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## Application of superspace symmetry to optical and magnetic resonance spectra of incommensurably modulated crystals

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The superspace description of incommensurable crystals is used to calculate the symmetry adapted crystal field potential for an incommensurable crystal. With this crystal field potential the perturbation of the high temperature phase energy levels by the incommensurable modulation can be calculated using perturbation theory. The results of such calculations on  $\text{ThBr}_4$  are compared with the experimental results obtained from optical and magnetic resonance spectroscopy.

### 1. Introduction

Incommensurable crystals occupy a special place within solid state physics. On the one hand they possess a long range order leading to a periodic distortion of the crystalline structure; on the other hand, the lack of three-dimensional lattice translation defies the classification of incommensurable crystals in terms of crystallographic space groups.

For a description of incommensurable crystals, an extended form of the Landau theory for structural phase transitions can be used [1, 2]. An alternative description was developed by De Wolff, Janner and Janssen, in which the three-dimensional space is extended to a higher dimensional so-called superspace. In this space, superspace groups are defined analogously to the crystallographic space groups. This allows the symmetry properties of the incommensurable crystals to be defined in terms of superspace groups.

The most conspicuous change in structure on entering the incommensurable phase is the disappearance of the three-dimensional lattice translation symmetry. The absence of the lattice translation symmetry leads to very characteristic lineshapes in optical and magnetic resonance spectra, resembling those of a powder spectrum. The calculation of magnetic resonance spectra using the Landau theory of phase transitions is well established, and is based on the variation with position of the phase and the amplitude of the modulation wave in the incommensurable crystal [2–4]. In this paper we present an alternative way to calculate the optical and magnetic resonance spectra of incommensurable crystals using the theory of superspace symmetry of incommensurable crystals as developed by De Wolff, Janner and Janssen [5–8]. This theory has the advantage over Landau theory that the incommensurable phase has a well defined symmetry, making it possible to calculate the form of the crystal field potential. From the crystal field thus found the parameters can be calculated that determine the optical and magnetic resonance spectra.

We have organized this paper as follows: first we calculate the crystal field operator for an incommensurable crystal, which, in the following section, we shall use to calculate the form of the optical and magnetic resonance spectra for a specific incommensurable crystal, thorium tetrabromide,  $\text{ThBr}_4$ . We conclude with a discussion of our results.

## 2. The crystal field operator in incommensurable crystals

We derive the crystal field operator for an incommensurable crystal in order to be able to use the symmetry relations that hold in an incommensurable crystal for the determination of the form of optical and magnetic resonance spectra for these crystals.

The crystal field potential is defined as

$$V(\mathbf{r}) = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'. \quad (1)$$

It can be written as a Fourier sum over vectors  $\mathbf{K}$  and  $\mathbf{q}$ , where

$$\mathbf{K} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*, \quad (2)$$

with  $\mathbf{a}^*$ ,  $\mathbf{b}^*$  and  $\mathbf{c}^*$  the basis vectors of the reciprocal lattice  $A_0^*$ , and  $\mathbf{q}$  is the wavevector of the incommensurable modulation

$$\mathbf{q} = \alpha\mathbf{a}^* + \beta\mathbf{b}^* + \gamma\mathbf{c}^*, \quad (3)$$

with at least one of  $\alpha$ ,  $\beta$ , or  $\gamma$  irrational. Thus, the Fourier expansion becomes:

$$V(\mathbf{r}) = V_0(\mathbf{r}) + \sum_{\lambda \neq 0} V_\lambda(\mathbf{r}), \quad (4)$$

where

$$V_\lambda(\mathbf{r}) = \sum_{\mathbf{K} \in A_0^*} \hat{V}_\lambda(\mathbf{K} + \lambda\mathbf{q}) \exp [i(\mathbf{K} + \lambda\mathbf{q}) \cdot \mathbf{r}], \quad (5)$$

where  $\lambda$  runs over positive and negative integers.

The fact that the crystal field potential must be real is used to write  $V(\mathbf{r})$  as a sum over positive values of  $\lambda$  only:

$$V(\mathbf{r}) = V_0(\mathbf{r}) + \sum_{\lambda > 0} \sum_{\mathbf{K} \in A_0^*} \hat{V}_\lambda(\mathbf{K} + \lambda\mathbf{q}) \exp [i(\mathbf{K} + \lambda\mathbf{q}) \cdot \mathbf{r}] \\ + \hat{V}_\lambda^*(\mathbf{K} + \lambda\mathbf{q}) \exp [-i(\mathbf{K} + \lambda\mathbf{q}) \cdot \mathbf{r}]. \quad (6)$$

To find the crystal field potential at the position  $\mathbf{r} + \mathbf{t}$ , where  $\mathbf{t}$  is a vector of the high temperature lattice, the translation operator  $P_{\{1|\mathbf{t}\}}$  is applied to the potential  $V(\mathbf{r})$ :

$$P_{\{1|\mathbf{t}\}}V(\mathbf{r}) = V(\mathbf{r} - \mathbf{t}) = V_0(\mathbf{r}) + \sum_{\lambda > 0} \sum_{\mathbf{K} \in A_0^*} \hat{V}_\lambda(\mathbf{K} + \lambda\mathbf{q}) \exp [i(\mathbf{K} + \lambda\mathbf{q}) \cdot \mathbf{r}] \exp [-i\lambda\mathbf{q} \cdot \mathbf{t}] \\ + \hat{V}_\lambda^*(\mathbf{K} + \lambda\mathbf{q}) \exp [-i(\mathbf{K} + \lambda\mathbf{q}) \cdot \mathbf{r}] \exp [i\lambda\mathbf{q} \cdot \mathbf{t}]. \quad (7)$$

From the expression it is clear that in the incommensurable phase the three-dimensional translation symmetry is lost due to the incommensurable nature of the wavevector  $\mathbf{q}$ , and the crystal field potential is no longer invariant under translations over a lattice vector  $\mathbf{t}$ . Because  $\mathbf{q}$  is incommensurable with the high temperature lattice vector  $\mathbf{t}$ , the phasefactor  $\mathbf{q} \cdot \mathbf{t}$  varies continuously as  $\mathbf{t}$  'moves' through the crystal.



The phase in the modulation wave is determined up to an arbitrary phase  $\phi_0$  because  $\mathbf{q} \cdot \mathbf{t}$  is the phase of  $\mathbf{r} + \mathbf{t}$  relative to the phase of  $\mathbf{r}$ . In the following we write for the phase in the modulation wave  $\mathbf{q} \cdot \mathbf{t} = \phi$ , thereby setting  $\phi_0 = 0$ .

We now express the crystal field potential in symmetry-adapted spherical harmonics. The decomposition of  $V(\mathbf{r}, \phi)$  into spherical harmonics  $Y_{lm}$  is achieved using the plane wave decomposition

$$\exp(i\mathbf{k} \cdot \mathbf{r}) = \sum_{l=0}^{\infty} \sum_{m=-l}^l 4\pi i^l j_l(kr) Y_{lm}^*(\vartheta, \varphi)_{\hat{\mathbf{k}}} Y_{lm}(\vartheta, \varphi)_{\hat{\mathbf{r}}}, \quad (8)$$

where  $j_l(kr)$  is a spherical Bessel function of order  $l$  with argument  $kr = |\mathbf{K} + \lambda\mathbf{q}||\mathbf{r}|$ . The crystal field potential in terms of spherical harmonics thus becomes:

$$V(\mathbf{r}, \phi) = V_0(\mathbf{r}) + \sum_{\lambda>0} \sum_{l,m} \{A_{lm}^\lambda Y_{lm}(\vartheta, \varphi)_{\hat{\mathbf{r}}} \exp(-i\lambda\phi) + A_{lm}^{*\lambda} Y_{lm}^*(\vartheta, \varphi)_{\hat{\mathbf{r}}} \exp(i\lambda\phi)\}, \quad (9)$$

with

$$A_{lm}^\lambda = \sum_{\mathbf{K} \in \Lambda_0^*} \hat{V}_\lambda(\mathbf{K} + \lambda\mathbf{q}) 4\pi i^l j_l(kr) Y_{lm}^*(\vartheta, \varphi)_{\hat{\mathbf{k}}}, \quad (10)$$

and  $\hat{\mathbf{k}}$  is the unit vector in the direction of  $\mathbf{K} + \lambda\mathbf{q}$ .

The phase dependent crystal field potential for incommensurable crystals, equation (9), is completely analogous to the crystal field potential in 'normal' crystals. In the latter, the number of terms in the expansion of the crystal field in spherical harmonics is restricted by the symmetry of the site for which the crystal field is determined. In an incommensurable crystal it is the site symmetry in superspace that determines the terms that are to be retained in the crystal field expansion in equation (9).

### 3. Superspace symmetry

In an incommensurable crystal with a displacive modulation, the atoms are displaced from their high temperature equilibrium positions by a periodic displacement:

$$\mathbf{r}(n, j) = \mathbf{r}_j + \mathbf{n} + \mathbf{f}_j u(\mathbf{q} \cdot (\mathbf{r}_j + \mathbf{n}) + \phi_j), \quad (11)$$

where  $\mathbf{r}_j$  gives the position of the atom with index  $j$  in the unit cell, and  $\mathbf{f}_j u(\mathbf{q} \cdot (\mathbf{r}_j + \mathbf{n}) + \phi_j)$  is the periodic displacement of the atom in the incommensurable phase. As was noted in the previous section, because of the incommensurable nature of the modulation, the phases  $\phi_j$  of the atoms are distributed uniformly and densely between 0 and  $2\pi$ , and therefore are taken as continuous variables. For the phase of the modulation wave we introduce the phase parameter  $v$ . A translation over a lattice vector  $\mathbf{t}$  changes the phase in the modulation wave by an amount  $\mathbf{q} \cdot \mathbf{t}$ , and thus the phase of the atom after translation is different from the phase before the translation, as can be seen from equation (11). The translation symmetry can be restored by accompanying the translation with a change in the phase such that

$$\mathbf{q} \cdot \mathbf{t} + v_1 = v \pmod{2\pi} \quad (12)$$

Thus, a lattice translation  $\mathbf{t}$  accompanied by a phase shift

$$v_1 = v - \mathbf{q} \cdot \mathbf{t} \pmod{2\pi} \quad (13)$$

leaves the crystal invariant.

Note that the parameter  $v$  defines a lattice direction with lattice parameter  $2\pi$ : if  $v$  is incremented by multiples of  $2\pi$  the amplitude of the modulation wave stays the same, just as a normal crystal is invariant for translations over a lattice vector  $\mathbf{K}$ . Therefore, the phase parameter  $v$  is considered to be an additional lattice coordinate that is needed to specify the position of the atoms. If there are more than one incommensurable wavevectors, more extra lattice directions can be specified. In this paper we shall restrict ourselves to a one-dimensional modulation.

The axis of the additional coordinate is chosen in the direction  $\mathbf{d}$  perpendicular to  $\mathbf{a}$ ,  $\mathbf{b}$ , and  $\mathbf{c}$ . The atoms now appear as strings along the  $\mathbf{d}$  direction of the four-dimensional superspace spanned by  $\mathbf{a}$ ,  $\mathbf{b}$ ,  $\mathbf{c}$ , and  $\mathbf{d}$  with positions

$$\mathbf{r}_{sj} = (\mathbf{r}_j + \mathbf{n} + \mathbf{f}_j u(\mathbf{q} \cdot (\mathbf{r}_j + \mathbf{n}) + \phi_j + v), v\mathbf{d}). \quad (14)$$

An incommensurable crystal can be considered as a cross-section of these strings of constant  $v$  of the four-dimensional space [5, 6, 9]. This description can be formalized by embedding the crystal in a  $(3 + 1)$ -dimensional superspace  $V_s$  [10]:

$$V_s = V \oplus V_1, \quad (15)$$

formed by the direct sum of the position or external space  $V$  in which the three high temperature lattice vectors  $\mathbf{a}$ ,  $\mathbf{b}$ , and  $\mathbf{c}$  are defined and the one-dimensional internal space  $V_1$  in which the vector  $\mathbf{d}$  is defined.

A vector in superspace is written as  $\mathbf{r}_s = (\mathbf{r}, \mathbf{r}_1)$ , where  $\mathbf{r}$  is a vector in the external and  $\mathbf{r}_1$  a vector in the internal space. The pattern of the strings considered above describes a modulated crystal which is invariant with respect to a translation of the lattice  $\Sigma$  with basis vectors

$$\mathbf{a}_s = (\mathbf{a}, -\alpha\mathbf{d}), \quad \mathbf{b}_s = (\mathbf{b}, -\beta\mathbf{d}), \quad \mathbf{c}_s = (\mathbf{c}, -\gamma\mathbf{d}), \quad \mathbf{d}_s = (0, \mathbf{d}). \quad (16)$$

The basis vectors for the reciprocal lattice  $\Sigma^*$  are orthogonal to these basis vectors and defined as:

$$\mathbf{a}_s^* = (\mathbf{a}^*, 0), \quad \mathbf{b}_s^* = (\mathbf{b}^*, 0), \quad \mathbf{c}_s^* = (\mathbf{c}^*, 0), \quad \mathbf{d}_s^* = (\mathbf{q}, \mathbf{d}^*). \quad (17)$$

The crystal field operator can be expanded as a Fourier sum in superspace [10]:

$$V_s(\mathbf{r}_s) = \sum_{h,k,l,\lambda} \hat{V}_{s\lambda}(\mathbf{k}_s) \exp(i\mathbf{k}_s \cdot \mathbf{r}_s), \quad (18)$$

where  $\mathbf{r}_s = (r_1, r_2, r_3, r_4)$  is a vector of the lattice  $\Sigma$ , equation (16), and  $\mathbf{k}_s = (h, k, l, \lambda)$  is a vector of the reciprocal lattice  $\Sigma^*$ , equation (17), and [11]

$$\hat{V}_{s\lambda}(\mathbf{k}_s) \equiv \hat{V}_\lambda(\mathbf{K} + \lambda\mathbf{q}). \quad (19)$$

Although an incommensurable crystal does not belong to a three-dimensional space group, in the four-dimensional superspace it is possible to find a superspace group  $G_s$  for which the crystal is invariant. The elements of  $G_s$  are defined by an external part  $g$ , operating on  $V$ , and an internal part  $g_1$ , operating on  $V_1$ :

$$\begin{aligned} g_s &= (g, g_1) \\ g &= \{R|\mathbf{t}\} \\ g_1 &= \{\epsilon|\mathbf{t}_1\} \end{aligned} \quad (20)$$

Because  $V_1$  is one-dimensional,  $\epsilon = \pm 1$ . Different notations for the elements of  $G_s$  are

in use. In the split basis notation the elements of  $G_s$  are defined as

$$g_s = \{R, \epsilon | (\mathbf{t}, t_1)\}, \quad (21)$$

and in the lattice basis notation as

$$g_s = \{R_s | \mathbf{t}_s\}. \quad (22)$$

We now use the invariance of the superspace crystal for transformations  $g_s \in G_s$  to derive the transformation properties of the incommensurable crystal under the external part  $g$  of  $g_s$ . In the appendix we derive that

$$P_g V_\lambda(\mathbf{r}) = V_{\epsilon\lambda}(\mathbf{r}) \exp(2\pi i \epsilon \lambda t_1). \quad (23)$$

The extra phase factor  $\exp(2\pi i \epsilon \lambda t_1)$  can be interpreted as a 'correction' for the change in phase associated with the change in position after the transformation  $g$ .

On the other hand, we can expand  $V_\lambda(\mathbf{r})$  in terms of irreducible basis functions  $\phi_{p,i}(\mathbf{r})$ , of the high temperature space group  $G_0$ :

$$V_\lambda(\mathbf{r}) = \sum_{p,i} c_{p,i}^\lambda \phi_{p,i}(\mathbf{r}), \quad (24)$$

where  $c_{p,i}^\lambda$  is the expansion coefficient of the  $i$ th basis function  $\phi_{p,i}$  of the  $p$ th irreducible representation of  $G_0$ . Under an element  $g = \{R | \mathbf{t}\}$  of the group of  $\mathbf{q}$ ,  $G_q$ , the coefficients  $c_{p,i}^\lambda$  transform as:

$$P_g c_{p,i}^\lambda = \sum_j \exp(-i\lambda \mathbf{q} \cdot \mathbf{t}) D_{ij}^p(R) c_{p,j}^\lambda, \quad (25)$$

where  $D_{ij}^p(R)$  are the matrix elements of the  $p$ th irreducible representation of the point group of  $\mathbf{q}$ . For the elements of  $G_q$ ,  $\epsilon = +1$  since  $R\mathbf{q} = \mathbf{q}$  [7]. Comparing equation (23) with (25) gives:

$$\sum_j \exp(-i\lambda \mathbf{q} \cdot \mathbf{t}) D_{ij}^p(R) c_{p,j}^\lambda = \exp(2\pi i \lambda t_1) c_{p,i}^\lambda. \quad (26)$$

This expression can be simplified further using (cf. equation (13))

$$t_1 = t_4 - \frac{\mathbf{q} \cdot \mathbf{t}}{2\pi}. \quad (27)$$

Thus, equation (26) becomes

$$\sum_j D_{ij}^p(R) c_{p,j}^\lambda = \exp(2\pi i \lambda t_4) c_{p,i}^\lambda. \quad (28)$$

The above expression imposes restrictions on the irreducible representations that can be present in the expansion of the crystal field operator in terms of  $\lambda$ ; however, it is not limited to the crystal field operator alone: it holds for any scalar operator and can be extended to tensor operators of higher rank [8].

#### 4. Application to ThBr<sub>4</sub>

Thorium tetrabromide, ThBr<sub>4</sub>, occurs in two modifications. Below 700 K, the  $\alpha$ -form with space group symmetry  $I4_1/a$  ( $C_{4h}^6$ ) is stable. The high temperature form,  $\beta$ -ThBr<sub>4</sub>, is stable above 700 K but is often obtained as a metastable form at lower temperatures when crystals are grown from the melt [12].  $\beta$ -ThBr<sub>4</sub> exhibits a



Table 1. Character table of the  $\tau^4$  representation of the group of  $\mathbf{q}$ ,  $I4_1md$ ;  $\mathbf{t} = (0, 1/2, 1/4)$ .

$\{E 0\}$	$\{C_{4z}^+ \mathbf{t}\}$	$\{C_{2z} 0\}$	$\{C_{4z}^- \mathbf{t}\}$	$\{\sigma_{yz} 0\}$	$\{\sigma_d \mathbf{t}\}$	$\{\sigma_{xz} 0\}$	$\{\sigma_{d'} \mathbf{t}\}$
1	$\bar{1}$	1	$\bar{1}$	$\bar{1}$	1	$\bar{1}$	1

structural phase transition to an incommensurable phase at 95 K, as was discovered with Raman spectroscopy [13]. Later, elastic and inelastic neutron scattering experiments revealed the structural and dynamic characteristics of the phase transition [14, 15]. It was found that the phase transition originates in a frozen optical soft mode that transforms as the  $\tau^4$  representation of  $I4_1md$ , the group of the wavevector  $\mathbf{q}$ . The characters of this representation are given in table 1. Measurements of the  $\mathbf{q}$  vector from 95 K down to 1.5 K shows that the length of the modulation wavevector is almost independent of temperature, with a value  $q = (0.3115 \pm 0.0015)c^*$ .

The superspace group of  $\text{ThBr}_4$  in the notation of De Wolff, Janner and Janssen is  $I4_1/amd(00\gamma)(s0s0)$  [16, 17]. In this notation, the direction of the wavevector  $\mathbf{q}$  is indicated after the space group symbol of the high temperature phase:  $\mathbf{q} = (0, 0, \gamma)$ , see also equation (3). The expression (s0s0) gives the fractional lattice translations in the direction of  $\mathbf{d}_s$  (see equation (16)). The position of the symbol, 0 or s, corresponds with the position of the generator in the space group symbol; 0 indicates no internal translation while s corresponds to an internal translation  $t_4 = 1/2$ . Thus, both the fourfold screw axis,  $4_1$ , and the mirror plane m are associated with an internal translation  $t_4 = 1/2$ .

To determine the crystal field potential of  $\text{ThBr}_4$  in the incommensurable phase, the crystal field potential is expanded in irreducible basis functions of the group of  $\mathbf{q}$ ,  $I4_1md$  with corresponding point group  $C_{4v}$ . The character table of  $C_{4v}$  is given in table 2. This expansion is subject to the restrictions imposed by equation (28). Application of these conditions shows that the expansion of  $V(\mathbf{r})$  in irreducible basis functions contains only basis functions that transform as  $\Gamma_4$  for odd values of  $\lambda$ , and basis functions that transform as  $\Gamma_1$  for even values of  $\lambda$ . The symmetry-adapted spherical harmonics that transform according to the  $\Gamma_4$  representation are [18]

$$-\frac{1}{2}i\sqrt{2}(Y_{lm} - Y_{l-m}), \quad (29)$$

where  $l$  takes only even values, and the values of  $m$  are given by

$$m = 2 + 4n \quad 2 \leq m \leq l, \quad (30)$$

with  $n$  integer, while symmetry-adapted spherical harmonics for the  $\Gamma_1$  representation are

$$\frac{1}{2}\sqrt{2}(Y_{lm} + Y_{l-m}) \quad (31)$$

Table 2. Character table of  $C_{4v}$ .

$C_{4v}$	$E$	$C_{2z}$	$C_{4z}^\pm$	$\sigma_{yz}, \sigma_{xz}$	$\sigma_d, \sigma_{d'}$
$\Gamma_1$	1	1	1	1	1
$\Gamma_2$	1	1	1	-1	-1
$\Gamma_3$	1	1	-1	1	-1
$\Gamma_4$	1	1	-1	-1	1
$\Gamma_5$	2	-2	0	0	0

Again,  $l$  is even, but now  $m$  takes the values

$$m = 4n \quad 0 \leq m \leq l. \quad (32)$$

When these restrictions are imposed on the general form of the crystal field potential as given by equation (9), the crystal field potential becomes

$$\begin{aligned} V(\mathbf{r}, \phi) = & V_0(\mathbf{r}) + \sum_{\lambda \text{ odd}} \sum_{l \text{ even}} \sum'_{m=2} iA_{lm}^\lambda (-Y_{lm} \exp(-i\lambda\phi) + Y_{l-m} \exp(i\lambda\phi)) \\ & + \sum_{\lambda \text{ even}} \sum_{l \text{ even}} \sum'_{m=0} A_{lm}^\lambda ((Y_{lm} \exp(-i\lambda\phi) + Y_{l-m} \exp(i\lambda\phi)), \end{aligned} \quad (33)$$

where the prime on the summation sign indicates that the  $m$  values increase by increments of 4. To bring out the  $\phi$  dependence more explicitly, this is written as

$$\begin{aligned} V(\mathbf{r}, \phi) = & V_0(\mathbf{r}) + \sum_{\lambda \text{ odd}} \cos \lambda\phi \sum_{l \text{ even}} \sum'_{m=2} iA_{lm}^\lambda (-Y_{lm} + Y_{l-m}) \\ & - \sum_{\lambda \text{ odd}} \sin \lambda\phi \sum_{l \text{ even}} \sum'_{m=2} A_{lm}^\lambda (Y_{lm} + Y_{l-m}) \\ & + \sum_{\lambda \text{ even}} \cos \lambda\phi \sum_{l \text{ even}} \sum'_{m=0} A_{lm}^\lambda (Y_{lm} + Y_{l-m}) \\ & - \sum_{\lambda \text{ even}} \sin \lambda\phi \sum_{l \text{ even}} \sum'_{m=0} iA_{lm}^\lambda (Y_{lm} - Y_{l-m}). \end{aligned} \quad (34)$$

To calculate the optical or EPR spectra of  $\text{ThBr}_4$  in the incommensurable phase, the crystal field potential at the optical or paramagnetic active thorium site has to be determined. In the frozen soft mode that determines the incommensurable phase, only terms with  $\lambda = 1$  contribute to the displacements of the bromine atoms [14]. Therefore, we shall consider only these terms in the expansion of the crystal field potential. A further reduction in the number of terms is obtained by making use of the accidental symmetry of the thorium site. The frozen soft mode can be written as the sum of two symmetry adapted eigenvectors, one that reduces the thorium site symmetry from  $D_{2d}$  to  $D_2$  and one that leaves the  $D_{2d}$  symmetry unaltered. Through the particular mixing of these two modes, the site symmetry of the thorium position is  $D_{2d}$  for phases  $\phi = 0, \pi$  and  $D_2$  for all other phases [4, 14, 19]. This accidental symmetry implies that terms with  $D_2$  symmetry must vanish for  $\phi = 0, \pi$ . This leaves the following expansion for the crystal field potential at the thorium sites

$$V(\mathbf{r}, \phi) = V_0(\mathbf{r}) + \sin \phi \sum_{l \text{ even}} \sum'_{m=2} A_{lm}^1 (Y_{lm} + Y_{l-m}). \quad (35)$$

The form of  $V_0(\mathbf{r})$  is determined by the  $D_{2d}$  site symmetry of the high temperature phase:

$$V_0(\mathbf{r}) = A_0^2 Y_{20} + A_0^4 Y_{40} + A_4^4 (Y_{44} + Y_{4-4}) + A_0^6 Y_{60} + A_4^6 (Y_{64} + Y_{6-4}). \quad (36)$$

## 5. Optical experiments on $\text{ThBr}_4$

The incommensurable modulation manifests itself in the optical spectra of  $\text{ThBr}_4$  doped with actinide ions. Krupa and co-workers have observed the characteristic singularities in absorption and emission spectra  $\text{Pa}^{4+}$  in  $\text{ThBr}_4$  and in the isomorphous compound  $\text{ThCl}_4$  [20, 21]. The optical spectra of  $\text{ThBr}_4$  doped with  $\text{U}^{4+}$  ( $5f^2$ ) were studied by Delamoye *et al.* [22, 23]. The spectra show a continuous distribution



of  $U^{4+}$  sites bounded by two edge singularities. Selective excitation experiments showed that the lines could be assigned to a continuous distribution of sites with  $D_2$  symmetry; the singularities are attributed to sites with  $D_2$  symmetry and sites with  $D_{2d}$  symmetry.

The symmetry spectra could be explained by assuming that the energy levels depend on the phase in the modulation wave according to

$$E^j(\phi) = E_0^j + \eta^2(\alpha_j + \beta_j \sin^2 \phi) \pm \gamma_j \eta \sin \phi, \quad (37)$$

where  $j$  is the index of the energy levels of a  $U^{4+}$  ion in the  $ThBr_4$  host and  $\eta$  corresponds to the amplitude of the modulation. The coefficient  $\gamma_j$  equals zero for states which transform according to the irreducible representations  $\Gamma_1$ ,  $\Gamma_2$ ,  $\Gamma_3$ , and  $\Gamma_4$  of the group  $D_{2d}$ , and is non-zero for states that transform as  $\Gamma_5$ .

To see how these results compare with the results that are obtained from the application of the  $\phi$ -dependent crystal field potential, we determine the effect of the modulation on the energy levels by considering the  $\phi$ -dependent part of  $V(\mathbf{r}, \phi)$  as a small perturbation:

$$V_1(\mathbf{r}, \phi) = \sin \phi \sum_{\text{even } l} \sum_{m=2} A_{lm}^1 (Y_{lm} + Y_{l-m}). \quad (38)$$

As was shown earlier,  $V_1(\mathbf{r}, \phi)$  transforms according to the  $\Gamma_4$  representation of  $C_{4v}$ . The unperturbed states of the  $U^{4+}$  ions transform according to one of the irreducible representations of  $D_{2d}$ . To first order in the energy, the only non-zero matrix elements are between states that belong to the twofold degenerate  $\Gamma_5$  representation of  $D_{2d}$ . The perturbation splits the degenerate energy level into two non-degenerate levels with energies:

$$E_{\pm} = E_0 \pm E_1 \sin \phi. \quad (39)$$

The energy levels that belong to the one-dimensional representations of  $D_{2d}$  are changed only in second order, in agreement with the experimental observation that  $\gamma_j$  in equation (37) is non-zero only for states that transform according to the  $\Gamma_5$  representation.

## 6. EPR experiments on $ThBr_4$

The results of EPR experiments on  $ThBr_4$  doped with  $Pa^{4+}$  in the incommensurable phase were reported in a series of earlier papers [4, 19, 24]. To explain the spectra, a heuristic model was proposed in which it was assumed that the parameters of the spin Hamiltonian all varied linearly with the amplitude of the incommensurable modulation. With this heuristic model excellent agreement with the experimental spectra was obtained [4, 19, 24]. Here we use the symmetry adapted crystal field to calculate the effect of the incommensurable modulation on the spin Hamiltonian parameters of  $Pa^{4+}$  in  $ThBr_4$ . Because all observed EPR transitions are within the ground doublet formed by states  $|1\rangle$  and  $|\overline{1}\rangle$  that transform according to the  $\Gamma_7$  representation of the double group  $\overline{D}_{2d}$ , we calculate only the perturbation of the ground state. The term of  $V(\mathbf{r}, \phi)$ , with  $\lambda = 1$  connects the ground state with the excited states that transform according to the  $\Gamma_6$  representation. In this way, the first excited state is mixed with the ground state, and to first order the ground state becomes:

$$|1\rangle_{\phi} = |1\rangle + \epsilon \sin \phi |2\rangle, \quad (40)$$

where  $\epsilon$  is a small constant that depends on the strength of the perturbation and hence on the amplitude of the modulation. The  $g$  values for the ground state are determined by diagonalization of the matrix [25]

$$\begin{pmatrix} \langle 1 | L_i + 2S_i | 1 \rangle_\phi & \langle 1 | L_i + 2S_i | \overline{1} \rangle_\phi \\ \langle \overline{1} | L_i + 2S_i | 1 \rangle_\phi & \langle \overline{1} | L_i + 2S_i | \overline{1} \rangle_\phi \end{pmatrix}, \quad (41)$$

and are found to be [27]

$$g_x(\phi) = g_x^0 + g_1 \sin \phi + \dots, \quad (42)$$

$$g_y(\phi) = g_y^0 - g_1 \sin \phi + \dots, \quad (43)$$

$$g_z(\phi) = g_z^0 + g_2 \sin^2 \phi + \dots. \quad (44)$$

An important point to note is that the matrix elements of the hyperfine interaction are proportional to the matrix elements of the Zeeman interaction because both the Zeeman interaction and the hyperfine interaction are vector operators which operate within the same  $j$  manifold [25]. Therefore, the phase dependence of the hyperfine interaction is the same as for the Zeeman interaction. The quadrupole interaction is the scalar product of two tensor operators of rank two [26]. Therefore, the matrix elements of the quadrupole operator are not proportional to those of the Zeeman and hyperfine interactions, but transform as irreducible tensor operators of rank 2:

$$V_{xx} - V_{yy} = \sqrt{\frac{3}{2}}(U_2^{(2)} + U_{-2}^{(2)}), \quad (45)$$

$$V_{zz} = 2U_0^{(2)}, \quad (46)$$

where the quadrupole coupling constant  $V_{zz}$  and  $V_{yy}$  are elements of the quadrupole matrix

$$\mathbf{V} = \begin{pmatrix} V_{xx} & 0 & 0 \\ 0 & V_{yy} & 0 \\ 0 & 0 & V_{zz} \end{pmatrix}. \quad (47)$$

Evaluation shows that  $V_{xx} - V_{yy}$  is proportional to the amplitude of the modulation, and that  $V_{zz}$  is proportional to the square of the modulation amplitude [25].

The phase dependence of the spin Hamiltonian parameters as calculated with the phase dependent crystal field potential is in agreement with the phase dependence of the spin Hamiltonian parameters observed experimentally [4, 19–24]. From the fact that the  $z$  components of the  $g$  tensors of the two sites are equal within the experimental uncertainties, and that the same holds for the  $z$  components of the hyperfine tensors of the two sites, it is concluded that the coefficient of the quadratic term  $g_2$  in equation (44), and the corresponding term for the hyperfine interaction, are smaller than the experimental uncertainties in the  $g$  and  $A$  values. The agreement of the measured quadrupole tensor with the calculated tensor is more difficult to establish because of the large uncertainty in the directions of the principal axes. It was found [4] that the  $z$  components of the quadrupole tensors of both sites are equal, in agreement with the quadratic dependence on the modulation amplitude of  $V_{zz}$ . The linear dependence on the modulation amplitude of  $V_{xx} - V_{yy}$  is not so easy to establish experimentally because the principal directions of the quadrupole tensor are inaccurate. If, however, it is assumed that the quadrupole tensors of both sites are rotated with respect to one another by  $90^\circ$  around the  $z$  axis, like the  $\mathbf{g}$  and



A tensors, the experimental observations are in agreement with the theoretical dictions.

## 7. Conclusion

We have found the crystal field operator for an incommensurable crystal by extending the three-dimensional space to a higher-dimensional superspace. The symmetry properties of the crystal in this phase were used to derive constraints on the form of the crystal field operator. We compared the experimental results from optical and electron paramagnetic resonance studies on  $\text{ThBr}_4$  in the incommensurable phase with calculations using the symmetry adapted crystal field potential. The results were found to be in excellent qualitative agreement. We propose that this method may also be used as an aid in the interpretation of the optical and magnetic resonance spectra when ambiguities such as pinning effects complicate interpretation.

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## Appendix

In this appendix we derive equation (23). To begin we need to calculate the dot product  $\mathbf{k}_s \cdot \mathbf{r}_s$  in the split basis notation. With respect to this basis, the vectors  $\mathbf{k}_s$  and  $\mathbf{r}_s$  take the following form:

$$\begin{aligned} \mathbf{k}_s &= h\mathbf{a}_s^* + k\mathbf{b}_s^* + l\mathbf{c}_s^* + \lambda\mathbf{d}_s^* \\ &= (h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* + \lambda\mathbf{q}, \lambda\mathbf{d}^*) \\ &= (\mathbf{K} + \lambda\mathbf{q}, \lambda\mathbf{d}^*) = (\mathbf{k}, \mathbf{k}_I), \end{aligned} \quad (\text{A } 1)$$

$$\begin{aligned} \mathbf{r}_s &= r_1\mathbf{a}_s + r_2\mathbf{b}_s + r_3\mathbf{c}_s + r_4\mathbf{d}_s \\ &= \left( r_1\mathbf{a} + r_2\mathbf{b} + r_3\mathbf{c}, \left( -\frac{\mathbf{q} \cdot \mathbf{r}}{2\pi} + r_4 \right) \mathbf{d} \right) = (\mathbf{r}, \mathbf{r}_I). \end{aligned} \quad (\text{A } 2)$$

The incommensurable crystal belongs to a four-dimensional superspace group  $G_s$ , thus, the crystal field operator  $V_s(\mathbf{r}_s)$  is invariant for transformations  $g_s \in G_s$ :

$$P_{g_s} V_s(\mathbf{r}_s) = V_s(\mathbf{r}_s), \quad (\text{A } 3)$$

or,

$$\sum_{\mathbf{K}, \lambda} \hat{V}_{s\lambda}(\mathbf{k}_s) \exp(\mathbf{k}_s \cdot g_s^{-1} \mathbf{r}_s) = \sum_{\mathbf{K}, \lambda} \hat{V}_{s\lambda}(\mathbf{k}_s) \exp(\mathbf{k}_s \cdot \mathbf{r}_s). \quad (\text{A } 4)$$

First we rewrite the left hand side:

$$\sum_{\mathbf{K}, \lambda} \hat{V}_{s\lambda}(\mathbf{k}_s) \exp(\mathbf{k}_s \cdot g_s^{-1} \mathbf{r}_s) = \sum_{\mathbf{K}, \lambda} \hat{V}_{s\lambda}(\mathbf{K} + \lambda\mathbf{q}) \exp(g_s \mathbf{k}_s \cdot \mathbf{r}_s), \quad (\text{A } 5)$$

where we have used the definition in equation (19). This can be expanded further in



the split basis notation:

$$\begin{aligned} & \sum_{\mathbf{K}, \lambda} \hat{V}_\lambda(\mathbf{K} + \lambda\mathbf{q}) \exp(g_s \mathbf{k}_s \cdot \mathbf{r}_s) \\ &= \sum_{\mathbf{K}, \lambda} \hat{V}_\lambda(\mathbf{K} + \lambda\mathbf{q}) \exp [iR(\mathbf{K} + \lambda\mathbf{q}) \cdot \mathbf{r} + 2\pi i \lambda \epsilon r_1 - iR(\mathbf{K} + \lambda\mathbf{q}) \cdot \mathbf{t} - 2\pi i \lambda \epsilon t_1]. \end{aligned} \quad (\text{A } 6)$$

Because of the invariance condition, this must be identical to

$$\sum_{\mathbf{K}, \lambda} \hat{V}_\lambda(\mathbf{K} + \lambda\mathbf{q}) \exp [i(\mathbf{K} + \lambda\mathbf{q}) \cdot \mathbf{r} + 2\pi i \lambda r_1]. \quad (\text{A } 7)$$

To compare equations (A 6) and (A 7) we change the summation in the latter. The summation over  $\mathbf{K}$  is replaced by  $R\mathbf{K}$  and the summation over  $\lambda$  is replaced by a summation over  $\epsilon\lambda$ :

$$\sum_{\mathbf{K}, \lambda} \hat{V}_\lambda(R\mathbf{K} + \epsilon\lambda\mathbf{q}) \exp [i(R\mathbf{K} + \epsilon\lambda\mathbf{q}) \cdot \mathbf{r} + 2\pi i \epsilon \lambda r_1] \quad (\text{A } 8)$$

We now use the relation  $R\mathbf{q} = \epsilon\mathbf{q}$  (see, e.g., Janner and Janssen [7]) to obtain

$$\sum_{\mathbf{K}, \lambda} \hat{V}_{\epsilon\lambda}(R(\mathbf{K} + \lambda\mathbf{q})) \exp [iR(\mathbf{K} + \lambda\mathbf{q}) \cdot \mathbf{r} + 2\pi i \epsilon \lambda r_1]. \quad (\text{A } 9)$$

We can now compare this with equation (A 6) to find the condition for equivalence:

$$\hat{V}_\lambda(\mathbf{K} + \lambda\mathbf{q}) = \hat{V}_{\epsilon\lambda}(R(\mathbf{K} + \lambda\mathbf{q})) \exp [iR(\mathbf{K} + \lambda\mathbf{q}) \cdot \mathbf{t} + 2\pi i \epsilon \lambda t_1]. \quad (\text{A } 10)$$

Now, we want to compare the transformation  $g_s$  in four-dimensional space with the effect of the external part  $g$  of  $g_s$  on the crystal in real space, i.e., we want to compare  $P_{g_s} V_s(\mathbf{r}_s)$  with  $P_g V(\mathbf{r})$ . We write

$$P_g V(\mathbf{r}) = \sum_{\mathbf{K}, \lambda} \hat{V}_\lambda(\mathbf{K} + \lambda\mathbf{q}) \exp [iR(\mathbf{K} + \lambda\mathbf{q}) \cdot \mathbf{r} - iR(\mathbf{K} + \lambda\mathbf{q}) \cdot \mathbf{t}]. \quad (\text{A } 11)$$

Substitution of the invariance condition gives

$$\begin{aligned} P_g V(\mathbf{r}) &= \sum_{\mathbf{K}, \lambda} \hat{V}_{\epsilon\lambda}(R(\mathbf{K} + \lambda\mathbf{q})) \exp [iR(\mathbf{K} + \lambda\mathbf{q}) \cdot \mathbf{r} + 2\pi i \epsilon \lambda t_1] \\ &= \sum_{\lambda} V_{\epsilon\lambda}(\mathbf{r}) \exp [2\pi i \epsilon \lambda t_1], \end{aligned} \quad (\text{A } 12)$$

which gives the desired relation, equation (23).

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