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Optical absorption spectrum of dilute U^{4+} impurities in incommensurate $ThBr_4$: lineshape analysis

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Résumé. — Les transitions de champ cristallin des ions U^{4+} dilués dans $ThBr_4$ donnent lieu à des bandes d'absorption caractérisées par des singularités de bord. On montre que les spectres observés sont compatibles avec l'existence d'une distorsion sinusoidale qui module les positions d'équilibre des ions Br^- et réduit la symétrie du site de l'ion actinide de D_{2d} à D_2 . L'observation de singularités spectrales correspondant à des sites de symétrie D_{2d} résulte de l'accrochage partiel de l'onde incommensurable sur les ions U^{4+} .

Abstract. — Crystal-field transitions associated with U^{4+} impurities diluted in $ThBr_4$ give rise to broad absorption bands characterized by edge singularities. We show that the experimental spectra are consistent with the known occurrence of a sinusoidal distortion which modulates the Br^- ion equilibrium positions, thus reducing the actinide site-symmetry from D_{2d} to D_2 . The observation of spectral singularities corresponding to D_{2d} -sites is interpreted as resulting from the partial pinning of the incommensurate modulation by the U^{4+} impurities.

Pure β - $ThBr_4$ is diamagnetic and free of optical absorption over a wide range of wavelengths. Thus, it is often used as a host material for tetrapositive actinide ions in magnetic and optical studies. U^{4+} is most frequently used because of its relatively simple electronic structure ($5f^2$) as well as for practical reasons. In one such study [1], the complete visible and infrared absorption (and emission) spectra of dilute U^{4+} impurities have been examined. The spectra, obtained at low temperature (~ 4 K), could not be interpreted on the basis of the « accepted » β - $ThBr_4$ structure (space group D_{4h}^{19}). Many more lines were observed than could possibly be due to crystal-field transitions associated with the $5f^2$ electrons on the U^{4+} ions. Furthermore, instead of the usual (sharp) zero-phonon transition lines, broad bands with two edge singularities were observed.

Subsequently, Raman [2] and neutron diffraction [3] studies have established that $ThBr_4$ undergoes a displacive phase transition, at $T_c = 95$ K, from the room-temperature β -phase into an incommensurately-modulated structure.

The object of this letter is to show that the observed U^{4+} absorption spectra are consistent with the known wavevector and point-symmetry characteristics of the condensed modulation. The situation here is similar to that encountered in the discussion of NMR, NQR and EPR lineshapes in incommensurate systems [4], as both the light-absorption and the resonance techniques are sensitive to the *local* value of the phase of the frozen wave. Unfortunately, the optical technique, which operates on a very short characteristic time-scale, is only useful at low temperatures, where thermal broadening of the spectral lineshapes is still tolerable ($T \lesssim 15$ K).

From the analysis below, it appears that the U^{4+} ions do not sample the same distribution of « local phases » as the Th^{4+} ions, which they replace. This illustrates another basic difficulty, inherent to the use of impurity probes in incommensurate structures, namely that the local value of the phase is influenced by the nature of the impurity itself, the latter acting to some degree as a phase-pinning centre.

1. Experimental absorption spectra. — Figure 1 shows the essential features of the U^{4+} electronic absorption spectra measured at 4.2 K, in thorium tetrabromide single-crystals. Two distinct sets of absorption bands are obtained depending upon the electric polarization of the incident radiation :

i) When the incident light is polarized along the crystallographic four-fold axis (E_{\parallel}), the absorption spectrum consists of doublet-lines with two edge-singularities. The frequency separation between the singularities (i.e. the bandwidth) is typically of the order of 8 cm^{-1} .

ii) When the incident light is polarized in the basal plane (E_{\perp}), the absorption bands are broader (40 to 80 cm^{-1}) and consist of three peaks with, as in the E_{\parallel} -case, two edge-singularities.

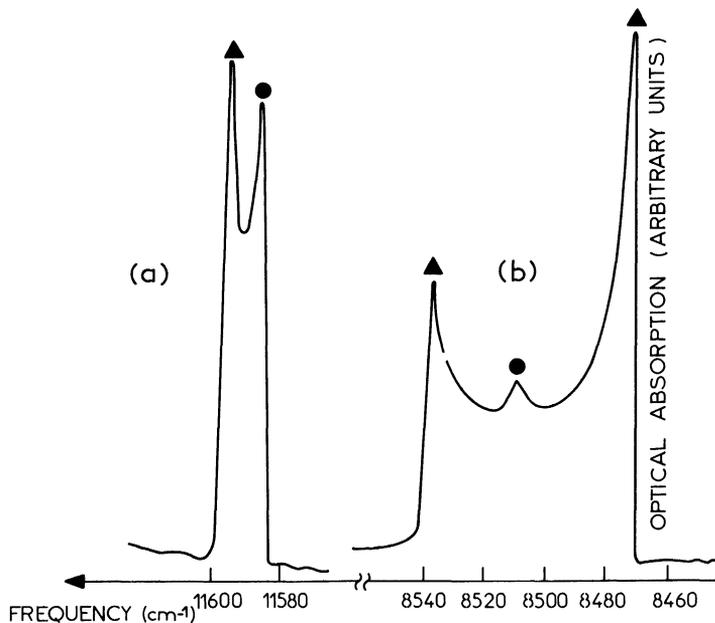


Fig. 1. — Typical absorption bands from U^{4+} in $ThBr_4$ at liquid helium temperature. The incident-light electric polarization is parallel (a) and perpendicular (b) to the tetragonal c -axis. The instrumental frequency resolution is of the order of 2 cm^{-1} .

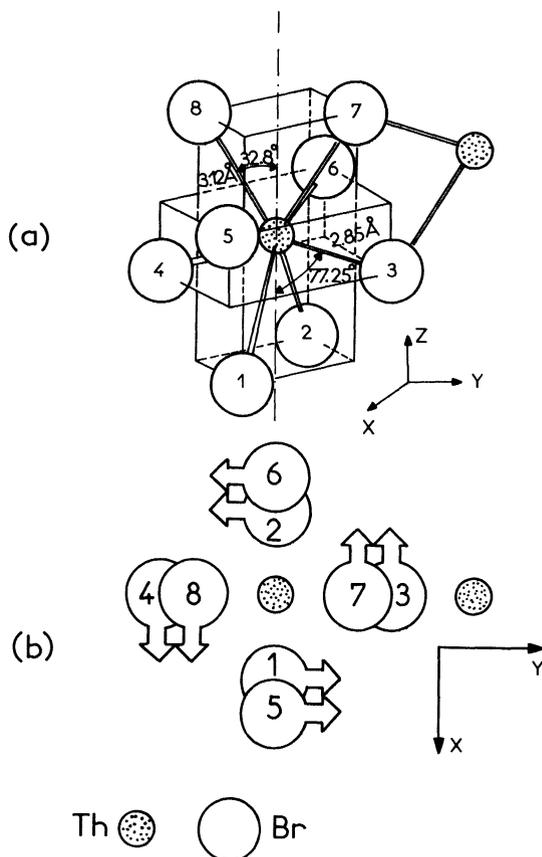


Fig. 2. — Primitive unit cell of β -ThBr₄ : (a) perspective view ; (b) looking down the tetragonal axis. The arrows in (b) correspond to the unit vectors \mathbf{e}_k in equation (1).

2. **Crystal structure below T_c .** — The high-temperature structure [5] of ThBr₄ (β -structure) is shown in figure 2. Below T_c , neutron diffraction data show that the modulation wavevector \mathbf{q}_s is directed along the tetragonal c -axis

$$q_s = \frac{2\pi}{c} \zeta_s \quad (a = 8.93 \text{ \AA} ; \quad c = 7.96 \text{ \AA} \text{ at R.T.})$$

with $\zeta_s = 0.310 \pm 0.005$.

No appreciable variation of ζ_s is observed upon cooling, down to 4 K. The combined analysis of Raman, infrared and inelastic neutron scattering data ($T > T_c$), together with the observation of systematic satellite-reflection extinction rules ($T < T_c$), allows the symmetry [3] of the soft optic branch to be identified (τ_4 in Kovalev's notation [6]). Furthermore, since higher-order satellite-reflections are hardly visible (even at 4 K), one may assume a purely sinusoidal modulation, in which case the atomic displacements below T_c , \mathbf{u}_{lk} , may be written simply in terms of the soft-mode eigenvectors :

$$\mathbf{u}_{lk} = \eta \mathbf{e}_k \cos \{ \mathbf{q}_s \cdot \mathbf{r}_{lk}^0 - \varepsilon_k \theta \} . \tag{1}$$

The quantities appearing in the expression above are defined as follows :

\mathbf{r}_{lk}^0 ($\equiv \mathbf{l} + \mathbf{r}_k^0$) is the position vector of the k th atom in the l th primitive unit cell. Each such cell contains two Th^{4+} ions at $(0, 0, 0)$ and $(0, 1/2, 1/4)$ and 8 Br^- ions. Since the positions of the Th^{4+} ions are *unaffected* by a modulation of τ_4 -symmetry, we need only consider the Br^- displacements in equation (1), i.e. $k = 1, 8$. As shown in figure 2a, the 8 Br^- ions may be chosen in such a way as to generate the complete first and second nearest-neighbour shells around the Th^{4+} ion located at the origin. η is a temperature-dependent amplitude factor which may be taken as the order parameter of the modulated phase, and \mathbf{e}_k is a unit vector in the x or y direction (cf. Fig. 2b). θ is a parameter entering the expression of the soft-mode eigenvector. Its value is *a priori* unknown. Since ε_k is defined as $+1(-1)$ for $k = 1$ to 4 (5 to 8), θ is seen to control the phase difference between the displacements of the Br^- ions located above and those located below the Th^{4+} ion at the origin.

3. **Actinide site-symmetry below T_c .** — In the high-temperature phase the Th^{4+} site-symmetry is D_{2d} . This is seen most clearly in figure 2a, by considering the two pseudo-tetrahedra generated by the Br^- ions labelled (1, 2, 7, 8) and (3, 4, 5, 6) respectively. Each tetrahedron is separately invariant under the point-symmetry operations S_4^z , C_2^z , C_2^{xy} ($\equiv C_2'$) and σ_d . As a result of the Br^- displacements given in equation (1), each tetrahedron experiences both a rotational displacement as well as a twist-deformation :

- i) The twist component of the displacements destroys both S_4^z and σ_d for each tetrahedron.
- ii) The rotational component of the displacements rotates the C_2' -axes by different amounts for the two tetrahedra. Thus C_2' , in general, disappears as a site-symmetry element. The resulting actinide site-symmetry is thus C_2 .

If however, the rotational components happen to be equal for the two tetrahedra, C_2' survives as a site-symmetry element, and the actinide site-symmetry, to the extent that it is determined by the surrounding eight Br^- ions *alone*, is D_2 rather than C_2 . The condition for this to happen may be written as :

$$\sum_{k=1,2,7,8} \frac{\mathbf{u}_{lk} \cdot \mathbf{e}_k}{\rho_k} = \sum_{k=3,4,5,6} \frac{\mathbf{u}_{lk} \cdot \mathbf{e}_k}{\rho_k} \quad (2)$$

where ρ_k stands for the distance of ion k to the $\bar{4}$ -axis. With the help of table I, we find that condition (2) is satisfied, *simultaneously for all values of l* , if :

$$\theta = 2 \pi \zeta_s z - \tan^{-1} \left\{ \frac{\frac{1}{2} - x - x \cos\left(\frac{\pi \zeta_s}{2}\right)}{x \sin\left(\frac{\pi \zeta_s}{2}\right)} \right\} \simeq 21.6^\circ. \quad (3)$$

It is remarkable that the preliminary analysis of the satellite-reflection intensities [3], measured at 55 K, yields :

$$\theta = 20.2 \pm 3^\circ$$

in excellent agreement with the condition expressed in equation (3). We do not wish to elaborate, here, on the possible significance of this apparent « coincidence », only to point out that it would appear to suggest that the concept of local symmetry plays an important role, at least in this type of incommensurate structures.

In the following analysis we shall assume that condition (2) is sufficiently close to being fulfilled at 4 K, that the uranium site-symmetry is effectively D_2 . In the preceding discussion we

Table I. — Cartesian components of the Br^- position vectors r_k^0 and rotational eigenvectors e_k . The R.T. values of the parameters x and z below are 0.311 and -0.08 , respectively [7].

k	r_k^0	e_k
1	$\frac{1}{2} - x, 0, z - \frac{1}{4}$	0, 1, 0
2	$x - \frac{1}{2}, 0, z - \frac{1}{4}$	0, $\bar{1}$, 0
3	0, x, z	$\bar{1}$, 0, 0
4	0, \bar{x}, z	1, 0, 0
5	$x, 0, \bar{z}$	0, 1, 0
6	$\bar{x}, 0, \bar{z}$	0, $\bar{1}$, 0
7	$0, \frac{1}{2} - x, \frac{1}{4} - z$	$\bar{1}$, 0, 0
8	$0, x - \frac{1}{2}, \frac{1}{4} - z$	1, 0, 0

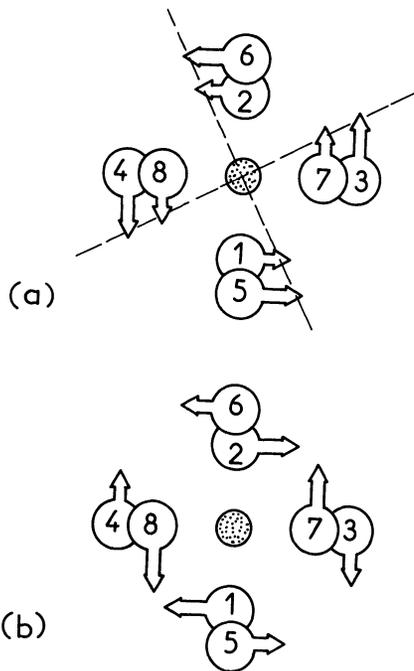


Fig. 3. — Character of Br^- displacements for $\varphi_1 = 0$ (a) and $\varphi_1 = \pi/2$ (b). The resulting actinide site-symmetry is D_{2d} in (a) and D_2 in (b).

have only considered the actinide site at (0, 0, 0). Similar arguments can be put forward concerning the symmetry of the (0, 1/2, 1/4) sites. Since no new physical result is introduced by including these latter sites we shall ignore them altogether.

With the help of table I and introducing the local phase angle φ_l :

$$\varphi_l = \mathbf{q}_s \cdot \mathbf{l} \pmod{\pi} \quad \left(|\varphi_l| < \frac{\pi}{2} \right)$$

we obtain :

$$\mathbf{q}_s \cdot \mathbf{r}_{lk}^0 = \varphi_l + \begin{cases} \pm 2 \pi \zeta_s z & (k = 3, 4, 5, 6) \\ \pm 2 \pi \zeta_s (\frac{1}{4} - z) & (k = 1, 2, 7, 8) \end{cases} \quad (4)$$

Inserting (4) into (1), it is easy to study the character of the site-distortion as a function of cell index l (cf. Fig. 3) :

— for sites such that $\varphi_l \simeq 0$, the Br^- displacements correspond to a pure rotation, by the same angle, of the two Br^- tetrahedra. For such sites the D_{2d} -symmetry is preserved, or nearly so ;

— for sites such that $\varphi_l \simeq \pm \pi/2$, we obtain a pure twist-deformation and the resulting site symmetry is D_2 ;

— for intermediate values of φ_l , both components are present in comparable amounts and the site-symmetry is again D_2 .

4. Crystal-field energy. — Since Th^{4+} and U^{4+} have almost identical ionic radii the strain field associated with the substitution of one by the other may be safely neglected. Also, for dilution levels of the order of 1 %/100, the U^{4+} ions may be treated as isolated impurities, randomly distributed throughout the host lattice. Neglecting second-order perturbations, the U^{4+} electronic levels, $E^{(j)}$, may be written as :

$$E^{(j)} = E_e^{(j)} + E_{so}^{(j)} + \mathcal{E}^{(j)}$$

where $E_e^{(j)}$, $E_{so}^{(j)}$ and $\mathcal{E}^{(j)}$ are the electrostatic, spin-orbit and crystal-field energies, the latter being defined as :

$$\mathcal{E}^{(j)} = \sum_{k=1}^8 \sum_{n,m} a_{n,m}^{(j)} B_m^n(\mathbf{r}_k) \quad (5)$$

where the a_{nm} 's are numerical coefficients and the B_m^n 's are crystal-field parameters which depend upon the position \mathbf{r}_k of the surrounding ligand (Br^-) ions. The values of n and m to be included in the summation on the right-hand side of equation (5) are restricted by the symmetry of the free-ion electronic state under consideration and by the symmetry of the ligand field potential. For f-electrons in a D_{2d} -field, referred to its principal axes, we have ($T > T_c$) [7] :

$$\mathcal{E}_0^{(j)} = \sum_{k=1}^8 \sum_{p=0}^3 a_{2p,0}^{(j)} B_0^{2p}(\mathbf{r}_k^0) + a_{4,4}^{(j)} B_4^4(\mathbf{r}_k^0) + a_{6,4}^{(j)} B_4^6(\mathbf{r}_k^0). \quad (6)$$

The corresponding crystal-field states are either singlet-states (Γ_1 , Γ_2 , Γ_3 and Γ_4) or doublet-states (Γ_5). Below T_c , the substitution :

$$\mathbf{r}_k^0 \rightarrow \mathbf{r}_k^0 + \mathbf{u}_{lk}$$

in equation (6) gives rise to a cell-dependent correction term, $\Delta_1 \mathcal{E}_l^{(j)}$, to $\mathcal{E}_0^{(j)}$. Furthermore the presence of additional correction terms due to the lower site-symmetry (D_2 instead of D_{2d})

lifts the degeneracy of the Γ_5 -states :

$$\epsilon_l^{(j)} = \epsilon_0^{(j)} + \Delta_1 \epsilon_l^{(j)} \pm \Delta_2 \epsilon_l^{(j)}$$

where

$$\Delta_2 \epsilon_l^{(j)} = \begin{cases} 0 & \text{if } (j) = \Gamma_1, \Gamma_2, \Gamma_3 \text{ or } \Gamma_4 \\ \sum_{k=1}^8 \sum_{p=1}^3 a_{2p,2}^{(j)} B_2^{2p}(\mathbf{r}_k^0 + \mathbf{u}_{lk}) + a_{6,6}^{(j)} B_6^6(\mathbf{r}_k^0 + \mathbf{u}_{lk}) & \text{if } (j) = \Gamma_5 \end{cases}$$

As expected from perturbation theory arguments $\Delta_1 \epsilon_l^{(j)}$ ($\Delta_2 \epsilon_l^{(j)}$) varies quadratically (linearly) with the modulation amplitude η . Moreover, since $\Delta_2 \epsilon_l^{(j)}$ must vanish for $\varphi_l = 0$, we may write to lowest-order in η :

$$\epsilon_l^{(j)} = \epsilon_0^{(j)} + \eta^2 \{ \alpha_j + \beta_j \sin^2(\varphi_l) \} \pm \gamma_j \eta \sin(\varphi_l) \tag{7}$$

where α_j , β_j and γ_j are coefficients, and γ_j vanishes for non-degenerate ($T > T_c$) states.

Although equation (7) has been obtained here in a semi-intuitive fashion, it may be formally derived by considering the explicit dependence of the B_m^n coefficients upon the displaced Br⁻ coordinates.

Figure 4 shows the various types of «energy bands» resulting from equation (7). On each site the possible electronic transition frequencies $\nu^{jj'}$ are given by :

$$\nu^{jj'} = \epsilon_l^{(j)} - \epsilon_l^{(j')}$$

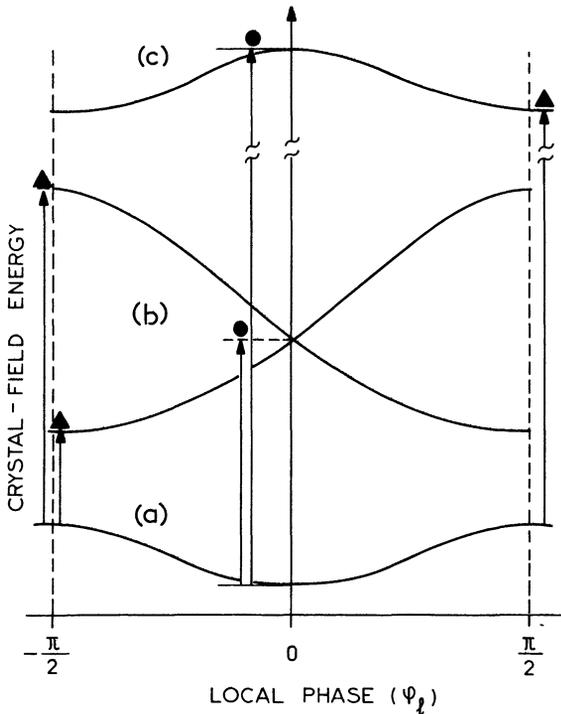


Fig. 4. — Examples of energy levels $\epsilon_l^{(j)}$ obtained from equation (7) : (a) singlet-state $\beta > 0$ (ground-state); (b) doublet-state $\beta > 0$; (c) singlet-state $\beta < 0$. Vertical arrows correspond to transitions giving rise to spectral singularities (cf. Fig. 1).

and the spectral density of the corresponding absorption bands as :

$$I_{(v)}^{j0} \propto \left| \frac{dv_l^{j0}}{d\varphi_l} \right|^{-1}$$

where the superscript (0) refers to the electronic ground-state. The observed spectral singularities correspond to the condition :

$$\frac{d\mathcal{E}_l^{(j)}}{d\varphi_l} = \frac{d\mathcal{E}_l^{(0)}}{d\varphi_l}. \quad (8)$$

From Zeeman absorption spectroscopy and by analogy with what is found in other host materials we know that the U^{4+} ground-state is non-degenerate in D_{2d} -symmetry. Thus, we see in figure 4, that condition (8) is satisfied when :

- i) $\varphi_l = 0, \pm \frac{\pi}{2}$ for initially (i.e. $T > T_c$) non-degenerate excited states.
- ii) $\varphi_l = \pm \frac{\pi}{2}$ for initially degenerate excited states.

In both cases only two (edge-) singularities are found. We note in passing that the simplicity of the present result depends strongly on condition (2) being fulfilled : the above analysis carried out taking C_2 as the actinide site-symmetry below T_c predicts that the spectral singularities should not, in general, correspond to simple values of φ_l .

5. Discussion. — For $T > T_c$, group-theoretical arguments show that electronic transitions involving a degenerate (non-degenerate) final-state are obtained with the $E_{\perp}(E_{\parallel})$ incident-light polarization. Thus the model presented here accounts for the following two observations :

- i) The occurrence of relatively narrow doublet-lines in the E_{\parallel} -polarization, as bandwidths in that case are proportional to the *square* of the modulation amplitude η (a small quantity, even at 4 K).
- ii) The occurrence of broad bands in the E_{\perp} -polarization the bandwidths in that case being proportional to η rather than η^2 .

Implicit in the above statement is the assumption that the coefficients $\{\beta_j\}$ and $\{\gamma_j\}$ in equation (7) are of same order of magnitude. In fact these coefficients are complicated functions of the $a_{n,m}^{(j)}$'s and of the spatial derivatives of the $B_m^n(\mathbf{r}_k)$'s, all quantities whose numerical values are largely unknown. However, there appears to be no fundamental reason why the β_j 's ($(j) = \Gamma_1, \Gamma_2, \Gamma_3, \Gamma_4, \Gamma_5$) should be systematically larger than the γ_j 's ($(j) = \Gamma_5$), and thus we feel justified in assuming that they are in general comparable.

In addition a number of previously unexplained experimental features, can now be accounted for. For instance, it is possible, using a tunable laser, to excite certain sites selectively and to observe the corresponding fluorescence spectrum. This technique allows one to identify the transitions, and in particular the singularities, which originate from the same sites. Not surprisingly, the experiment [8] shows that one of the two singularities (marked \blacktriangle) in figure 1a is associated with both edge singularities in figure 1b, while the other (marked \bullet) is associated with the third peak in figure 1b. Clearly the former corresponds to sites with $\varphi_l = \pm \pi/2$ while the latter corresponds to $\varphi_l = 0$. What is not clear at this point is why the additional peak in figure 1b occurs at all, since the corresponding transitions do not satisfy condition (8).

Nevertheless, the occurrence of the third peak in the E_{\perp} -spectra is systematic. Additional proof that it arises from $\varphi_l = 0$ transitions may be obtained by applying a magnetic field in the crystal basal plane, whose effect is to lift the final-state degeneracy : as expected, the third peak generally splits (linearly with applied field) while none of the other singularities is modified.

A possible interpretation for this anomalous « third peak » is to postulate that the U^{4+} ions *pin* the phase of the modulation, in such a way as to minimize their energy. This energy, or at least that part of it which is dependent upon the phase of the modulation, can be approximated by the 5f crystal-field energy and with our (*ad hoc*) choice of $\beta_0 > 0$, this situation leads to an excess of U^{4+} sites with $\varphi_1 \simeq 0$: this is qualitatively what is needed in order to account for the occurrence of the third peak in figure 1b.

The last question which must be answered is why the pinning process remains incomplete : if it were complete one would only observe sharp lines corresponding to $\varphi_1 = 0$. Here we must invoke some competition between the U^{4+} ions and other phase-pinning defects, or competition between the individual U^{4+} ions themselves : even for a dilution level of 1 ‰ the average U^{4+} - U^{4+} distance is only of the order of 2 wavelengths of the modulation ($\simeq 6c$) and it is quite plausible that they are not able to minimize their energies independently of one another. This last point is strongly supported by the finding that a sample with a dilution level of $\sim 10^{-4}$, rather than 10^{-3} , exhibits a comparatively stronger « third peak ». Further work on the isomorphous $ThCl_4$ system, where the U^{4+} concentration may be varied over a much wider range, is in progress.

A more detailed account of this work will be given elsewhere.

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