only two allowed

dipolar electric transitions: $\Gamma_4 \rightarrow \Gamma_5$ (σ polarization) and $\Gamma_4 \rightarrow \Gamma_1$ (π polarization). So the results on $\text{ThSiO}_4:\text{U}^{4+}$ appear as essential to improve the calculations of the usual spectroscopic parameters (the Slater's parameters F^k , the spin-orbit constant ξ and the crystal field parameters B_q^k) for the two other crystals $\text{ThCl}_4:\text{U}^{4+}$ and UCl_4 . These calculations are underway.

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Neutron Diffraction Study of $\text{U}_{0.5}\text{Np}_{0.5}\text{O}_2$

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A neutron powder diffraction study of $\text{U}_{0.5}\text{Np}_{0.5}\text{O}_2$ has been performed recently at the D2 spectrometer of the ILL high flux reactor. Neutron diffraction patterns were recorded for the temperature range $3 \leq T \leq 293$ K. This compound crystallizes in the CaF_2 -type structure. The lattice parameter has been found to be $a = 5.4624(3)$ Å in the temperature range $3 \leq T \leq 37$ K. A magnetic ordering was observed below $T_N \cong 12$ K, in agreement with the previous Mössbauer experiments [1]. Surprisingly the observed magnetic order is different from the one previously found in UO_2 [2]. Actually only one weak magnetic reflection quite near to the $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ line referred to the nuclear unit cell was observed; the high Miller indice reflections are probably too small due to the magnetic form factor to be seen. The magnetic order is compatible with the ordered moment $-0.6 \mu_B$ per Np atom – observed by Mössbauer resonance. A striking fact is the large width of the magnetic reflection which decreases only slightly with T remaining higher by a factor of about 5 as compared to the width of the 1,1,1 nuclear reflection; this fact is probably to be attributed to a short range of the magnetic order (a correlation length of about 20 Å has been found). Moreover clustering effects of Np and U ions should be excluded.

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