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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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.