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## Transferred hyperfine interaction of a $\text{Yb}^{3+}$ trigonal centre in $\text{KMgF}_3$

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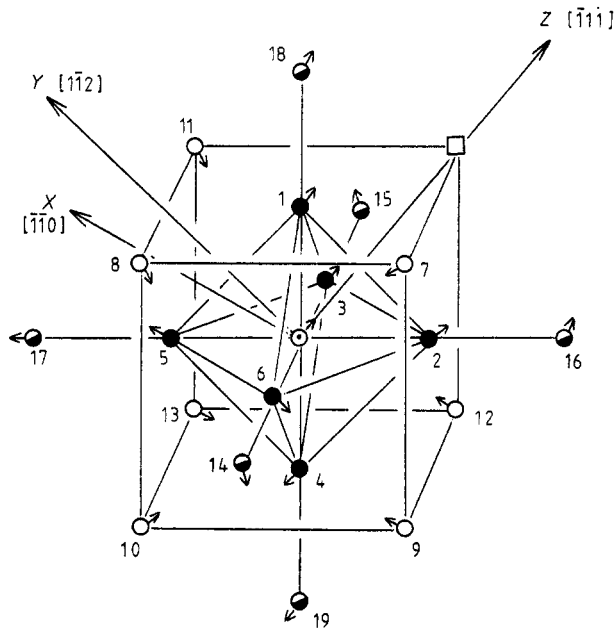
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**Abstract.** The investigation of a  $\text{Yb}^{3+}$  trigonal centre in  $\text{KMgF}_3$  was carried out by means of ENDOR. Expressions for the frequencies for ENDOR transitions in trigonally distorted complexes for arbitrary magnetic field orientation with respect to the crystallographic axes were obtained. A structural model of the centre was determined. The parameters of interaction of  $\text{Yb}^{3+}$  with  $\text{F}^-$  ions of the nearest environment were also determined. A method to determine the absolute signs of the crystal-field parameters  $B_4^3$  and  $B_6^3$  was suggested. The microscopic calculation of crystal lattice deformation in  $\text{KMgF}_3$  near a paramagnetic impurity was carried out. The microscopic analysis of transferred hyperfine interaction parameters for an ion in a non-S state and having a local non-cubic symmetry, taking into account the effects of the spin polarisation of the outer filled 5s and 5p shells of the rare-earth ion, has been carried out for the first time.

### 1. Introduction

Recently, new concepts about the interaction between an impurity paramagnetic ion in a dielectric crystal and nuclear moments forming the nearest environment (the transferred hyperfine interaction (THFI)) were developed by Anikeenok and Eremin (1981), Anikeenok *et al* (1982, 1984, 1986a, b) and Falin *et al* (1989). They enabled the variety of experimental data for impurity rare-earth ions (IREIS) in fluorides with cubic local symmetry to be explained for the first time. In the studies of Anikeenok *et al* (1986a), Eremin and Falin (1987) and Eremin and Khutsishvili (1988) these concepts were used to explain the experimental data for IREIS for sites having a local symmetry lower than cubic ( $\text{CaF}_2$ ,  $\text{SrF}_2$ :  $\text{Ce}^{3+}$  and  $\text{CaF}_2$ :  $\text{Tb}^{3+}$ ). The local deformation model was known for different types of IREI in fluorite-type crystals (Malkin *et al* 1970, Davydova *et al* 1978), thus determining the successful results of the works of Anikeenok *et al* (1986a), Eremin and Falin (1987) and Eremin and Khutsishvili (1988). The attempts to apply new THFI theory to low-symmetry IREI in crystals with a structure differing from that of fluorite were hampered by the absence of corresponding local deformation models of these centres.

The present work is concerned with the experimental results of the THFI investigation of trigonal  $\text{Yb}^{3+}$  in  $\text{KMgF}_3$  by means of ENDOR (the EPR and optical spectra of this complex were studied by Abraham *et al* (1971) and Antipin *et al* (1977)). The microscopic calculations of crystal lattice local deformation near the implantation centre and THFI parameters were carried out.



**Figure 1.** The model of the  $\text{Yb}^{3+}$  trigonal centre in  $\text{KMgF}_3$ , and the structure deformation of the crystal near the rare-earth ion:  $\odot$ ,  $\text{Yb}^{3+}$ ;  $\bullet$ ,  $\text{F}^-$ ;  $\circ$ ,  $\text{K}^+$ ;  $\ominus$ ,  $\text{Mg}^{2+}$ ;  $\square$ , vacancy.

## 2. Experiment

$\text{KMgF}_3:\text{Yb}^{3+}$  crystals were grown by the Czochralski method. The concentration of  $\text{Yb}^{3+}$  was 0.01%. The experiment was carried out using an X-band ENDOR spectrometer at  $T = 4$  K.

The present study confirmed the model of the trigonal complex  $[\text{YbF}_6]^{3-}$  suggested by Abraham *et al* (1971) (figure 1).

The  $\text{Yb}^{3+}$  ground state is  $^2F_{7/2}$ . The Kramers doublet  $\Gamma_4^{(1)}$  is the lowest. The spin Hamiltonian describing the interaction of  $\text{Yb}^{3+}$  with fluorine nuclei has the form

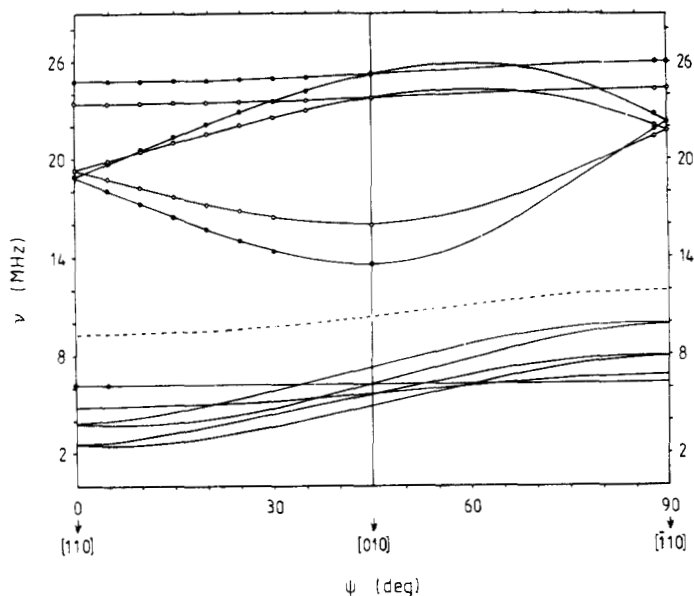
$$\mathcal{H} = \beta H g S + \sum_{i=1}^6 (\mathbf{S} \mathbf{A}^{(i)} \mathbf{I}_i^F - g_n^F \beta_n H \cdot \mathbf{I}_i^F) \quad (1)$$

where  $S = I^F = \frac{1}{2}$ ,  $\mathbf{A}^{(i)}$  is a THFI tensor and  $i$  labels the nuclei.

$\mathbf{A}^{(i)}$  for each  $\text{F}_i^-$  ion from the nearest environment is defined by the local symmetry. As the local symmetry of  $\text{F}_i^-$  is  $C_3$ , the THFI tensor describing the interaction between  $\text{Yb}^{3+}$  and, for example,  $\text{F}_1^-$  in the  $x, y, z$  coordinate system (figure 1) may be written as

$$\mathbf{A}^{(1)} = \begin{pmatrix} A_1 & 0 & 0 \\ 0 & A_2 & A_4 \\ 0 & A_5 & A_3 \end{pmatrix}.$$

THFI tensors of  $\text{Yb}^{3+}$  for  $\text{F}_2^-$  and  $\text{F}_3^-$  ions may be obtained by consecutive rotation of the coordinate system through  $120^\circ$  about an axis of symmetry, because the vacancies  $\text{F}_{4,5,6}^-$  are not equivalent to  $\text{F}_{1,2,3}^-$ .



**Figure 2.** Angular dependence of ENDOR lines in the (001) plane: ●, ○, experiment; —, calculated, using (2) and table 1.

By diagonalisation of the one-particle nuclear Hamiltonian, obtained by averaging (1) over electron variables up to second-order perturbation theory and using selection rules for ENDOR transitions, general expressions for ENDOR transition frequencies were obtained for the arbitrary orientation of a magnetic field  $H$  with respect to the crystallographic directions:

$$\nu_i^2 = a_i^2 C_1^2 + (d_i C_2 + C_5)^2 + (C_3 + d_i C_4)^2 \quad (2)$$

where  $i \equiv F_1^-, F_2^-, F_3^-$ ,

$$C_1 = \{(g_{\perp}/g)[(A_1 u - \mu(u)(A_2 A_3 - A_4 A_5)] - \nu_L\} \sin \theta$$

$$C_2 = \{(g_{\perp}/g)[A_2 u - \mu(u)A_1 A_3] - \nu_L\} \sin \theta$$

$$C_3 = \{(g_{\parallel}/g)[A_3 u - \mu(u)A_1 A_2] - \nu_L\} \cos \theta$$

$$C_4 = (g_{\perp}/g)[A_4 u + \mu(u)A_1 A_5] \sin \theta$$

$$C_5 = (g_{\parallel}/g)[A_5 u + \mu(u)A_1 A_4] \cos \theta$$

$$a_1 = \cos \varphi \quad d_1 = \sin \varphi$$

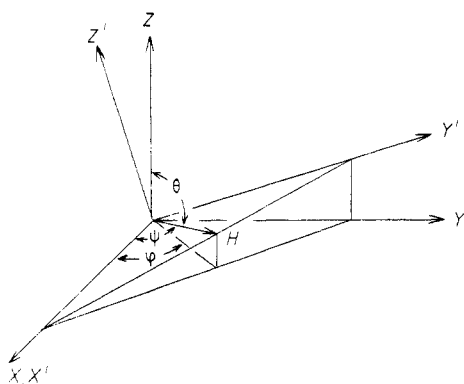
$$a_{2,3} = \frac{1}{2}(\cos \varphi \pm \sqrt{3} \sin \varphi) \quad d_{2,3} = \frac{1}{2}(\sqrt{3} \cos \varphi \mp \sin \varphi)$$

$$a_i^2 + d_i^2 = 1 \quad \mu(u) = [S(S+1) - u^2]/2g\beta H$$

$$\nu_L = g_n^F \beta_n H.$$

The signs + and - in  $a_i$  and  $d_i$  refer to  $F_2^-$  and  $F_3^-$ , respectively;  $\theta$  and  $\varphi$  are the polar angles;  $u$  is the magnetic quantum number of an electron spin. For  $F_{4,5,6}^-$ , expressions for the frequencies of ENDOR transitions are similar.

To identify unambiguously the structure of the nearest environment and THFI parameters, the angular dependence of ENDOR spectra was recorded (figure 2). The strong



**Figure 3.** The relation between the magnetic and crystallographic directions.

anisotropy of the intensity of ENDOR signals, preventing the recording of the total angular dependence of ENDOR spectra, should be noted. In previously investigated complexes  $\text{CaF}_2:\text{Er}^{3+}$ ,  $\text{KMgF}_3:\text{Dy}^{3+}$ ,  $\text{Er}^{3+}$  (Grachev *et al* 1987, 1989) the angular dependence was studied in the (110) crystal plane. It allowed to pass through all main crystallographic directions by a single rotation of the magnetic field. In the present case, owing to the low intensity of ENDOR signals in this plane, the measurements, in general, were carried out in the (001) plane. The relation between magnetic and crystallographic directions is shown in figure 3, where  $\theta$  and  $\varphi$  are defined as follows. For the (001) plane,

$$\theta = \cos^{-1}\{[(\cos \psi^1)/2\sqrt{3}][1/\cos^2 \psi^1 + 2 - (1 - \tan \psi^1)^2]\}$$

$$\varphi = \cos^{-1}[(1/2m)(\cos \psi/\cos \psi^1)]$$

$$m = \{[\frac{1}{6}[1/\cos^2 \psi^1 - 1 + \sqrt{2}(\cos \psi/\cos \psi^1)]]^{1/2}\}$$

$$\psi^1 = \psi - \frac{1}{4}\pi.$$

For the (110) plane,

$$\theta = \cos^{-1}[(1/\sqrt{3}) \sin \psi]$$

$$\varphi = \tan^{-1}(\sqrt{\frac{2}{3}} \tan \psi).$$

The spectra and angular dependence of ENDOR lines show that the nearest environment of  $\text{Yb}^{3+}$  consists of six fluorine ions, divided into two non-equivalent groups. The compensation of an extra positive charge of  $\text{Yb}^{3+}$  occurs most probably owing to a vacancy at the site of one of the nearest  $\text{K}^+$  ions (ENDOR of  $\text{K}^+$  was not detected). A least-squares computer fit analysis of the experimental data was carried out using (2). The THFI parameters obtained are given in table 1 and are compared with the experimental data of Falin *et al* (1977) on cubic  $\text{Yb}^{3+}$  in  $\text{KMgF}_3$ .

### 3. Analysis and discussion

The effective operator of the interaction of 4f electrons with a ligand nuclear spin  $I$  is

$$\mathcal{H} = \sum_k b^{(j)k} (\{\mathbf{R}^{(j)} I^{(1)}\}^{(k)} \mathbf{C}^{(k)}) \quad (3)$$

where  $\mathbf{R}^{(j)}$  are irreducible tensor operators,  $I^{(1)}$  the spherical components of the nuclear

**Table 1.** Spin-Hamiltonian parameters ( $g_{\parallel} = 1.844$  and  $g_{\perp} = 2.896$  from Abraham *et al* (1971)). The experimental data is for the cubic centre from Falin *et al* (1977) given in the  $x$ ,  $y$ ,  $z$  coordinate system (figure 1).

	I	II	Cubic
$A_1$	30.93(5)	28.19(5)	29.21
$A_2$	14.34(5)	16.83(5)	17.35
$A_3$	18.80(5)	17.40(5)	23.28
$A_4$	2.74(5)	0.93(5)	-8.39
$A_5$	22.09(5)	17.75(5)	-8.39

spin  $I$ ,  $b^{(j)k}$  the combinations of the transfer integrals and  $\mathbf{C}^{(k)}$  the spherical tensors of the angles  $\theta$  and  $\varphi$ . The reduced matrix elements of the operators  $W^{(1k)k'}$  and  $V^{k'}$  for the ground state have been calculated and are listed in the appendix.

The implantation of an impurity ion in a crystal lattice leads to the redistribution of the electron charge, which changes the force constants of the ions in a crystal matrix surrounding the impurity, and thus leads to the displacement of the ion into new equilibrium positions. The values of the displacement and the induced dipolar moments of the ions were calculated using the condition of minimum energy of a crystal bond according to Ivanenko and Malkin (1969). The set of linear algebraic equations has the form

$$\left(\frac{\partial E}{\partial X_{\alpha i}}\right)_0 + \sum_k \left(\frac{\partial^2 E}{\partial X_{\alpha i} \partial X_{\beta j}}\right) X_{\beta j} = 0 \quad (4)$$

$$\alpha, \beta = x, y, z$$

where  $X_j$  is the displacement vector of ion  $j$ . The derivatives of non-Coulomb energy were expressed via force constants, responsible for the interaction between different ions of a crystal. The Coulomb part of the energy bond change was derived by expanding in series the interaction energy between point ions and dipoles in harmonic approximation.

In the calculations the displacements of the five coordination spheres, formed by  $\text{F}^-$ ,  $\text{K}^+$  and  $\text{Mg}^{2+}$  near  $\text{Yb}^{3+}$  were taken into account. While calculating the non-Coulomb energy the force constants of bonds of ions in crystal lattice were taken to be the same as in a regular  $\text{KMgF}_3$  crystal (Rousseau *et al* 1974). The force constants of a  $\text{Tm}^{3+}-\text{F}^-$  bond in  $\text{CaF}_2$  (Malkin 1976) corrected to another length of a bond were chosen as initial values for force constants of a  $\text{Yb}^{3+}-\text{F}^-$  bond. Then they were varied to achieve the best fit to the energy level diagram and  $g$ -factors of the trigonal centre, estimated on the basis of a given local deformation, with experimental data of Abraham *et al* (1971) and Antipin *et al* (1977). The crystal-field parameters  $B_n^m$  of  $\text{Yb}^{3+}$  necessary to obtain the above values were calculated within the point exchange charge model (Malkin 1976).

The polarisation of ions was not taken into account in deformation calculations.

The calculation of the local deformation enabled us to obtain a model of the impurity centre  $\text{Yb}^{3+}$  (figure 1) and to make a quantitative estimate of the inter-ion distances (table 2). Figure 1 and table 2 demonstrate that the first and third coordination spheres, formed by  $\text{F}^-$  and  $\text{Mg}^{2+}$  ions, respectively, have a tendency to be expanded and the second coordination sphere ( $\text{K}^+$  ions) to be compressed.

**Table 2.** Lattice deformation of KMgF<sub>3</sub> near the trigonal centre Yb<sup>3+</sup>.

	Number of ions (figure 1)	R (Å)	θ (deg)
F <sup>-</sup>	1-3	2.199	58.01
F <sup>-</sup>	4-6	2.269	125.73
K <sup>+</sup>	7, 11, 12	3.012	74.75
K <sup>+</sup>	8, 9, 13	3.135	114.94
Mg <sup>2+</sup>	14, 17, 19	4.368	126.30
Mg <sup>2+</sup>	15, 16, 18	4.106	55.22

The calculated crystal-field parameters  $B_n^m$  accounting for local deformation have the following values:  $B_2^0 = -63 \text{ cm}^{-1}$ ,  $B_4^0 = -176 \text{ cm}^{-1}$ ,  $B_6^0 = 42 \text{ cm}^{-1}$ ,  $B_4^3 = 5568 \text{ cm}^{-1}$ ,  $B_6^3 = 246 \text{ cm}^{-1}$  and  $B_6^6 = 389 \text{ cm}^{-1}$ . The experimental and calculated Stark structures of the ground terms of Yb<sup>3+</sup> in KMgF<sub>3</sub> are given in figure 4.

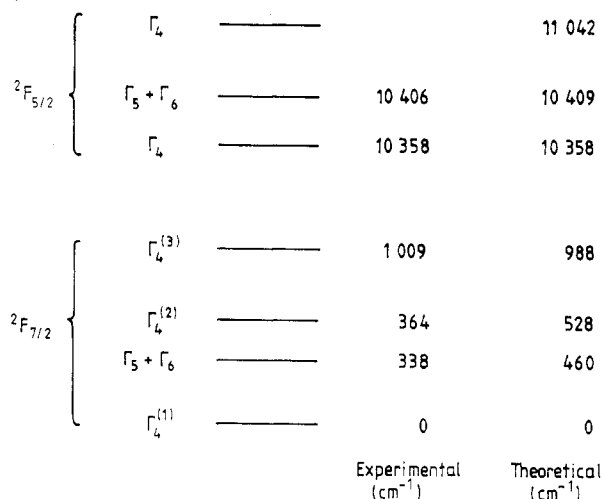
The wavefunction of a ground state within the given microscopic model of a centre was the following:

$$\Psi(\pm\frac{1}{2}) = \mp 0.359 09 |\pm\frac{7}{2}\rangle \mp 0.515 27 |\pm\frac{1}{2}\rangle \pm 0.778 17 |\mp\frac{5}{2}\rangle. \quad (5)$$

To analyse the THFI parameters, the  $\Psi$  function was transformed into the coordinate system shown in figure 1 and had the form

$$\Psi^1(\pm\frac{1}{2}) = \mp 0.359 09 |\pm\frac{7}{2}\rangle \pm i0.515 27 |\pm\frac{1}{2}\rangle \mp 0.778 17 |\mp\frac{5}{2}\rangle. \quad (6)$$

It should be noted that the calculation of the THFI parameters requires accurate determination of the wavefunction of a ground state. The value of THFI depends on the relative signs of the  $|\pm\frac{7}{2}\rangle$ ,  $|\pm\frac{1}{2}\rangle$ ,  $|\mp\frac{5}{2}\rangle$  components in (5) and (6), which are defined by the signs of  $B_4^3$  and  $B_6^3$ . However, the relative signs of  $B_4^3$  and  $B_6^3$  usually remain uncertain (Abragam and Bleaney 1972). Now it becomes possible to control the sign of the crystal-field parameters  $B_4^3$  and  $B_6^3$  by using the THFI parameters.

**Figure 4.** Calculated and experimental (Antipin et al 1977) Stark structure of ground terms of Yb<sup>3+</sup> in KMgF<sub>3</sub>.

The calculation of the THFI components  $\mathbf{A}^{(i)}$  was carried out accounting for all the mechanisms proposed by Anikeenok *et al* (1986a), Eremin and Falin (1987) and Eremin and Khutsishvili (1988). The overlap integrals were calculated with the Hartree–Fock wavefunctions of  $\text{Yb}^{3+}$  (Eremin *et al* 1977) and fluorine (Clementi and Roetti 1974). The distances  $\text{Yb}^{3+}\text{-F}^-$  were taken from the deformation model of a centre. The radial 5s and 5p functions were taken from Van Piggelen *et al* (1980) and the 5d, 6s and 6p functions from Rajnak (1963) for  $\text{Tm}^{3+}$ . The mixing of 1s and 2s shells of  $\text{F}^-$  was taken into account. The transfer integrals have the following values: for  $R = 2.2 \text{ \AA}$ ,  $\gamma_{4fs} = 0.01$ ,  $\gamma_{4f\sigma} = -0.055$ ,  $\gamma_{4f\pi} = 0.055$ ,  $\gamma_{5ds} = 0.02$ ,  $\gamma_{5d\sigma} = -0.15$ ,  $\gamma_{5d\pi} = 0.15$ ,  $\gamma_{5ps} = 0.01$ ,  $\gamma_{5p\sigma} = -0.1$  and  $\gamma_{5p\pi} = 0.1$ ; for  $R = 2.27 \text{ \AA}$ ,  $\gamma_{4fs} = 0.007$ ,  $\gamma_{4f\sigma} = -0.05$ ,  $\gamma_{4f\pi} = 0.055$ ,  $\gamma_{5ds} = 0.01$ ,  $\gamma_{5d\sigma} = -0.1$ ,  $\gamma_{5d\pi} = 0.1$ ,  $\gamma_{5ps} = 0.01$ ,  $\gamma_{5p\sigma} = -0.1$  and  $\gamma_{5p\pi} = 0.1$ . The covalency parameters for 6s and 6p shells which are very uncertain are considered to be equal to  $\gamma_{5d}$ . The energies of electron transfer were estimated by the same method used by Anikeenok *et al* (1984) and Falin *et al* (1989):  $\Delta_{2p4f} = 6 \times 10^4 \text{ cm}^{-1}$ ,  $\Delta_{2s4f} = 2.4 \times 10^5 \text{ cm}^{-1}$ ,  $\Delta_{2p5d} = 1.5 \times 10^5 \text{ cm}^{-1}$ ,  $\Delta_{2s5d} = 3.3 \times 10^5 \text{ cm}^{-1}$ ,  $\Delta_{5s6s} = 3.7 \times 10^5 \text{ cm}^{-1}$ ,  $\Delta_{5p6p} = 2 \times 10^5 \text{ cm}^{-1}$  and  $\Delta_{5s5d} = 3.3 \times 10^5 \text{ cm}^{-1}$ . The radial integrals were taken to be the same as in the work of Falin *et al* (1989). The 4f–5d interaction parameters  $G^1$ ,  $G^3$  and  $G^5$  were taken from Starostin *et al* (1975) for  $\text{Yb}^{2+}$  and the 4f–6s interaction parameter  $G^3 = 2359 \text{ cm}^{-1}$  from Goldschmidt (1978).

The theoretical results are given in table 3. The values of the separate calculations are given in the third to eleventh columns: the dipole–dipole contribution  $H_{d-d}$  accounting for multipole corrections; the contribution  $H_{4f}$  due to the effect of overlap and covalency of 4f shell; the contributions  $H_{5d}$  and  $H_{6s}$  due to the electron transfer to the empty 5d and 6s shells respectively; the contribution  $H_d$  due to the effect of the mixing of 4f and 5d states by the field of virtual hole  $\text{F}^-$ ; the contribution  $H_{oc}$  due to the effects of an odd crystal field on  $\text{Yb}^{3+}$ ; the contributions  $H_{5s \rightarrow 5d}$ ,  $H_{5s \rightarrow 6s}$  and  $H_{5p \rightarrow 6p}$  due to the effects of the spin polarisation of 5s and 5p shells. The total values of THFI are given in the last column. Comparing tables 1 and 3 one can see that the theoretical values are in satisfactory agreement with the experimental values. It should be noted that the calculated values of THFI are very sensitive to the angles  $\theta_1$  and  $\theta_2$  and the best fit of the theory and experiment is achieved, when  $\theta'_1 = 50^\circ$  and  $\theta'_2 = 131^\circ$  (table 4). The difference between  $\theta_2$  and  $\theta'_2$  is insignificant. The strong difference between  $\theta_1$  and  $\theta'_1$  indicates the essential role of the vacancy, the influence of which was not taken into account in full measure in the calculation of local deformation and THFI.

The calculation of THFI in the cubic centre  $\text{KMgF}_3$ :  $\text{Yb}^{3+}$  favours this conclusion. The results of calculations are given in table 5. This table is more complete than that given by Anikeenok *et al* (1984), where the contribution to THFI connected with the polarisation of the 5s and 5p shells was not taken into account. In this case, good agreement with experiment shows the correctness of the approximations made in the calculations of THFI.

In conclusion it should be noted that, to create an adequate model of low-symmetry IREIS in crystals, local deformation and THFI calculations should probably be carried out self-consistently.

### Acknowledgments

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Table 3. Calculated values of  $\mathbf{A}^{(l)}$  for  $\text{KMgF}_3$ ;  $\text{Yb}^{3+}$ .

	$H_{0-d}$	$H_{4f}$	$H_{5d}$	$H_{6s}$	$H_d$	$H_{6c}$	$H_{5s-5d}$	$H_{5c-6s}$	$H_{5p-6p}$	Total
$A_1$ (MHz)	9.50	17.10	-6.91	0.20	9.11	-1.19	0.63	-0.22	-0.37	27.86
$A_2$ (MHz)	-10.93	18.83	-5.03	0.53	8.57	-2.00	0.48	-0.48	-0.37	9.62
$A_3$ (MHz)	1.12	18.61	-3.41	0.24	8.72	-1.86	0.39	-0.24	-0.52	21.06
$A_4$ (MHz)	-12.77	-3.10	2.45	0.21	-2.68	-0.27	-0.48	-0.16	0.05	-16.76
$A_5$ (MHz)	-9.33	10.02	-0.59	0.15	3.46	-1.58	-0.18	-0.12	-0.40	1.43
$A_1$ (MHz)	8.64	16.46	-3.74	0.07	5.97	1.10	0.44	-0.18	-0.21	28.59
$A_2$ (MHz)	-8.27	18.55	-2.92	0.24	6.07	1.96	0.34	-0.37	-0.40	15.20
$A_3$ (MHz)	-0.20	16.89	-2.91	0.11	5.80	1.47	0.39	-0.20	-0.31	21.03
$A_4$ (MHz)	-12.29	1.29	0.72	0.12	0	0.61	-0.15	-0.14	-0.13	-9.97
$A_5$ (MHz)	-8.99	1.92	0.41	0.09	0.22	0.66	-0.16	-0.10	-0.19	-6.14

Table 4. Calculated values of  $\mathbf{A}^{(0)}$  for  $\text{KMgF}_3: \text{Yb}^{3+}$ .

	$H_{d-d}$	$H_{4f}$	$H_{5d}$	$H_{6s}$	$H_d$	$H_{6c}$	$H_{5s \rightarrow 5d}$	$H_{5s \rightarrow 6s}$	$H_{5p \rightarrow 6p}$	Total
$A_1$ (MHz)	9.50	16.73	-6.84	0.20	8.90	-1.42	0.60	-0.22	-0.36	27.08
$A_2$ (MHz)	-7.16	20.94	-5.55	0.47	9.06	-2.97	0.25	-0.43	-0.64	13.97
$A_3$ (MHz)	-1.64	15.82	-5.02	0.28	7.91	-1.63	0.60	-0.27	-0.31	15.74
$A_4$ (MHz)	-13.97	8.39	-0.04	0.23	2.88	-1.61	-0.10	-0.18	-0.26	-4.65
$A_5$ (MHz)	-10.23	-3.10	1.89	0.17	-2.45	-0.20	-0.39	-0.13	0.01	-14.44
$A_1$ (MHz)	8.65	16.04	-3.71	0.07	5.80	1.19	0.42	-0.18	-0.21	28.07
$A_2$ (MHz)	-6.21	17.66	-2.93	0.21	5.67	2.20	0.22	-0.34	-0.50	15.99
$A_3$ (MHz)	-1.72	14.16	-2.64	0.13	4.97	1.23	0.46	-0.22	-0.19	16.19
$A_4$ (MHz)	-12.77	7.27	-0.08	0.13	2.07	1.21	0.01	-0.14	-0.26	-2.56
$A_5$ (MHz)	-9.35	-4.79	1.16	0.09	-1.97	-0.06	-0.26	-0.10	0	-15.27

Table 5. Calculated and experimental (Fain *et al* 1977) values of THFI parameters.

	$H_{d-d}$	$H_{4f}$	$H_{5d}$	$H_{6s}$	$H_d$	$H_{5s \rightarrow 5d}$	$H_{5s \rightarrow 6s}$	$H_{5p \rightarrow 6p}$	Total	Experimental
$A_1$ (MHz)	9.71	16.49	-6.82	0.2	9.43	0.85	-0.22	-0.39	29.25	29.21
$A_2$ (MHz)	-9.63	22.69	-5.40	0.49	10.07	0.23	-0.43	-0.56	17.46	17.35
$A_3$ (MHz)	0.04	19.53	-6.07	0.34	9.72	0.53	-0.32	-0.47	23.30	23.28
$A_4 = A_5$ (MHz)	-13.68	4.38	1.01	0.2	0.45	-0.44	-0.15	-0.12	-8.34	-8.39

**Appendix. The reduced matrix elements of  $W^{(1k)k'}$  and  $V^{k'}$  for the states  $4f^{13} 2F_{7/2}$** 

$$\begin{aligned}
\left(\frac{7}{2}\right\| W^{(10)1} \left\|\frac{7}{2}\right) &= \left(\frac{3}{7}\right)^{1/2} \\
\left(\frac{7}{2}\right\| W^{(12)1} \left\|\frac{7}{2}\right) &= -\frac{1}{7}(30)^{1/2} \\
\left(\frac{7}{2}\right\| W^{(12)3} \left\|\frac{7}{2}\right) &= \frac{1}{7}(3 \times 5 \times 11)^{1/2} \\
\left(\frac{7}{2}\right\| W^{(14)3} \left\|\frac{7}{2}\right) &= -\frac{2}{7}(2 \times 3)^{1/2} \\
\left(\frac{7}{2}\right\| W^{(14)5} \left\|\frac{7}{2}\right) &= \frac{1}{7}(2 \times 3 \times 5 \times 13)^{1/2} \\
\left(\frac{7}{2}\right\| W^{(16)5} \left\|\frac{7}{2}\right) &= -\frac{1}{7}(6)^{1/2} \\
\left(\frac{7}{2}\right\| W^{(16)7} \left\|\frac{7}{2}\right) &= (3 \times 5)^{1/2} \\
\left(\frac{7}{2}\right\| V^1 \left\|\frac{7}{2}\right) &= \frac{9}{7}(2)^{1/2} \\
\left(\frac{7}{2}\right\| V^3 \left\|\frac{7}{2}\right) &= 2\left(\frac{11}{7}\right)^{1/2} \\
\left(\frac{7}{2}\right\| V^5 \left\|\frac{7}{2}\right) &= \frac{1}{7}(2 \times 11 \times 13)^{1/2}.
\end{aligned}$$

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