Electron paramagnetic resonance studies of Gd^{3+} in $K_2Zn(SO_4)_26H_2O$

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Abstract. A single crystal of $K_2Zn(SO_4)_26H_2O$ doped with Gd^{3+} was studied by EPR at room temperature and at $-150\,^{\circ}C$ using an X-band spectrometer. There are two magnetically equivalent spectra characterized by the main Stevens constants $b_2^0 = 0.029$ cm^{-1} and $b_2^2 = 0.0217$ cm^{-1}. The spectra are described by a general spin Hamiltonian and all constants have been determined. The zero-field splitting of the energy levels is of the order of 0.3 cm^{-1} and EPR lines exist at very low fields, which are identified. The spectra are temperature dependent. This is interpreted as an anisotropic modification of the Gd^{3+} environment. The analysis of the pseudo-symmetry of the fourth order term of the spin Hamiltonian shows a strong modification of the local structure. The coordination polyhedra of Gd^{3+} are different from Zn and K polyhedra. The comparison with other results from the double sulphate family is made.

1. Introduction

This EPR investigation of $K_2Zn(SO_4)_26H_2O$ belongs to a series of works on the different double sulphates of general formula $M_1M_2(SO_4)_2nH_2O$ ($n = 2, 4, 6$) doped with Fe^{3+} or Gd^{3+} impurities [1–3].

The principal aim of all these studies is to obtain a description of the local environment of paramagnetic centres in such a type of lattice, to look for a possible charge compensation mechanism and for the influence of the number of water molecules on the EPR spectra.

Although the crystal structures of kronkite ($n = 2$), astrakanite ($n = 4$) or tutton salts ($n = 6$) are quite similar (crystals are monoclinic with space group C_{2h}^5) it is important to mention several peculiarities for each series of samples both in structural and in EPR aspects.

From previous results it was possible to conclude that Fe^{3+} in kronkite $K_2Cd(SO_4)_22H_2O$ and astrakanite $Na_2Zn(SO_4)_24H_2O$ replace the M_2 ion (Cd^{2+} and Zn^{2+}) and modified only slightly the local structure. For Gd^{3+} the situation is different. There is surely a very strong distortion of the local structure around Gd^{3+} and the accurate location of Gd^{3+} is doubtful.

On the other hand, many crystals of the tutton salt family with paramagnetic impurities of the iron group or the rare-earth group may exhibit a zero-field resonance [4]. This resonance arises when the zero-field splitting between two energy levels is nearly equal to the energy of the microwave radiation. Particular attention was made for identification of the low-field transitions and their frequency and temperature dependences.

2. Experimental details

We used a high-quality single crystal of $K_2Zn(SO_4)_26H_2O$ grown in similar conditions as other previously studied double sulphates [3] and doped with Gd^{3+} ($\sim$0.05%). The crystal we studied had well developed natural faces and was oriented using its morphology. The crystal structure of this compound is similar to the structure of other isomorphous tutton salts [5]. A part of the structure is schematically presented in figure 1.
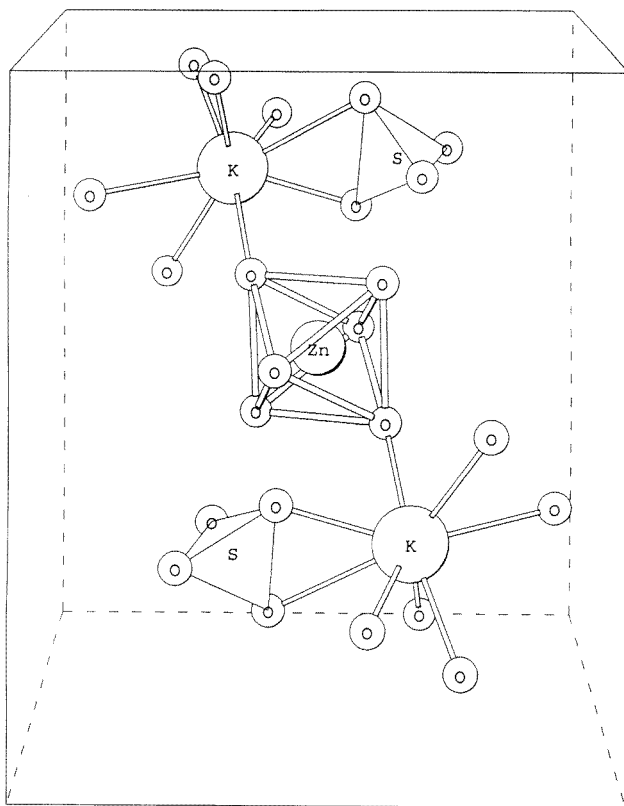

Figure 1. Part of the structure of $K_2Zn(SO_4)_26H_2O$. The perspective is along c^*. The a axis ($a = 0.942$ nm) is horizontal. Axis b ($b = 1.972$ nm) is vertical. Only one unit cell formula is shown. All oxygen atoms around Zn belong to water molecules.

The EPR spectra were recorded at X-band with an EPR spectrometer 'Varian 4502' equipped with a variable temperature unit using liquid nitrogen cooling in the temperature range 150–420 K. The magnetic field was measured with a Hall gaussmeter calibrated using a proton probe.

The angular dependences of the spectra were studied in the three orthogonal planes ab, bc^* and c^*a at room temperature and at $-150\,°C$. Two magnetically equivalent spectra related by the symmetry laws of the crystal structure were observed; they are superimposed for $H \parallel b$ and in the ac plane. The angular dependence in the ac plane is presented in figure 2. In this angular dependence, it is observed that when H is at $26°$ from $\boldsymbol{c}$ toward $\boldsymbol{a}$ the lines of the spectrum are greatly split. For this particular orientation, the magnetic field of the $-5/2 \rightarrow -3/2$ transition reaches its maximum value and many transitions are

observed. This particular orientation is near an EPR axis (principal axis of the second rank tensor of the crystal field). Later on this particular orientation will be called z_0. Figure 3 presents the EPR spectra for three characteristic orientations of the crystal with respect to the magnetic field.
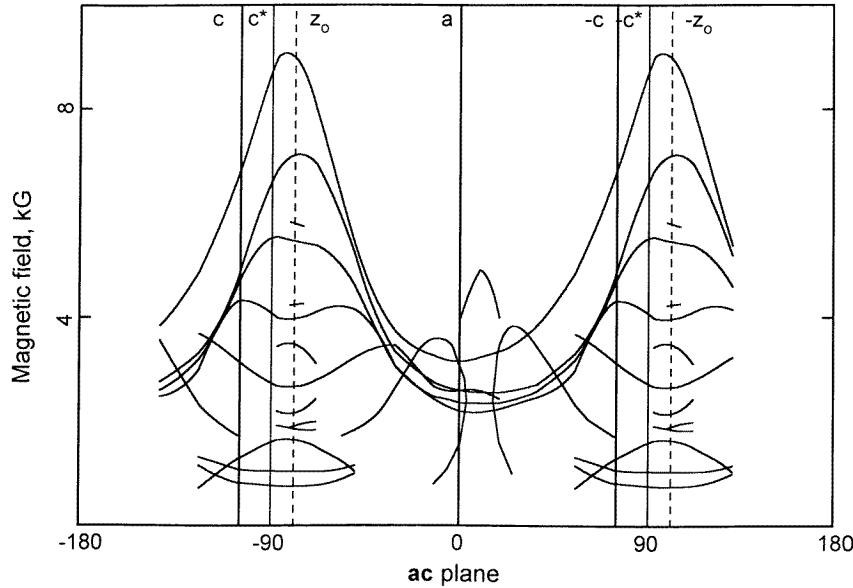

Figure 2. Angular dependence of EPR spectra of Gd^{3+} in $K_2Zn(SO_4)_26H_2O$ at room temperature in the ac plane of the crystal. Angles are given in degrees. The angle between c axis and a axis is 105 degrees. The particular axes z_0 correspond to the maximum of the $-5/2 \rightarrow -3/2$ transition in the ac plane. The frequency is about 9.4 Ghz.

The temperature dependences of EPR spectra were measured for the two particular orientations of the magnetic field $H \parallel b$ and $H \parallel z_0$. For temperature measurements some spectra were recorded at different frequencies (9.2 and 9.4 GHz).

3. Experimental results

For Gd^{3+} (electron configuration $4f^7$, $S = 7/2$, $^8S_{7/2}$-state ion) the EPR spectra are described by the spin Hamiltonian

$$H_s = \sum_{ij} g_{ij} \beta H_i S_j + \sum_{m=-2}^{2} B_2'^m O_2'^m + \sum_{m=-4}^{4} B_4'^m O_4'^m + \sum_{m=-6}^{6} B_6'^m O_6'^m \qquad (1)$$

where $O_n'^m$ are normalized Steven's operators, g_{ij} are the components of the **g** matrix and $B_n'^m$ are the fine structure constants (coefficients relating the normalized constants to the Stevens ones are given in [1] and [6]).

Because of the presence of many forbidden transitions, a sure identification of all transitions at one time is difficult and doubtful. So, the spin-Hamiltonian constants were calculated in two steps. First, using some allowed transitions (which were easily identified) for many different orientations of the magnetic field with respect to the crystal, we calculated approximative constants, considering an isotropic g factor and neglecting the sixth order
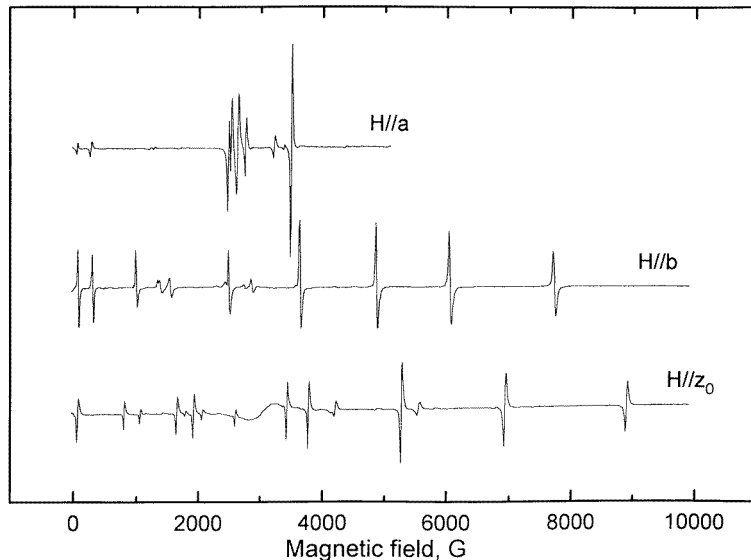
Figure 3. EPR spectra of Gd^{3+} in $K_2Zn(SO_4)_26H_2O$ at room temperature for three diferent orientations of the magnetic field. The spectra are recorded at 9.4 GHz.
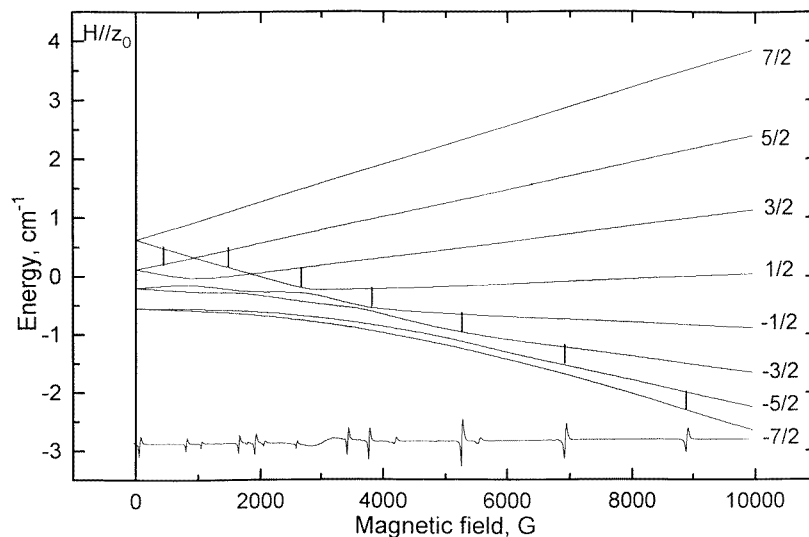
Figure 4. Diagram of the energy levels of Gd^{3+} in $K_2Zn(SO_4)_26H2O$ for $H \parallel z_0$. The allowed transitions for 9.4 GHz are shown by vertical lines, that correspond to the lines of the experimental spectrum presented in the bottom of the figure. The amplitude of the spectrum is given in arbitrary units.

constants. In a second step, we calculated (using the obtained constants) diagrams of the energy levels as a function of the magnetic field (figure 4) and diagrams of the differences between the energy levels for particular orientations of the magnetic field. It was then possible to identify all transitions as shown for example in figure 5 for $\Delta M = \pm 1$ transitions and in figure 6 for $\Delta M = \pm 2$ ones.

Figure 5. (Top) Diagram of the energy level difference of the $\Delta M = 1$ transitions of Gd^{3+} in K$_2$Zn(SO$_4$)$_2$6H$_2$O for $H \parallel b$. The energy corresponding to the microwave frequency 9.4 GHz is shown by a dotted line. (Bottom) Experimental spectrum recorded at 9.4 GHz (the amplitude is in arbitrary units).
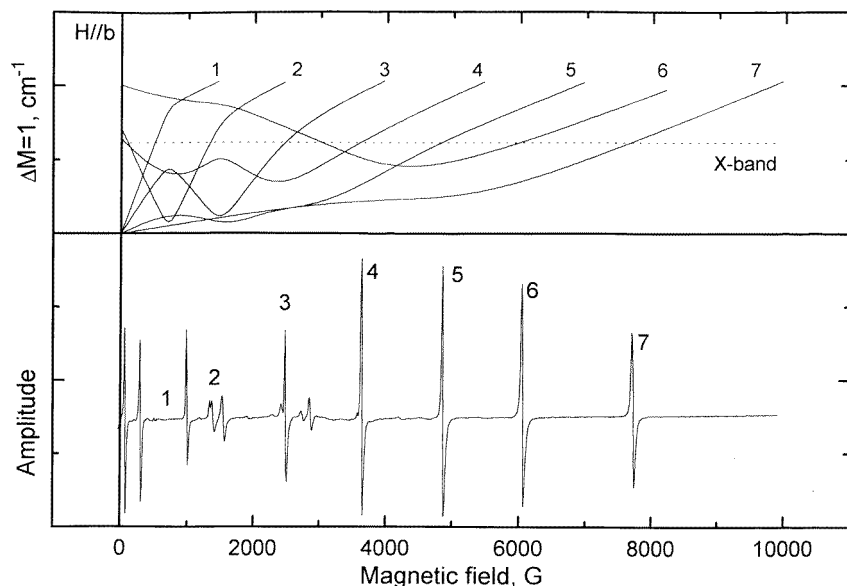
Since all transitions were identified, the spin-Hamiltonian constants were calculated. For the final computation, we used the magnetic fields (and frequencies) of 200 transitions belonging to 40 different spectra recorded in the three crystallographic planes. Our computing program is based on direct diagonalizations of the energy matrices and the 33 constants are determined using an iterative process. The fine structure constants are given in table 1: the standard deviation between the calculated and experimental positions of EPR lines was 15 G.

Diagrams of the difference of the energy levels as a function of the magnetic field are very useful not only to identify the transitions, they also explain strong variations of the EPR spectra with the frequency. For example for H parallel to z_0 transitions $1/2 \rightarrow -3/2$ (at $\sim$2000 Gauss) can be observed at 9.4 GHz but not at 9.2 GHz (figure 6).

EPR lines for the magnetic field close to zero were particularly studied for $H \parallel b$ and for $H \parallel z_0$: they are the superposition of one allowed transition $1/2 \rightarrow -1/2$ of relatively small intensity and a strong forbidden transition $3/2 \rightarrow -1/2$. From our calculations these lines can be observed in the absence of constant magnetic field at 9.9 GHz at room temperature. For $H \parallel a$ and for many intermediate orientations these lines are weak (figure 3).

Previous studies of Gd^{3+} in other double sulphates [1–3] were performed at 77 K. To compare the results of the present study with to the others, we looked for a possible variation of the spectra as a function of temperature.

Figure 7 presents the temperature dependences for $H \parallel z_0$. Changes in the EPR spectra are clearly observed especially at high fields. The EPR line shift for some transitions is of the order of a few hundred gauss.

The Gd^{3+} spin-Hamiltonian constants at $-150\,^\circ$C were calculated. They are given in table 1 for comparison with the constants calculated at room temperature.
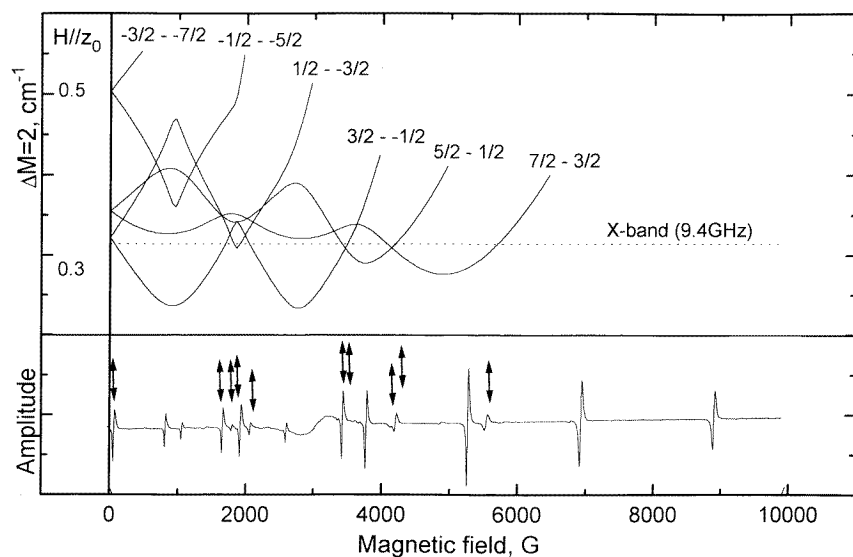
Figure 6. (Top) Diagram of the energy level difference of the $\Delta M = 2$ transitions of Gd^{3+} in $K_2Zn(SO_4)_26H_2O$ for $H \parallel z_0$. The energy corresponding to the microwave frequency 9.4 GHz is shown by a dotted line. (Bottom) Experimental spectrum recorded at 9.4 GHz (the amplitude is in arbitrary units). The observed $\Delta M = 2$ of the experimental spectrum are indicated by arrows.

Table 1. Normalized constant $B_n^{\prime m}$ of the spin Hamiltonian of Gd^{3+} in $K_2Zn(SO_4)_2^*6H_2O$. Axis x is parallel to the crystallographic a axis, z is parallel to axis b of the crystal. This coordinate system is the same as used in previous double sulphates [1–3]. All constants are given in units of 10^{-4} cm^{-1}.

m	$B_2^{\prime m}$		$60B_4^{\prime m}$		$1260B_6^{\prime m}$	
	20 °C	−150 °C	20 °C	−150 °C	20 °C	−150 °C
0	−243.95	−258.22	15.10	14.18	0.42	0.43
1	56.18	63.61	−4.59	−5.56	−0.28	−1.21
−1	8.99	34.72	−4.78	−6.77	−0.58	−0.56
2	−121.4	−133.95	1.98	0.45	0.54	0.81
−2	148.95	163.60	3.43	4.07	0.46	0.17
3			−1.89	−0.61	−0.27	1.65
−3			−0.33	2.75	−1.05	1.09
4			−10.29	−11.97	0.32	1.68
−4			−0.51	−0.41	0.07	2.16
5					−0.68	3.08
−5					−0.47	4.25
6					0.73	−2.93
−6					−0.27	0.28

From the second order constants we computed the orientations of the second order tensors and their principal values. The results are presented in table 2 for low- and high-temperature measurements. It is observed that there is no strong divergence for the two temperatures. The parameter of axiality $\lambda = b_2^2/b_2^0$ is smaller at $-150\,°$C. This value is very similar to the one of Gd^{3+} in kronkite [2] ($\lambda = 0.731$) but far from the λ in the astrakanite ($\lambda = 0.1372$).
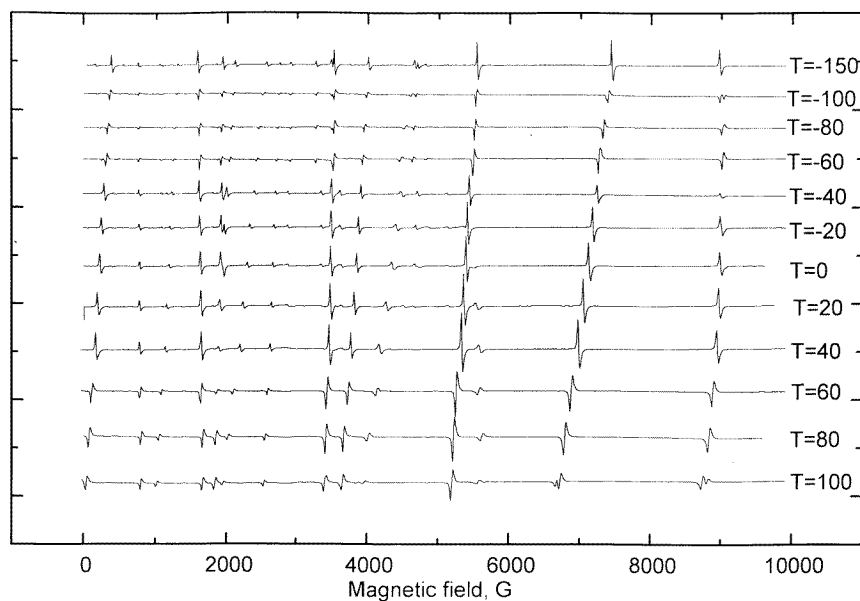
Figure 7. Temperature variation of the EPR spectrum of Gd^{3+} for $H \parallel z_0$. Microwave frequency was 9.2 GHz. Temperatures are given in Celsius.

Table 2. Characteristics of the second order term of the spin Hamiltonian. Angles θ and φ are the spherical coordinates of the principal axes X, Y, Z (EPR axes) in the reference coordinate system $x \parallel a$, $z \parallel b$. b_2^0 and b_2^2 are the classical Stevens constants.

Axes of	20 °C		−150 °C	
Gd^{3+} KZS6H$_2$0	θ	φ	θ	φ
X	79.0	−26.4	80.4	−26.7
Y	168.6	169.4	169.1	−178.4
Z	86.9	64.2	84.9	64.2
b_2^0	289.9		317.0	
b_2^2	216.7		221.0	
$\lambda = b_2^2/b_2^0$	0.75		0.69	

From the fourth order constants which are mainly induced by the nearest neighbours of S state ions, we tried to obtain more information about the environment of Gd^{3+} in the crystal.

For this purpose we looked for the pseudo-symmetry characteristics of the fourth order tensor of the spin Hamitonian following the pseudo-symmetry method presented first by Michoulier and Gaite [7] and used in papers concerning other double sulphates [1–3].

The basic pseudo-symmetry method consists of looking for the minima of ε_n functions depending on the orientations of the reference frame with respect to the crystal, n being the order of the symmetry axis.

The ε_n functions are defined by:

$$\varepsilon_n = ((B_4'^0)^2 + (B_4''^n)^2 + (B_4'^{-n})^2)/\Sigma(B_4''^m)^2 \qquad \text{for } n = 3 \text{ and } 4. \qquad (2)$$

The ε_n are zero in the case of perfect n-fold symmetry and their values are characteristic of the distortion of the environment of the studied ions.

The results are presented in table 3. Only the results concerning the fourfold pseudo-symmetry axes (F_1, F_2 and F_3) are presented although all pseudo-symmetries (with $n = 3$) were investigated.

Table 3. Characteristics of the fourfold pseudo-symmetries of the fourth order term of the spin Hamiltonian of Gd^{3+} and of the ones of the fourth order development of the crystal field at Zn and K positions. Angles θ and φ are the spherical coordinates of the axes in the reference coordinate system defined in table 2.

Axes	n	Gd^{3+}: 20 °C			Gd^{3+}: −150 °C		
		ε_n	θ	φ	ε_n	θ	φ
F_1	4	0.027	8.3	40.2	0.011	11.1	50.9
F_2	4	0.046	89.1	−44.1	0.019	91.2	−44.8
F_3	4	0.019	81.7	45.6	0.004	79.0	44.9

Axes	n	Zn inside 6 H_2O			K inside 8 O		
		ε_n	θ	φ	ε_n	θ	φ
F_1	4	0.000 45	48.4	−7.9	0.19	16.1	76.6
F_2	4	0.000 77	65.9	105.9	0.22	83.8	−41.4
F_3	4	0.000 26	51.5	217.1	0.28	100.0	47.4

From these results, it is observed that the fourth order term of the spin Hamiltonian (H_4) is characteristic of a Gd^{3+} environment having a high pseudo-symmetry; the ε_n being much lower than the ones observed for astrakanite and kronkite. Because all ε_n values were of the same order of magnitude, it can be concluded that the environment of Gd^{3+} has an environment with nearly cubic symmetry.

To locate Gd^{3+} in the structure there are several possibilities. In simple cases one can compare the orientations of the pseudo-symmetry axes obtained from EPR to the directions of the bonds linking the possible substituted ion to its nearest neighbours.

In another way, from the crystallographic data one can calculate at given structural positions the fourth order development V_4 of the crystal field expressed in terms of Tesseral harmonics, as described by Hutchings [8], which directly correspond to the normalized Stevens operators. Since the constants A_4^m of this development are obtained, the pseudo-symmetry of V_4 may be determined in the same way that for H_4 [9].

To perform these computations we used the atomic reduced coordinates of another tutton salt from Montgomery [5] and the unit cell parameters of KZS.

We calculated the pseudo-symmetry axes of V_4 at the Zn and K positions as represented in figure 1. The results are given in table 3. As could be immediately deduced from the observation of figure 1, the environment of Zn is much more symmetric than the one of K.

For the comparison of the orientations of the fourfold axes of Gd^{3+} with the M_1–O or M_2–O directions, we used the structural data of Montgomery *et al* [5] and Kumaraswamy *et al* [10] which are given in table 4.

The comparison of tables 4 and 2 shows there are no correlations between Zn–O or K–O directions and the EPR axes. The comparison of tables 4 and 3 shows there are also no correlations between Zn–O or K–O directions and the fourfold pseudo-symmetry axes of Gd^{3+}. In addition the fourfold pseudo-symmetry axes are far from the axes of the

Table 4. Direction of the vectors joining principal atoms of any double sulphates calculated from indicated references. The spherical angles θ and φ are calculated in the same coordinate system in order to compare directions with tables 2 and 3.

Direction	θ	φ
Kumaraswamy *et al* [10]		
Ni(Zn)–NH$_4$	29	80
Ni(Zn)–O	65	−10
Montgomery *et al* [5]		
V(Zn)–S	70.9	46.5
V(Zn)–N	26.5	32.9
N(K)–S	132.4	56.7
V(Zn)–O$_s$ (3)	57.0	55.7
V(Zn)–O$_s$ (4)	80.4	55.6
V(Zn)–O$_s$ (5)	77.9	39.1
V(Zn)–O$_s$ (6)	69.2	35.6
V(Zn)–O (7)	50.8	70.0
V(Zn)–O (8)	47.9	114.0
V(Zn)–O (9)	115.4	0.5

non-substituted octahedra of zinc and of potassium (table 3). However, the fourfold axes of potassium sites are closer to the ones of Gd^{3+}.

4. Discussion and conclusion

Some conclusions may be given: first, we have a high pseudo-symmetry of the local structure around Gd^{3+}; second the probability of the location of Gd^{3+} in the Zn site is less that in the K position, if one considers that the pseudo-symmetry axes of Gd^{3+} are closer to the one of the K site.

The ε_n values for the fourfold axes of Gd^{3+} are much better than the same ε_n of the potassium site but very poor in comparison with the ε_n of the zinc position. Next, these ε_n values of Gd^{3+} for F_1, F_2 and F_3 are quite similar and are near a cubic symmetry. It seems such a situation is possible if the absolutely non-symmetric environment of the potassium site (see figure 1 and ε_n values for the K site in table 3) will be strongly modified when a gadolinium replaces potassium. Of course, a non-local charge compensation takes place, which is suggested by the absence of a strong axial symmetry.

For Gd^{3+} in kronkite the values of ε_n are about 0.2, which correspond to a highly distorted local environment with respect to cubic symmetry. For Gd^{3+} in astrakanite the pseudo-symmetries (ε_n) are of the same order of magnitude. In both cases it was seen that there is no relation between the orientations of the fourfold pseudo-symmetry axes and special directions to nearest oxygens, as for the present study. In kronkite it was supposed that in the saturated solution there exist complexes of Gd^{3+} which are fixed on the growing step by a kind of epitaxial mechanism. Such a process can explain the local distortion around Gd^{3+} that we observed.

Similar deformation of the host lattice near Gd^{3+} was observed by other authors [11].

In the study of Gd^{3+} in the family of the double sulphates it was expected that it would be a relation between the norm of the fourth order constants of the spin Hamiltonian and the number of water molecules. In fact we did not observe a significant relation. Of course such a relation would exist only if Gd^{3+} is at the same position (M_2) with a variable

number of oxygens and water molecules. In these compounds, the Gd^{3+} may have similar environments.

It is interesting to make some remarks on the EPR spectra of $K_2Zn(SO_4)_2 6H_2O$.

The zero-field splitting is of the same order of magnitude as the energy of the microwave radiation at the X band. A great number of transitions were observed. We think this crystal could be a good example to look for some additional terms ($g\beta H S^3$, $g\beta H S^5$, $g\beta H S^7$) in the spin Hamiltonian as proposed by Claridge *et al* for Fe^{3+} in $CaWO_4$ [12].

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