dence in K_f and K^*_{app} values probably reflects the excitation conditions employed rather than the establishment of excited-state equilibrium.

Electronic spectra of adducts of $(Me_5C_5)_2Yb$ have been examined in toluene solution. The solid has been isolated as a mono-THF adduct (P. L. Watson, *J. Chem. Soc., Chem. Comm.*, 652 (1980)) and as a mono-Et_2O adduct (R. A. Anderson, *et al., Inorg. Chem., 19,* 2999 (1980)), orange and yellow-green compounds, respectively. Toluene solutions retain these colors. The THF adduct exhibits bands at 445, 505, and 790 nm in toluene with absorptivities of ~410, 320, and 190 M^{-1} cm^{-1}, respectively; corresponding values for the Et_2O adduct are 460 and 690 nm with absorptivities of ~410 and 180 M^{-1} cm^{-1}, respectively. Both species are reluctant to add a second equivalent of base to their coordination sphere; a K_f value of ~10 M^{-1} for formation of the bis-THF adduct was measured from spectral changes accompanying titration of the mono-THF adduct with THF. For adducts of $(Me_5C_5)_2Yb$ involving one equivalent of base, the lowest-energy absorption band appears particularly sensitive to the identity of the base, red-shifting as the base is changed from Et_2O to THF to pyridine (λ_{max} ~ 800 nm). The direction of the shift is consistent with an assignment for the band of $Yb \rightarrow \pi^*(Me_5C_5)$, *i.e.,* metal-to-ligand charge transfer (MLCT). Supporting this assignment are photolysis experiments in which irradiation of the THF adduct in toluene, either alone with UV excitation or in a C_6H_5Cl/toluene mixture with visible and near-IR excitation, leads to Yb(III) products with quantum efficiencies of ~10^{-1}.

The mono-THF adduct emits at 295 K in toluene solution when excited with visible light; the emission band is broad (~90 nm fwhm) with a maximum at 935 nm. Additionally, the adduct exhibits a novel chemiluminescent reaction indicative of the strong reducing power of these Yb(II) species: upon addition of O_2-saturated toluene to a toluene solution of the adduct, a sharp emission band is observed at ~985 nm. This band is also observed in photoluminescence of the product solution and is characteristic of an Yb(III) species. The species and mechanism responsible for the chemiluminescence will be discussed.

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Physico-chemical Studies of Uranyl Fluoride Complexes

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B7

Mössbauer Spectroscopy and X-Ray Diffraction Studies of Neptunium Intermetallics under High Pressure[†]

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The magnetic properties of intermetallic compounds of the light actinides vary from primary local moment behaviour through itinerant electron magnetism to non-magnetic behaviour. A dominant parameter determining the magnetic character is the interatomic separation of the actinide ions which experimentally can be varied by the application of high pressure. To study the microscopic magnetic behaviour we performed Mössbauer experiments on $NpAl_2$, $NpOs_2$, $NpCo_2Si_2$, and NpAs using the 60 keV transition in ^{237}Np. The magnetic hyperfine field B_{hf} and the isomer shift S, which are a measure of the ordered magnetic moment and the s-electron-density at the nucleus, respectively, as well as the magnetic ordering temperatures have been determined at various pressures up to 70 kbar and in the temperature range from 1.6 K to 77 K. In addition, the lattice parameter variation of $NpAl_2$ was measured up to 100 kbar at room temperature by X-ray diffraction.

We obtained the following results:

(i) In the cubic Laves phase compounds $NpAl_2$ and $NpOs_2$ with a Np–Np distance at ambient pressure of 3.371 Å and 3.258 Å, respectively, we observed a strong decrease of B_{hf} and Curie temperature with pressure indicating a progressive delocalization of the 5f electrons. This is markedly confirmed by the isomer shift. In addition, line broadenings are observed which point towards fluctuation phenomena and show that the delocalization process is of a dynamical nature [1–3].

(ii) The X-ray measurements demonstrate an increase of the compressibility of $NpAl_2$ by a factor of 5 when a pressure of 80 kbar is applied. This behaviour further supports the picture of 5f delocalization with reduced atomic volume. A collapse of volume on account of 5f delocalization

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has been predicted theoretically for Am metal [4], but could not yet be experimentally verified for this element.

(iii) In $NpCo_2Si_2$ which has a tetragonal structure and a nearest neighbour distance of 3.877 Å the magnetic hyperfine field remains constant under pressure. It indicates that in this compound the 5f electrons are well localized. The Néel temperature T_N increases with smaller volume. The variation of T_N can be explained quantitatively in terms of the rigid spin model of Ruderman-Kittel-Arrott [5, 6]

(iv) NpAs which has an even larger Np–Np separation of 4.128 Å shows a complex hyperfine pattern at 70 kbar consisting of several subspectra. Two different lattice structures coexist: The NaCl type structure and an unknown high pressure phase. The hyperfine field belonging to the former is only slightly (~4%) reduced when pressure (70 kbar) is applied and illustrates its highly localized property. The subspectrum of the latter structure gives a reduction of B_{hf} of ~16% with respect to the values of the NaCl phase.

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B8

f-Electron Elements as Coordination Centres and their Spectroscopic Properties

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B9

5f Actinide Ions as Spectroscopic Probes of Incommensurate Phases

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For ten years the incommensurate phases have been intensively studied mainly with techniques like: EPR, NMR, NQR and obviously with X-ray and neutron scattering, most of the investigated compounds being pure crystals.

It was of interest to take advantage of the sensitivity of the 5f ions to the environment to check how their electronic structure is affected when these ions are placed, as a dopant material, in an incommensurate phase.

We recently found that $ThBr_4$ showed a phase transition down 96 K and much experimental evidence tends to prove that it is an incommensurate phase. As we are mostly interested in optical properties of 5f ions such as Pa^{4+}, U^{4+}, Np^{4+} these elements in their tetravalent state were studied in $ThBr_4$ by optical spectroscopy. Their concentration in $ThBr_4$ doped crystals was about 0.1%. The absorption and emission spectra were recorded at liquid helium temperature where the structure of the host material, $ThBr_4$ was still incommensurate. In these conditions we have shown that the electronic levels are broadened whatever their degeneracy. In addition, the absorption and emission lineshape were found to be very unusual, showing two abrupt singularities on both edges of the line; the middle part was observed as a 'valley' where the intensities are less important compared to those of the edges.

This unusual lineshape is clearly interpreted taking into account the modulated structure of the matrix $ThBr_4$. It is consistent with the fact that broadening of the line and also the shape are due to the incommensurate phase where the modulated displacements of bromide ions from one unit cell to another give rise to multiple D_2 symmetry sites some other remaining D_2d. In these conditions tetravalent 5f ions placed in this type of structure are under the influence of the modulation of the crystal field parameters which are slightly different for each unit cell. The optical spectroscopy has revealed a continuum of energy for the levels located in the 'valley' of the absorption line, the edges corresponding to limit cases for the D_2 or the D_2d symmetries. Fluorescence study results of 5f ions in $ThBr_4$ are also in good agreement with the proposed model of the modulated structure.

In conclusion we have shown for the first time that an incommensurate structure could be detected through the optical properties of a 5f ion used as a probe. Further experiments on other types of ions are necessary to decide if the behaviour of 5f elements is unique or if it is a general phenomenon; but to-day it seems that trivalent 4f ions, in $ThBr_4$ are not sensitive to the modulation of the crystal field.