Superposition Model Analysis of the Spin Hamiltonian Parameters of Two Gd^{3+} Doped Thorium Dichalcogenides

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The spin Hamiltonian parameters of Gd^{3+} in a single crystal of Thorium disulfide (ThS_2) are analysed by means of the superposition model, in its most general form of a two exponents power law. In fact, the approximated one exponent power law is not suitable for this compound, where the ion-ligand distances show a quite large spread. The results of the analysis are then applied to the case of Gd^{3+} doped Thorium oxysulfide (ThOS), where the fitting of the experimental data is possible only assuming some distortion of the ligand cage.

1. Introduction

The superposition model (SPM) has been succesfully applied to the analysis of the spin Hamiltonian parameters describing the ground state splitting of S-state ions in many host matrices [1–7]. The main assumption underlying the SPM is that the total crystal field acting on the ion can be built up from individual contributions from each of the ions of the crystal. This essentially means that the crystal field interaction is considered as ruled up by overlap and covalence mechanisms and therefore it is sufficient to take into account contributions from the nearest neighbours only. This is also the principal limit of the SPM: in fact, in strongly ionic compounds, or when the dominant interaction is almost purely electrostatic, better results seem obtainable by the polarizable point charge model, at least for f^7 ions [8, 9]. However, in the quoted limit, the application of the SPM has given valuable results for the second degree and recently also for the fourth degree parameters [6].

The contribution to the parameters of each ion-ligand pair is given, apart from a geometrical factor depending on the angular coordinates of the ligand, by an "intrinsic parameter", the value of which depends on the ion-ligand distance. This dependence is usually explicited in terms of a simple power law, that is $\bar{b}_n(R_i) = \bar{b}_n(R_0)(R_0/R_i)^{t_n}$ [1], where R_i is the given distance and R_0 a fixed reference distance. In effect, this approximation is valid for small variations of R_i with respect to R_0 only. This derives from the fact that such a power law can be considered as an approximation of the sum of two opposing terms, as pointed out by Newman and Urban [1], in agreement with the low values of t_2 normally found for the second degree parameters, in the case of f^7 ions.

As far as we know, the SPM has never been successfully applied to compounds showing a large spread of ion-ligand distances. An attempt on $PbCl_2$ [10] has not given satisfactory results, owing probably also to the prevalent ionic character of the Pb-Cl bond. Therefore, we consider it necessary to analyze the most general form of the SPM as reported in Ref. [1], to show that the model can be applied also in the case of a relatively wide range of ion-ligand distances.

In this work we report the application of the SPM to a Gd^{3+} doped single crystal of Thorium disulfide (ThS_2), which has the same structure as $PbCl_2$, but appears more suitable for such application, owing to the more covalent character of the bonding with sulphur ligands. Using a power law with two exponents, we analyze the possible solutions for the parameters, obtained by numerical procedures, and apply the results to a second compound, namely Thorium oxysulfide (ThOS). One of the advantages of the SPM is the possibility to calculate the spin Hamiltonian parameters for a complex, using the intrinsic parameters obtained from other compounds. In this way, as we will show, one can also point out local distortions at the impurity site.

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We limit our analysis to the second degree parameters, for which the validity of the SPM has been confirmed.

In Sect. II we recall the crystal structures, the spin Hamiltonian parameters and all the useful experimental data for the two compounds under study. In Sect. III we give the general formulation of the SPM and a complete analysis of its application to ThS_2 and ThOS. Finally, in Sect. IV, the principal results are discussed.

2. Crystal Structures and Spin Hamiltonian Parameters

Both crystals, ThS_2 and ThOS, were grown at the Karlsruhe European Institute for Transuranium Elements, by means of a transport method already described [11]. Following the data of Zachariasen [12], the ThS_2 crystal belongs to the space group P_{mnb}-D_{2h}^{16} and has the same structure as $PbCl_2$, with lattice parameters $a=4.259(2)$ Å, $b=7.249(3)$ Å and $c=8.600(3)$ Å. The Th^{4+} ion coordinates nine Sulphur ligands with a resulting C_s site symmetry. In Table 1 we report, up to the last significant digit [12], the six distances of the ligands from the central ion and the coordination factors for the second degree parameters. It can be noted, as said in the Introduction, that the maximum variation of the distances is $\pm 7\%$ about their median value, to be compared with those, much smaller, normally found in the complexes analysed by the SPM [1].

ThOS crystal belongs to the space group $P_{4/nmm}$-D_{4h}^{7} and has the same structure as PbFCl, with lattice parameters $a=b=3.955(2)$ Å and $c=6.733(4)$ Å [12]. The Th^{4+} ion coordinates four oxygen and five sulphur ligands with a site symmetry C_{4v}. In Table 2 the same data as in Table 1 are listed, for the three different types of ligands, together with the in plane and z components of the distances.

The experimental spin Hamiltonian second degree parameters [11, 13] for both compounds are shown in Table 3.

3. Superposition Model

3.1. ThS_2

We consider the second degree parameters only, the values of which are to be fitted by the expression [1]:

$$b_2^m = \sum_i K_2^m(i)\,\bar{b}_2(R_i)\,, \tag{1}$$

where the coordination factors $K_2^m(i)$ are those listed in Table 1 and 2 for the two compounds under study.

Let us deal first with the case of ThS_2. This compound has S ligands only and three different second degree parameters, therefore it is more suitable for the determination of the single intrinsic parameter involved and of its dependence on the metal-ligand distance. Moreover, in this regard, the spread of these distances allows a complete check of the applicability of the superposition model.

The experimental conditions to be fulfilled are given by the values of b_2^0, b_2^1 and b_2^2, shown in Table 3. We have taken the value $b_2^1=0$, which corresponds to $\beta=-20.35°$ [13], the ratio b_2^0/b_2^2 and the value of b_2^0 because, in this form, the first two conditions become independent of the actual value of the intrinsic parameter $\bar{b}_2(R_0)$ and therefore allow an immediate test of the single exponent power law. In fact, they can be written as

$$\sum_i K_2^1(i)\,(R_i)^{-t_2}=0\,, \tag{2a}$$

$$\frac{\sum_i K_2^0(i)\,(R_i)^{-t_2}}{\sum_i K_2^2(i)\,(R_i)^{-t_2}}=\frac{b_2^0}{b_2^2}\,. \tag{2b}$$

The results of such a test are listed in Table 4, where the exponent $t_2=3$ corresponds to a pure

Table 1. Ligand distances (Å) and coordination factors in ThS_2. θ and φ identify the angular position of each ligand with respect to the crystal field reference frame.

	S_1	$S_2, S_{2'}$	S_3	$S_4, S_{4'}$	S_5	$S_6, S_{6'}$
R	2.74	2.80	2.94	3.00	3.05	3.13
$K_2^0=(3\cos^2\theta-1)/2$	0.989	0.128	−0.126	−0.276	0.092	−0.337
$K_2^1=3\sin 2\theta\cos\varphi$	−0.521	0.142	2.595	1.369	−2.933	−1.293
$K_2^2=(3\sin^2\theta\cos 2\varphi)/2$	0.011	−0.868	1.126	−0.231	0.908	−0.054

Table 2. Ligand distances and their in-plane and z components (Å), and coordination factors in ThOS.

	O	S_{I}	S_{II}
$R/$	2.39	2.98	3.01
$(x^2+y^2)^{1/2}$	1.98	2.80	0.00
z	− 1.35	1.03	3.01
K_2	− 0.025	− 0.321	1.000

Table 3. Experimental second degree parameters, in units of 10^{-4} cm^{-1} (from Refs. [11] and [13]).

	b_2^0	b_2^1	b_2^2
ThS_2	708.0 ± 0.6	0 ± 3	− 243.0 ± 1
ThOS	183.33 ± 0.02	—	—

Table 4. Comparison between experimental data for Gd^{3+} in ThS_2 and calculated values, following the single exponent power law.

	Expt.	$t_2=3$	$t_2=2.52$
β	− 20.35°	− 21.50°	− 20.35°
b_2^0/b_2^2	− 2.91	− 0.68	− 0.62

point charge approximation and the exponent $t_2=2.52$ satisfies exactly the condition (2a) and therefore gives just the experimental value of β, with the sign consistent with the provision of the point charge model [14]. It is clear that the single exponent power law is not able to fit all the experimental parameters simultaneously. This is not unexpected, taking into account the large spread of the ligand distances in ThS_2 and the limits of the single exponent power law [1].

Therefore, we have assumed a two exponents power law for the intrinsic parameter, as proposed by Newman and Urban [1], that is

$$\bar{b}_2(R)=A\left(\frac{R_0}{R}\right)^{t_A}+B\left(\frac{R_0}{R}\right)^{t_B}, \tag{3}$$

where, by definition, $A+B=\bar{b}_2(R_0)$ and A and B are opposite in sign to take into account that the main contributions to the crystal field effect are opposite in sign, as shown by the calculations of Wybourne and Newman [1, 15, 16]. In particular, it is $A<0$ and $t_A<t_B$. In fact, this assumption is the only one consistent with the previous literature, in particular as regards the negative sign for $\bar{b}_2(R_0)$ [1, 17].

Equation (3) contains five independent parameters, namely A, B, t_A, t_B and R_0. Therefore, the experimental conditions allow to determine three of them as functions of the other two. The rather large number of free parameters must not induce to think that it is always possible to find a solution. In fact, our intention is to check the suitableness of the two exponents power law in the most general way and to discuss the possible solutions, the range of which will be sensibly restricted by reasonableness criteria. Let us thus rewrite (3) in a more suitable form: introducing $\varrho=B/A$, Eq. (3) becomes

$$\bar{b}_2(R)=A\left(\frac{R_0}{R}\right)^{t_A}\left[1+\varrho\left(\frac{R_0}{R}\right)^{t_B-t_A}\right]. \tag{4}$$

One can note that the zero of the derivative of (4) corresponds to the condition

$$\left(\frac{R_0}{R_{\min}}\right)^{t_B-t_A}=-\frac{t_A}{\varrho\, t_B}. \tag{5}$$

From (5) it is possible to write

$$\varrho=-\left(\frac{R_{\min}}{R_0}\right)^{t_B-t_A}\frac{t_A}{t_B}=-\varrho_0\frac{t_A}{t_B}, \tag{6a}$$

where

$$\varrho_0=\left(\frac{R_{\min}}{R_0}\right)^{t_B-t_A}>0. \tag{6b}$$

When $\varrho_0=1$, we have $\varrho=-t_A/t_B$. On the other side, ϱ_0 can not be very different from unity, because it is not likely that the reference distance R_0 assumes values very different from $R_{\min}$.

To discuss the procedure of solution, let us write (4) as a function of $R_{\min}$, by means of (6a):

$$\bar{b}_2(R)=A\left(\frac{R_0}{R}\right)^{t_A}\left[1-\frac{t_A}{t_B}\left(\frac{R_{\min}}{R}\right)^{t_B-t_A}\right], \tag{7}$$

where the independent parameters are now A, t_A, t_B, R_0 and $R_{\min}$. Therefore, the conditions (2) can be written as

$$\sum_i\frac{K_2^1(i)}{R_i^{t_A}}\left[1-\frac{t_A}{t_B}\left(\frac{R_{\min}}{R_i}\right)^{t_B-t_A}\right]=0, \tag{8a}$$

$$\frac{\sum_i\frac{K_2^0(i)}{R_i^{t_A}}\left[1-\frac{t_A}{t_B}\left(\frac{R_{\min}}{R_i}\right)^{t_B-t_A}\right]}{\sum_i\frac{K_2^2(i)}{R_i^{t_A}}\left[1-\frac{t_A}{t_B}\left(\frac{R_{\min}}{R_i}\right)^{t_B-t_A}\right]}=\frac{b_2^0}{b_2^2} \tag{8b}$$

which leaves us with three parameters only, that is t_A, t_B and $R_{\min}$. Therefore, we can obtain two of

them as function of the third one:

$$t_B = t_B(t_A), \quad R_{\min} = R_{\min}(t_A). \tag{9}$$

The third experimental condition gives

$$\sum_i K_2^0(i) A \left(\frac{R_0}{R_i}\right)^{t_A} \left[1 - \frac{t_A}{t_B}\left(\frac{R_{\min}}{R_i}\right)^{t_B - t_A}\right] = b_2^0, \tag{10}$$

so that, remembering (9), A is a function of R_0 and t_A only:

$$A = R_0^{-t_A} f(t_A), \tag{11}$$

where $f(t_A)$ can be easily obtained from (10). Substituting (11) into (7), it turns out that $\bar{b}_2(R)$ does not depend explicitly on R_0.

Similarly, one can write for B:

$$B = R_0^{-t_B} g(t_A) \tag{12}$$

with $g(t_A) = \varrho f(t_A)$.

In this way, the two independent parameters left are t_A and R_0, as functions of which $R_{\min}$, t_B and A are to be determined. This has been performed by means of a self-consistent numerical procedure.

As regards Eqs. (9), the numerical analysis shows that solutions for the Eqs. (8) and (10) can be found in the range $5 \leqq t_A \leqq 9.37$ only. Figure 1 shows the dependence of t_B on t_A. On the contrary, the parameter $R_{\min}$ turns out to be practically insensitive to t_A. In fact, inside the quoted range, it is almost constant, that is $R_{\min} = 2.9846 \pm 0.0002$ Å. For this reason, in the actual numerical calculations we have preferred to use ϱ_0, defined by (6b), instead of $R_{\min}$ as a variable. In fact, it is more suitable a parameter, the value of which can vary inside a not negligible range.

Therefore, the procedure followed was based on (7), written in terms of ϱ_0:

$$\bar{b}_2(R) = A \left(\frac{R_0}{R}\right)^{t_A} \left[1 - \varrho_0 \frac{t_A}{t_B}\left(\frac{R_0}{R}\right)^{t_B - t_A}\right]. \tag{13}$$

For any fixed value of R_0, t_B and ϱ_0 have been numerically determined, by means of (8), as functions of t_A. Successively, the parameter A, which is only a factor in the expression for b_0^2, has been evaluated by means of (10). Because, as said, we have assumed $t_A < t_B$ and $A < 0$, it turns out that Eq. (10) can be satisfied only assuming a positive sign for the experimental crystal field parameter b_2^0.

To represent the solutions, we have chosen the parameter $\bar{b}_2(R_0) = A(1 + \varrho)$, $\bar{A} = A/\bar{b}_2(R_0)$, t_A, t_B

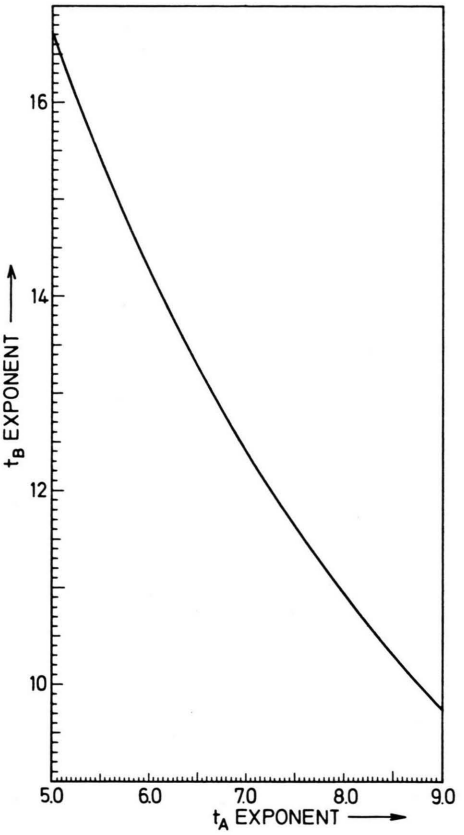

Fig. 1. Functional dependence of t_B on t_A, in the range of acceptable solutions.

and R_0 as more significant and more easily comparable with the previous literature [1, 10].

Figure 2 shows the variation of $\bar{A}$ as function of R_0, for different values of t_A. The same for $\bar{b}_2(R_0)$ is drawn in Figure 3. For each value of t_A the curves must have a minimum at $R_0 = R_{\min}(t_A)$; remembering that $R_{\min}$ is practically constant, all the minima are in the same position.

To show that the wide range of solutions displayed by Figs. 1, 2 and 3 is deceptive only, we have reported in Fig. 4 the intrinsic parameter $\bar{b}_2(R)$ versus $x = R/R_0$, for different values of t_A and for $R_0 = 3.00$ Å. The reduced abscissa has been taken to allow a direct comparison with the curve for the oxygen ligand [1], shown in the same Figure. Different choices of R_0 would lead to a displacement of the curves in Fig. 4, but would not have any effect on the curve for $\bar{b}_2(R)$, which, as said, does not depend on R_0. Apart from the unessential and small difference in the depth of the minima,

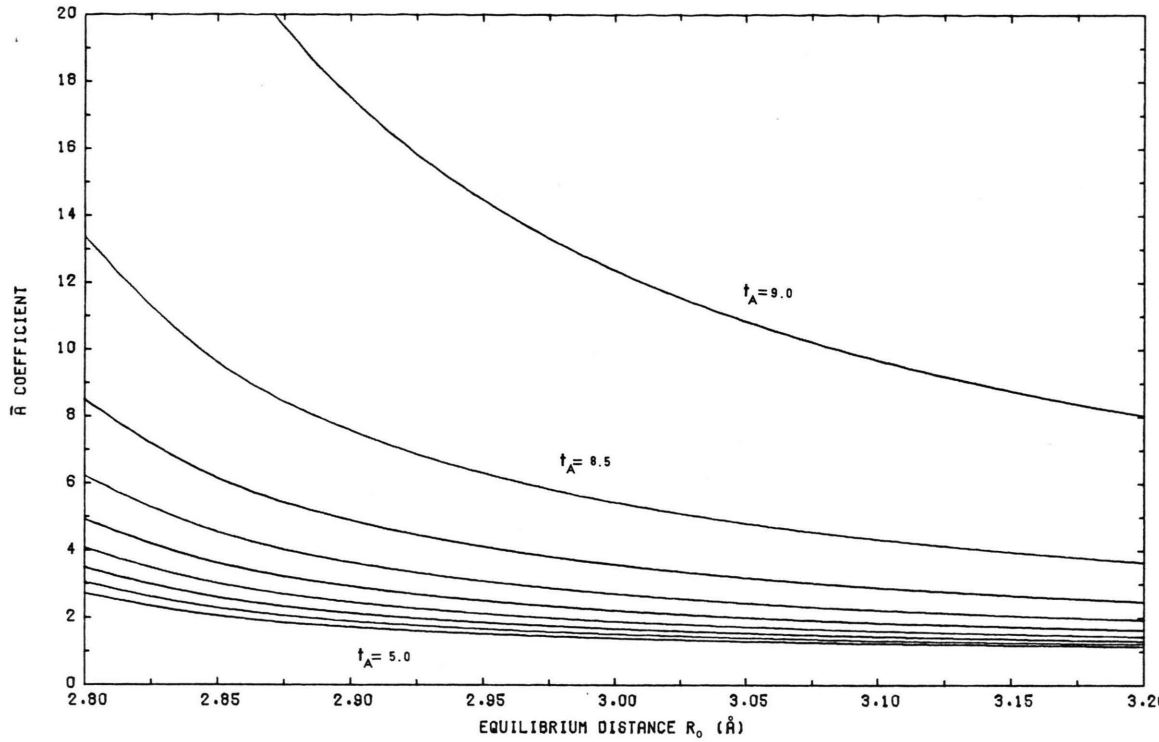

Fig. 2. Curves of the parameter $\bar{A}$ as function of R_0, for t_A varying by steps of 0.5.

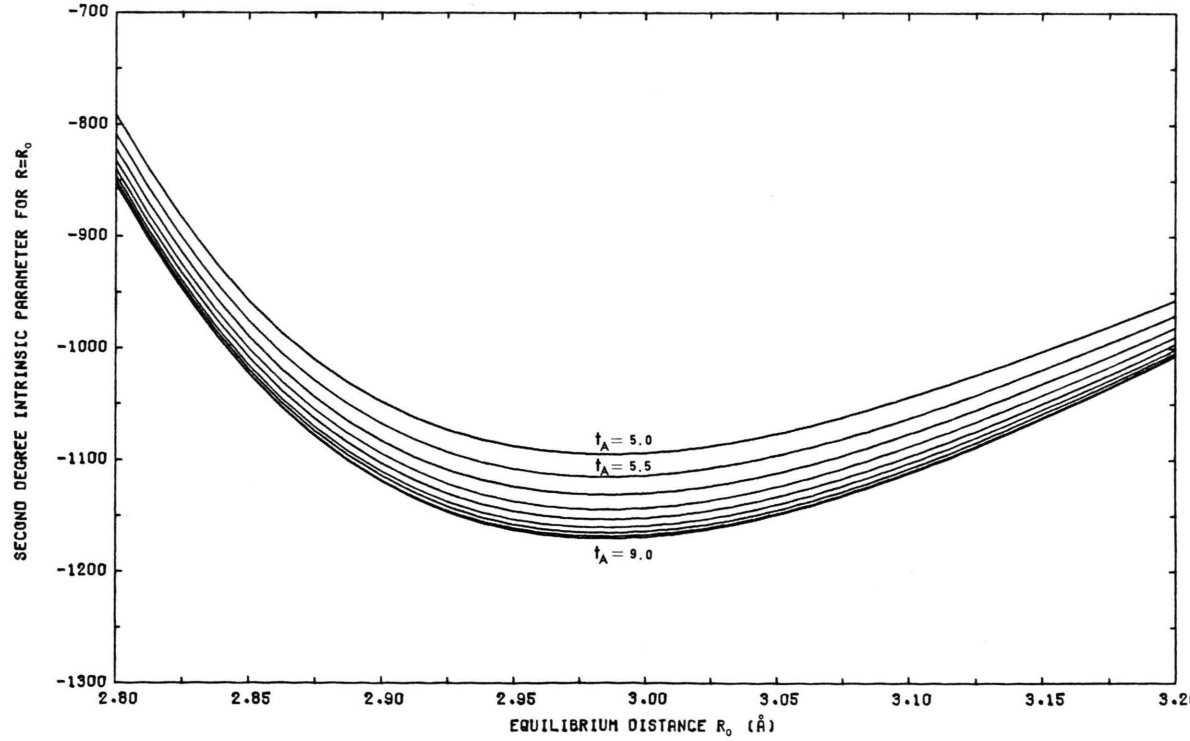

Fig. 3. Curves of $\bar{b}_2(R_0)$ (units of 10^{-4} cm^{-1}) as function of R_0, for t_A varying by steps of 0.5.

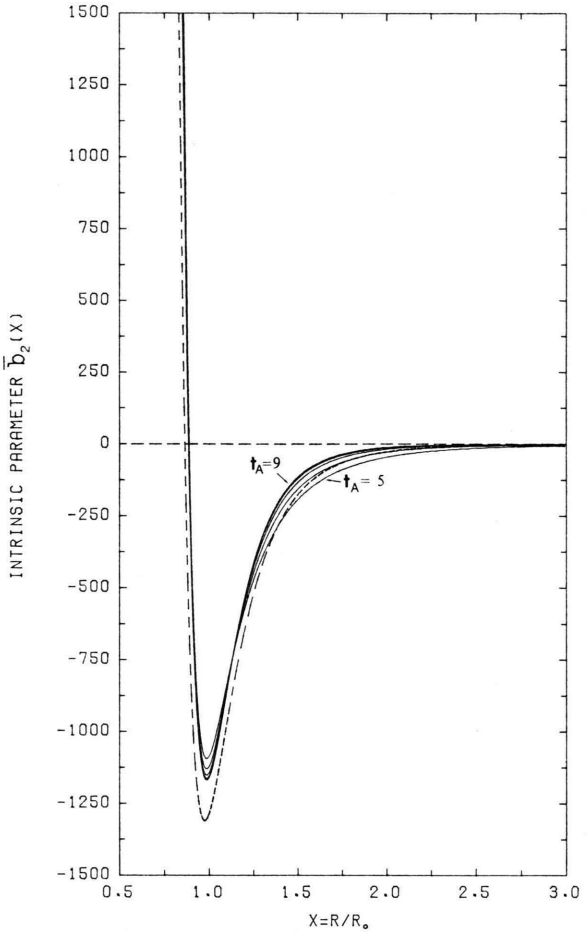

Fig. 4. Intrinsic parameter (units of 10^{-4} cm^{-1}) as function of the reduced distance, for $R_0 = 3.00$ Å. t_A varies as in Figure 2. The dashed curve refers to O ligands, as from [1].

all the curves are almost coincident and this shows that all the possible solutions, obtainable from Figs. 1, 2, and 3, represent practically the same physical situation. Therefore, we can choose anyone of these solutions, in particular that for which the coefficients $\bar{A}$ and $\bar{B}$ assume the values 3 and -2 respectively, as proposed tentatively in Ref. [1], and with $R_0 = 3.00$ Å, that is near the mean value of the ligand distances but slightly greater than $R_{\min}$ [1]. In this case the complete set of parameters results:

$$\bar{A} = 3\,, \quad \bar{B} = -2\,, \quad R_0 = 3.00\ \text{Å}\,,$$
$$t_A = 7.7\,, \quad t_B = 11.35\,,$$
$$\bar{b}_2(R_0) = -1161 \cdot 10^{-4}\ \text{cm}^{-1} \tag{14}$$

to be compared with the values given in Ref. [1] for oxygen ligands. It is to be noted that, if the ligand distances should allow to apply the single exponent power law, the expansion of (3) with the values (14) for the parameters should lead to an effective exponent $t_2 = 0.4$, in agreement with those previously found [1]. No significant alteration of the curves for $\bar{b}_2(R)$ is obtained when the parameters b_2^m are varied within the experimental errors.

In the above treatment, we have assumed an "undistorted" situation for the substituting Gd^{3+}, which is a "a posteriori" supported by the solutions we have found. Moreover, any significant displacement of the Gd^{3+} ion in the bc plane (other distortions are not allowed by symmetry reasons [13]) leads to unreasonable values for $\bar{b}_2(R_0)$. In fact, varying the fractional coordinates Y/b and Z/c of the Gd^{3+} ion by ± 0.005, which is half the error quoted in the original paper of Zachariasen [12], one obtains the sets of parameters shown in Tab. 5, where we have maintained, as a reference, a fixed value for t_A. It is apparent that the two exponents power law is very sensitive to the position of the Gd^{3+} and that the undistorted case gives the most reasonable solution. In fact, it is in agreement with the previous literature [17], where it is assumed that the value of $\bar{b}_2(R_0)$ for the Gd-S pair is of the same order as that for Gd-0. The case of equal displacements along b and c seems to give a not bad result, which, on the other hand, is less reasonable, because would lead to too large distortions in the case of ThOS, as it will appear in the following Section.

$\Delta(Y/b)$ (0.005)	$\Delta(Z/c)$ (0.005)	t_A	t_B	R_0 (Å)	$R_{\min}$ (Å)	$\bar{b}_2(R_{\min}) \cdot 10^4$ cm^{-1}
−	−	7.7	15.43	2.95	3.061	− 263
−	+	7.7	11.78	2.89	2.902	− 30880
+	−	7.7	9.38	3.54	3.130	− 326
+	+	7.7	11.49	2.94	2.935	− 4232
undistorted		7.7	11.35	3.00	2.985	− 1162

Table 5. Parameters of the two exponents power law, when the position of Gd^{3+} is varied in the bc plane, with respect to the undistorted structure of ThS_2 ($\bar{A} = 3$).

Table 6. Second degree parameters (units of 10^{-4} cm^{-1}) for Gd^{3+} in ThS_2 and direction of the crystal field principal axis, as deduced from the distortion diagrams [18], using the two exponents power law with the parameters (14).

$\Delta(Y/b)$ (0.005)	$\Delta(Z/c)$ (0.005)	β	b_2^0	b_2^2
−	−	− 19°	971.7	− 51.7
−	+	− 26°	448.0	− 565.6
+	−	− 17°	1124.4	1.8
+	+	− 22°	495.5	− 415.3

The high sensitivity of our treatment to the distortions is confirmed by the distortion diagrams, introduced in Ref. [18], from which we obtain the values of Tab. 6, to be compared with the experimental values given in Tabs. 3 and 4. On the other hand, such behaviour is not unexpected, taking into account that in ThS_2 there are six different ion-ligand distances. In fact, the curve of $\bar{b}_2(R)$ must pass through six different points and any displacement of the central ion, even small, changes the distribution of these points and their angular weight: consequently, the parameters of the function describing $\bar{b}_2(R)$ undergo even drastic variations. Therefore, our results can be considered as an indication that the Gd^{3+} ion does not induce noticeable distortions in the ThS_2 structure, apart from a possible isotropic expansion of the ligand cage (as a consequence of the smaller positive charge of the doping ion), which, on the other hand, would affect the value of R_0 only and not the behaviour of the curve for $\bar{b}_2(R)$.

3.2. ThOS

In this case, the ligands are of two different types and the experimental value is one only. For the intrinsic parameter $\bar{b}_2(R)$ relative to the sulphur ligands, we have taken the function characterized by the parameters (14). We want to point out once more that this choice is not at all restrictive, because all the possible solutions obtained in Sect. 3.1 lead practically to the same behaviour for the function $\bar{b}_2(R)$.

As regards the oxygen ligands, we have taken the same function $\bar{b}_2(R)$ used in Ref. [1], taking into account that in ThOS the distance Th-O lies inside the range considered in the quoted paper. This function is characterized by the parameters:

$$\begin{aligned} &\bar{A} = 3\,, \quad \bar{B} = -2\,, \quad R_0 = 2.24\ \text{Å}\,, \\ &t_A = 7\,, \quad t_B = 10\,, \\ &\bar{b}_2(R_0) = -1300 \cdot 10^{-4}\ \text{cm}^{-1}\,. \end{aligned} \tag{15}$$

The spin Hamiltonian second degree parameter is given by

$$\begin{aligned} b_2^0 = {} & 4K_2^0(\text{O})\,\bar{b}_2(R_0) + 4K_2^0(S_\text{I})\,\bar{b}_2(R_{S_\text{I}}) \\ & + K_2^0(S_\text{II})\,\bar{b}_2(R_{S_\text{II}})\,, \end{aligned} \tag{16}$$

where S_II labels the ligand along the z axis.

Introducing the coordination factors given in Table 3 and the quoted functions for $\bar{b}_2(R)$, the resulting value is more than twice the experimental one. This is due principally to the coordination factors used to evaluate b_2^0. In fact, for the ligand distances of ThOS, all the values of $\bar{b}_2(R)$ are of the same order, that is $\sim -1000 \cdot 10^{-4}$ cm^{-1}. On the other hand, from Table 3 we have

$$\begin{aligned} 4K_2^0(\text{O}) &= -0.100 \\ 4K_2^0(S_\text{I}) &= -1.283 \\ K_2^0(S_\text{II}) &= \frac{1.000}{0.383} \end{aligned} \tag{17}$$

and therefore it is apparent that a precise fit of the experimental value of b_2^0 for ThOS is impossible, in such conditions. Because the variations of the intrinsic parameters, necessary to obtain the right value of b_2^0, are too large to be reasonable, we have considered the possibility of some distortion, which can modify the values (17) of the coordination factors dramatically.

Taking into account that the ligand distances are shorter in ThOS than in ThS_2, it is not unlikely that the substitution of a tetravalent ion, as Th^{4+}, with the trivalent Gd^{3+} may lead to an enlargement of the negative ligand cage, as a consequence of the smaller positive charge at the center. On the other side, this distortion must be such that it does not modify the site symmetry, which remains the same after the introduction of the impurity, as shown by the EPR spectra [11]. In terms of polar coordinates, this means that the angle φ must remain unchanged for every ligand, while R and θ (except for S_II) can vary.

A general deformation of this type can be described as the combination of two elementary distortions, that is: a) a simultaneous variation of the z component of the distance of all the ligands of the same type; b) an isotropic variation of the dimensions of the coordination squares, at the vertices of which the 4 O and the 4 S_I are located. For the sake of simplicity we have assumed that S_II is always at the same distance from the center

as S_I: it will be seen that the small difference of 0.03 Å has no substantial influence on the results.

Remembering the sign of (17) and of the intrinsic parameters, Eq. (16) can be fitted, with reasonable values of the distortions, only taking the positive sign for the second degree parameter b_2^0.

Figure 5 shows the result of the analysis of the distortion a). It is apparent that no solution is possible moving both types of ligands toward the central ion. Moreover, the zone of minimum distortion corresponds to a simultaneous increase of the absolute value of the z component of the distance of all the ligands, as expected. The points labelled (1) and (2) in Fig. 7 are the solutions corresponding to the displacement of one type of ligands only, that is O and S respectively. The distortion corresponding to the point (1) is relatively smaller than that corresponding to the point (2), in agreement with the smaller undistorted distance of the O ligands. In fact, it is reasonable that, in order to reduce the absolute value of the second degree parameter, is a smaller displacement of the nearest ligands sufficient.

Figures 6 and 7 refer to the distortion b), taking also into account the preceding results. That is, Fig. 6 corresponds to the case of undistorted z component for the S ligands and Fig. 7 to the case of undistorted z component for the O ligands. The points (1) and (2) represent the same situations as in Figure 5.

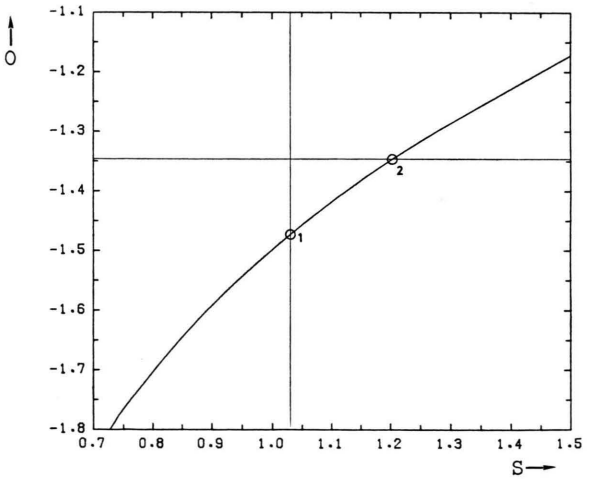

Fig. 5. Curve of the deformation of type a), which gives the right value of b_2^0 in ThOS. The coordinates are the z components of the S and O ligand distances (Å).

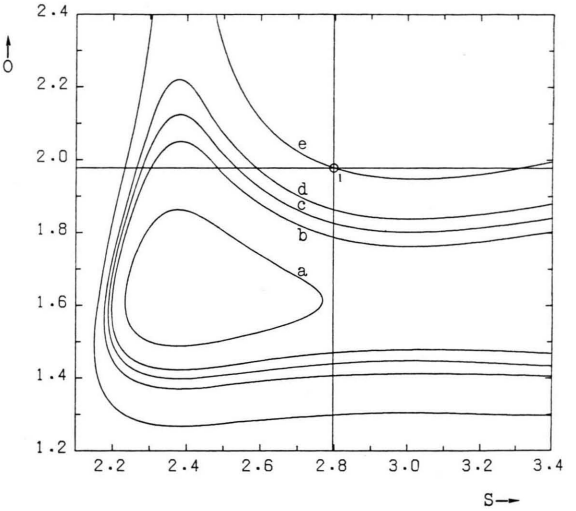

Fig. 6. Curves of the deformation of type b), for undistorted z component of the S ligands distance. The labels of the curves refer to the z component of the O ligands distance (Å): $a = -1.219$; $b = -1.317$; $c = -1.347$ (undistorted); $d = -1.377$; $e = -1.475$. The coordinates are the inplane distances from the z axis (Å).

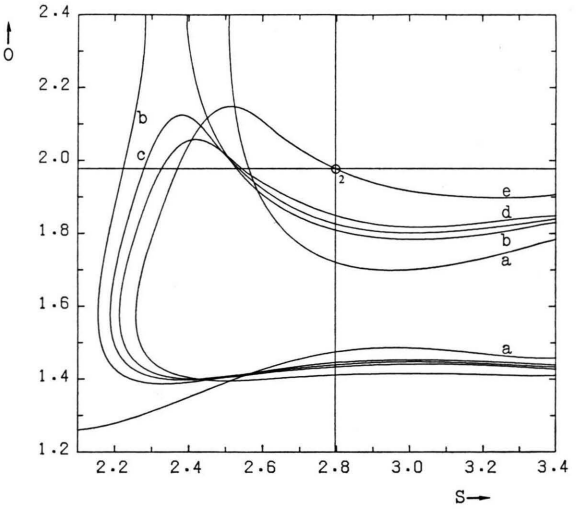

Fig. 7. Curves of the deformation of type b), for undistorted z component of the O ligands distance. The labels of the curves refer to the z component of the S ligands distance (Å): $a = 0.858$; $b = 1.000$; $c = 1.030$ (undistorted); $d = 1.060$; $e = 1.202$. The coordinates are the in-plane distances from the z axis (Å).

It can be noted that no solution is obtained by a simultaneous enlargement of the two coordination squares, at least for acceptable displacements along z. On the contrary, the solutions tend to accumulate in the region corresponding to the simultaneous shrinking of the two coordination squares.

Taking into account that the coordination factors appearing in (16) are crucially dependent on the angle θ, while the variation of the distances R_i influences the values of the intrinsic parameter only, the two most probable elementary distortions, deducible from Figs. 5, 6 and 7, correspond both to an increase for O ligands and a decrease for S ligands of the polar coordinate θ.

4. Conclusions

As shown, the application of the SPM, in the form of a two exponents power law, leads to a complete fitting of the experimental second degree parameters for a compound like ThS_2, whereas in the isostructural $PbCl_2$ the single exponent power law was not able to fit the experimental data [10]. It is to be noted that such fitting can be obtained with different sets of parameters for the power law, but that all these sets correspond to the same physical situation, leading to almost identical curves for the intrinsic parameter $\bar{b}_2(R)$.

One of the most useful properties of the SPM has been confirmed. In fact, the value of the intrinsic parameter obtained for ThS_2 has been used to fit the data in a compound of different structure and symmetry, that is ThOS. Moreover, in this procedure, the possibility to reveal environmental distortions, as those induced by the impurity ion [17] has been pointed out.

A still open question remains the comparison of the relative merit of the electrostatic [8, 9] and superposition model. Low temperature measurements have determined a negative sign [19] for b_2^0 in $BaCl_2$ [20] which is isostructural with ThS_2, in agreement with the results of electrostatic calculations [21]. Because Newman [10] has suggested, on the basis of a tentative application of the SPM to $PbCl_2$, that in such systems the second degree parameters b_2^0 should be positive, the authors of Ref. [20] conclude that, at least in these systems, the electrostatic model is to be preferred to the SPM. But we think that the problem is far from solution. In fact, there is no reason why the real sign of b_2^0 for ThS_2 must be the same as that for $BaCl_2$ and therefore opposite to our prevision on the basis of the SPM. The ligands are different and, above all, even small differences in the relative positions of the ions may lead to opposite results in otherwise isostructural compounds, owing to the crucial role of the coordination factors in the determination of the value and of the sign of the parameters. Unfortunately, the experimental determination of the sign of b_2^0 in ThS_2, which could directly support or refute the SPM conclusions, is not available at present [13]. However, if the sign of b_2^0 in ThS_2, resulting from our calculations, is correct, the following considerations must be taken into account:

a) The SPM may have different validity in ThS_2 and $BaCl_2$, owing to the different bond character of the ligands involved.

b) The suggestion of Newman [10] is not at all conclusive, because it derives from a very approximate application of the SPM to $PbCl_2$ in the form of the single exponent power law, not suitable for this case.

c) Anyhow, the results for $PbCl_2$ are not directly applicable to $BaCl_2$, which has a local structure different from that of $PbCl_2$ [22, 23], contrarily to the assumption of [21].

Our present aim is to try a complete analysis of the cases of $BaCl_2$ and $PbCl_2$, by means of the two exponent power law which we have used in this work.

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