The Refined Structure of ThS_2 and the Implications on the Superposition Model Analysis of ThS_2: Gd^{3+} Spin Hamiltonian Parameters

G. Amoretti *, G. Calestani **, and D. C. Giori *

University of Parma, Italy

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The crystal structure of ThS_2 has been refined starting from single crystal diffractometry data. The accurate determination of the positional parameters allows us to reexamine the SPM analysis of the second degree crystal field parameters for Gd^{3+} in ThS_2 matrix. The fitting of the EPR data is still possible by means of a suitable two exponents power law for the intrinsic parameter only if the substitutional Gd^{3+} ion displaces in the mirror (bc) plane with respect to the undistorted Th^{4+} site. The resulting increase of the mean metal-ligand distances agrees with the expected expansion of the ligand cage around the trivalent Gd ion. The applicability of the proposed method to examine the impurity induced distortions in an host crystal is discussed too.

1. Introduction

In a preceding paper [1] the superposition model (SPM) analysis was succesfully applied to the second degree crystal field parameters of substitutional Gd^{3+} in ThS_2 and ThOS matrices.

In particular, a two exponents power law for the intrinsic parameter $\bar{b}_2(R)$ was used to fit the experimental data in the case of ThS_2:Gd^{3+}, owing to the large spread of ion-ligand distances about a mean reference value R_0. The values of the structural parameters given by Zachariasen [2, 3] were assumed.

For the determination of the functional dependence of $\bar{b}_2$ on R a precise knowledge of the six considered n.n. metal-ligand distances is needed. In fact, small variations of the positional parameters characterizing the structure can induce an appreciable modification in the distribution of the quoted distances.

It must be noted that the values of the positional parameters given by Zachariasen were determined experimentally from photographic intensity measurements as regards Th atoms only. The other ones were calculated in order to obtain reasonable interatomic distances.

We have redetermined the crystal structure of ThS_2 starting from accurate single crystal diffractometry data and we have examined the consequences of this refinement on the SPM analysis.

In Section 2 the results of the structural investigation are given, while the application of the SPM is presented and discussed in Sections 3 and 4 respectively.

2. Crystal Structure Refinement

Crystal Data

ThS_2 is orthorhombic, space group Pmnb, structure-type $PbCl_2$. Cell parameters are $a = 4.273$ (2), $b = 7.267$ (3), $c = 8.615$ (4) Å, $V = 267.5$ (2) Å^3, $Z = 4$, $D_x = 7.35$, $\mu = 546.88$ cm^{-1} (Mo Kα).

Experimental

The prismatic single crystal used for the data collection ($0.36 \times 0.30 \times 0.58$ mm) was grown by chemical vapor transport using iodine as transporting agent in an evacuated (10^{-6} Torr) and sealed quartz bulb. The transport reaction occurred in a temperature gradient between 900 and 850 °C.

Intensity data were collected on an automated SIEMENS AED single crystal diffractometer using Zr-filtered Mo Kα radiation ($\lambda = 0.710688$ Å), θ range $2 < \theta < 45°$, $\omega - 2\theta$ scan.

Cell parameters were refined by least squares analysis of the setting angles of 16 selected reflections in the θ range 15 to 25°.

* Department of Physics and GNSM/CNR – Parma.
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** Istituto di Strutturistica Chimica and Centro di Studio per la Strutturistica Diffrattometrica del CNR – Parma.

Reprint requests to G. Amoretti, Department of Physics, Via M. D'Azeglio 85, 43100 Parma, Italy.

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4602 reflections ($\pm h, \pm k, l$) were collected of which 1603 with $I < 3\,\sigma(I)$ were considered unobserved. The 2999 observed reflections were corrected for Lorentz and polarisation effect.

Discontinuous absorption corrections were performed after measuring accurately the crystal size and indexing the natural faces, with a special routine of the SHELX 76 [4] system of crystallographic computer programs used in the structure refinement. The 2999 observed reflections were then merged to 895 unique reflections, which were used in the structure analysis.

Structure refinement

In all calculations un-ionized coherent scattering factors of Cromer and Mann [5] and anomalous scattering factors of Cromer and Lieberman [6] where used.

Since ThS_2 has the $PbCl_2$ structure type, one set of four thorium atoms and two sets of four sulphur atoms are in reflection planes at positions

$$\pm(\tfrac{1}{4}, y, z); \quad \pm(\tfrac{1}{4}, \tfrac{1}{2}+y, \tfrac{1}{2}-z).$$

Starting from the coordinates obtained by Zachariasen [2], the full matrix least squares refinement converged to $R = 0.075$ with all isotropic thermal parameters. The structure was then refined with anisotropic thermal parameters for all the atoms. Finally, the crystal size was refined, to check the absorption corrections, and the correction obtained by refining the size was applied to F_c. The final residuals were $R = 0.056$ and $R_w = 0.053$ with weights $w = 5.0191/(\sigma^2(F) + 0.005\,F^2)$. Fractional coordinates and thermal parameters are given in Table 1; bond distances and angles in Table 2.

On the basis of this refinement, the crystal structure of ThS_2 remains fundamentally as described by Zachariasen [2]: only small displacements in the atomic coordinates and consequently small variations of the bond distances were found.

Thorium atoms are coordinated by nine sulphur atoms at distances ranging from 2.796 (2) to 3.235 (2) Å. Three of the nine sulphur atoms lie on the same plane ($x = \frac{1}{4}$) of thorium; the remaining six are distributed on two planes adjacent to the preceeding one.

Lists of observed and calculated structure factors are available from the authors on request.

3. Superposition Model Analysis

In Fig. 1 the coordination of the metal ion in ThS_2 is shown. Just for comparison with Table 1 in

Table 1. Fractional atomic coordinates and thermal parameters ($\times 10^4$ Å^2). The thermal parameters are in the form $T = \exp[-2\,\pi^2(U_{11}\,h^2 a^{*2} + U_{22}\,k^2 b^{*2} + \ldots + U_{12}\,h\,k\,a^*\,b^*)]$.

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Th	1/4	0.24745 (3)	− 0.11982 (3)	42 (2)	52 (3)	61 (2)	− 11 (1)	0	0
S (1)	1/4	− 0.1403 (2)	− 0.0698 (2)	44 (6)	58 (6)	57 (6)	0 (4)	0	0
S (2)	1/4	− 0.0297 (2)	0.3338 (3)	8 (7)	59 (6)	68 (6)	8 (5)	0	0

Table 2. Bond distances (Å) and angles (°). The superscripts d, b and a, c refer respectively to the four equivalent positions quoted in the text.

Th−S(1)^{a}	2.796(2)	Th−S(2)^{a}	2.948(2)
Th−S(1)$^{b,b'}$	2.800(2)	Th−S(2)$^{c,c'}$	2.988(2)
Th−S(1)^{d}	2.851(2)	Th−S(2)$^{b,b'}$	3.235(2)
S(2)^{b}−Th−S(2)$^{b'}$	82.65(4)	S(1)^{b}−Th−S(1)$^{b'}$	99.47(5)
S(2)^{c}−Th−S(2)$^{b'}$	137.02(6)	S(1)^{d}−Th−S(2)$^{b,b'}$	66.59(2)
S(2)^{c}−Th−S(2)^{b}	77.73(3)	S(1)^{d}−Th−S(2)$^{c,c'}$	134.32(3)
S(2)^{c}−Th−S(2)$^{c'}$	91.27(4)	S(1)^{d}−Th−S(2)^{a}	114.62(5)
S(2)^{a}−Th−S(2)$^{b,b'}$	138.14(3)	S(1)^{d}−Th−S(1)$^{b,b'}$	68.71(2)
S(2)^{a}−Th−S(2)$^{c,c'}$	74.62(3)	S(1)^{a}−Th−S(2)$^{b,b'}$	66.27(2)
S(2)^{a}−Th−S(1)$^{b,b'}$	70.44(4)	S(1)^{a}−Th−S(2)$^{c,c'}$	70.85(2)
S(1)^{b}−Th−S(2)$^{b'}$	134.45(5)	S(1)^{a}−Th−S(2)^{a}	129.72(5)
S(1)^{b}−Th−S(2)^{b}	72.09(3)	S(1)^{a}−Th−S(1)$^{b,b'}$	129.73(3)
S(1)^{b}−Th−S(2)$^{c'}$	144.52(6)	S(1)^{a}− Th−S(1)^{d}	115.66(5)
S(1)^{b}−Th−S(2)^{c}	73.94(3)		

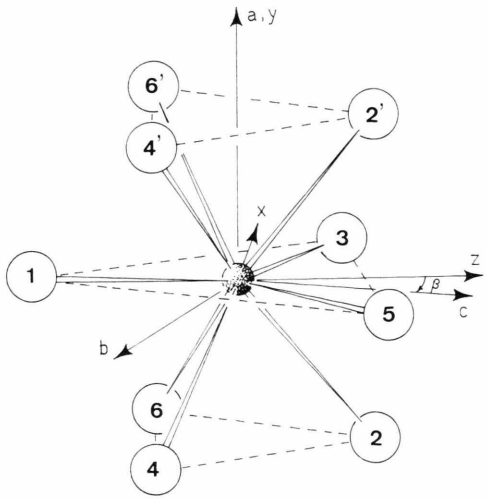

Fig. 1. Coordination structure at the Th^{4+} site in ThS_2. The crystal field reference frame (x, y, z) is also shown ($\beta = -20.35°$ with respect to the z-axis).

[1], we report in Table 3 the six n.n. metal-ligand distances and the second degree coordination factors, relative to the crystal field reference frame (see Figure 1).

We have maintained the same numbering of the ligands as in [1]. However it does no more correspond to the increasing order, as the $S_{4,4'}$ and S_5 ligand distances are now inverted.

In general the overall spread of distances is slightly increased ($\sim 13\%$). The mean distance passes from 2.954 Å to 2.960 Å as an effect of the slight dilatation of the lattice parameters quoted here with respect to the parameters given in [2].

The ligands in the mirror *bc* plane present the most significant modification of the distances distribution.

The coordination factors vary appreciably with respect to the values quoted in [1], confirming that an accurate determination of the positional parameters is needed, particularly in low symmetry systems.

We can now proceed to the SPM analysis of the second degree crystal field parameters for the substitutional Gd^{3+} ion in ThS_2 matrix.

In [1] the functional dependence of the second degree intrinsic parameter $\bar{b}_2(R)$ was written

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

The set of parameters values given in [1] was:

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

It has been shown in [1] that without loss of generality the coefficients $\bar{A}$ and $\bar{B}$ can be fixed at the quoted values, already proposed by Newman and Urban [7].

Moreover, a suitable value of the reference distance R_0 can be chosen to determine the values of t_A, t_B and $\bar{b}_2(R_0)$ from the fitting of the experimental data. Conversely, for a given value of t_A, the corresponding values of t_B, R_0 and $\bar{b}_2(R_0)$ can be found.

In [1] the effects of the possible distortions of the ligand cage were examined.

As an isotropic expansion of this cage affects only the value of R_0 and not the behaviour of $\bar{b}_2(R)$, only displacements of the Gd^{3+} ion in the mirror $(b\,c)$ plane were considered.

The conclusion was that the two exponents power law is very sensitive to the position of the paramagnetic ion and that the undistorted case corresponded to the most reasonable solution.

In fact, small displacements of the central ion gave rise to unphysical solutions for the two-exponents power law. Alternatively, the methods of distortion diagrams introduced in [8] showed that the experimental data could not be fitted with the assumption (2) for the parameters, when the Gd^{3+} ion was displaced.

If the refined structure is considered now, we can proceed to the same analysis as in [1], by fixing $\bar{A}$, $\bar{B}$ and the exponent t_A at the values in (2).

For each given displacement of the Gd^{3+} ion in the $(b\,c)$ plane we can try to find a solution of the fitting problem, which corresponds to a particular value of t_B, R_0 and $\bar{b}_2(R_0)$.

In principle we can obtain a map of the solutions for $\bar{b}_2(R)$: we assume that the zone of the $(b\,c)$ plane, where these solutions are physically more reasonable, corresponds to the most probable displacement of the paramagnetic ion.

In the case of ThOS:Gd^{3+}it was shown that the correct order of magnitude for $\bar{b}_2(R_0)$, as $R_0 = 3$ Å, is $-1000 \cdot 10^{-4}\ \text{cm}^{-1}$. Then, the solution (2) was suitable to fit the experimental value of b_2^0 in

Table 3. Ligand distances (Å) and coordination factors relative to the undistorted site in ThS_2. θ and φ give the angular position of each ligand with respect to the crystal field reference frame (Figure 1).

	S_1	$S_{2,2'}$	S_3	$S_{4,4'}$	S_5	$S_{6,6'}$
R	2.796	2.800	2.851	2.988	2.948	3.235
$K_2^0=(3\cos^2\theta-1)/2$	0.9947	0.1216	− 0.1465	− 0.3012	0.0267	− 0.3011
$K_2^1=3\sin 2\theta\cos\varphi$	− 0.3545	0.2240	2.5464	1.3039	− 2.8640	− 1.4349
$K_2^2=(3\sin^2\theta\cos 2\varphi)/2$	0.0053	− 0.8683	1.1465	− 0.2323	0.9733	− 0.0070

Table 4. Second degree parameters (units of $10^{-4}\,cm^{-1}$) and direction of the crystal field principal axis for selected values of the Gd^{3+} in plane displacements. They are deduced from the distortion diagrams [8], using the two exponents power law with the parameters (2).

$\Delta(Y/b)$ (0.005)	$\Delta(Z/c)$ (0.005)	β	b_2^0	b_2^2
−	−	− 32°	719	− 177
−	+	− 38°	377	− 627
undistorted		− 29°	516	− 376
+	−	− 22°	796	− 205
+	+	− 24°	355	− 512

Table 5. Parameters of the two exponents power law (with $A=3$) corresponding to the "equilibrium" position of Gd^{3+} in the ($b\,c$) plane (first row) and to a small area around it.

(Y/b)	(Z/c)	t_A	t_B	R_0 (Å)	R_{min} (Å)	$\bar{b}_2(R_{min})$ $\cdot 10^4\,cm^{-1}$
0.0085	− 0.0030	7.7	11.37	3.02	3.007	− 1159
0.0075	− 0.0040	7.7	14.50	2.92	3.020	− 668
0.0075	− 0.0020	7.7	9.94	3.19	2.984	− 1995
0.0095	− 0.0040	7.7	13.83	2.95	3.039	− 575
0.0095	− 0.0020	7.7	9.82	3.24	2.999	− 1631

$ThOS:Gd^{3+}$ without requesting too large distortions.

This suggests to search for the same kind of solution in the present case.

Table 4 shows the calculated values of β, b_2^0 and b_2^2 obtained from the distortion diagrams with $\bar{b}_2(R)$ given by (2), for selected values of the Gd^{3+} in plane displacements [9].

It is evident that in the undistorted case the experimental data cannot be fitted, while more suitable results can be obtained in the (+ −) quadrant of the ($b\,c$) plane.

In fact, from a map of solutions in this zone, we have found that the point $Y/b=0.0085$ and $Z/c=-0.0030$ corresponds practically to the same solution for $\bar{b}_2(R)$ as in [1].

Table 5 shows the results in a small area around this point.

4. Discussion

It must be noted that "a priori" a reasonable solution of the fitting problem with the expression (1) for $\bar{b}_2(R)$ does not exist necessarily. If it exists, Table 5 shows that it is very sensitive to small displacements around the "equilibrium" position.

This suggests that the present method can be used as a test to verify the reliability of the superposition model assumptions and to restrict the range of possible displacements of the impurity ion in a given host matrix.

The problem is to find a cryterion to decide on the reasonableness of the chosen solution for $\bar{b}_2(R)$ in a series of compounds. As regards Thorium dichalcogenides and oxichalcogenides, we wait for EPR studies on analogous compounds to get a further support of the present assumption.

In the case of isostructural ionic compounds, as in particular $PbCl_2$, $PbBr_2$, $BaCl_2$ and CaFCl, SrFCl, BaFCl, BaFBr, BaFI, the situation is not yet clear.

First of all, for $PbCl_2$ type compounds, at least two different attributions for the lattice and positional parameters exist, which lead to different values for the interionic distances and coordination factors.

In the case of the quoted PbFCl type compounds, where the structural information is accurate, although less critical for the application of the SPM, complete EPR data are available [10, 11]. However, an attempt to apply the model was unsuccessful [10].

Also a tentative analysis of distortions, following the same procedure as for $ThOS:Gd^{3+}$, leads to contradictory results.

Then, both the problems of the applicability of the SPM and of a realistic estimate of the intrinsic parameters remain open for these compounds.

Going back to ThS_2, we can see from Table 5 that R_0 is slightly increased with respect to the value chosen in [1], in accord with the dilatation of the lattice parameters and with the corresponding increase of R_{min}.

As regards the distortion of the ligand cage around Gd^{3+}, which is now required as a consequence of the refinement of the ThS_2 structure, we can make the following considerations.

The displacements of Gd^{3+} which have been found are of the same order as those quoted for ThOS:Gd^{3+} in [1].

We can examine the behaviour of the mean distance of the nearest neighbours from the central ion, as a function of the in-plane displacements of the ion itself. This distance increases as Gd^{3+} moves in the positive sense of both the *b* and *c* axes, more rapidly along the *b* axis.

Therefore, the "equilibrium" position corresponds to an increase of the mean distance (from 2.960 Å in the undistorted Th^{4+} site to 2.962 A in the Gd^{3+} site). This increase puts in evidence that the Gd^{3+} ion tends to maximize its distance from the surrounding ligands by a suitable in-plane displacement.

This is an other support to the present analysis, in agreement with the considerations on Gd^{3+} doped ThOS in [1].

We hope that the method proposed here to examine the structural distortions around an impurity S-state ion in an host matrix can be used successfully in other low symmetry systems.

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