EPR of Sm^{3+} in BaFCl single crystals

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Abstract
BaFCl single crystals doped with Sm^{3+} ions were studied by using the EPR method. Several types of paramagnetic Sm^{3+} centres were found. The parameters of the corresponding spin Hamiltonians were determined. Structural models and ground states of the observed centres are proposed.

1. Introduction

PbFCl (matlockite) structure hosts containing samarium impurities are photochromic materials of considerable potential for optical applications and thus are of timely interest. Members of this family of materials present reversible and stable optical spectral hole burning (OSHB) capability at the technologically important room temperature (RT) and are currently among the best performing materials. But fundamental research needs to be done on them to increase their actual performance. In particular, discussion is open about the mechanism(s) of OSHB, and the nature of the switched state is not elucidated. Some of the proposed models propose Sm^{3+} as an intervening species.

During our work in this domain we realized that to the best of our knowledge no published EPR results exist on Sm^{3+} in the matlockite hosts. There are in fact rather few EPR results available on Sm^{3+}. Results from early experiments are given in [1–4]. A more recent study on Sm^{3+} in KY$_3$F$_{10}$ [5] gives data on a tetragonal paramagnetic Sm^{3+} centre.

For this and the other reasons given above we investigated with EPR several pure matlockites doped with Sm^{3+} (a Kramers ion), and this paper presents new EPR results on BaFCl:Sm^{3+}.

2. Experimental details

Single crystals of BaFCl were grown either in a Bridgman furnace or pulled out of the melt in our Kyropoulos crystal growing facility. The powders together with either SmF$_3$ or Sm$_2$O$_3$ (typically 0.5–4‰) were melted in high purity graphite crucibles under an argon (5N7) atmosphere or 95% of this gas + 5% of H$_2$. Our crystal growth facility allowed very strict control of the growth conditions and the starting powders were of highest purity available
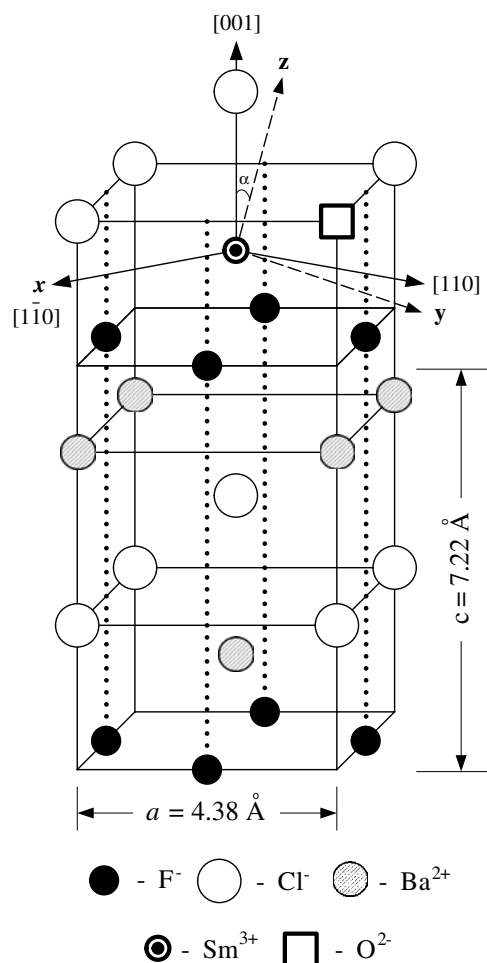
Figure 1. A fragment of the crystal structure of BaFCl.

(BaF_2: Merck suprapur, $BaCl_2$: Cerac suprapur, SmF_3, Sm_2O_3: Cerac 99.9%). Several samples were further hydrolyzed to enhance the Sm^{3+} concentration.

The matlockite host lattice forms a layer structure. Its unit cell is shown in figure 1. The layers are oriented perpendicular to c ([001]). The crystals cleave easily along these layers and we took advantage of this fact in orienting the samples. Laue photographs of the (001) planes served to obtain the Cl–Cl orientations in these planes: there is an important difference between the structure factors of the Cl$^-$ and of the F$^-$ ions, respectively, which allows for a rapid identification of the Cl–Cl axes by using the angles measured in the Laue diagram.

EPR spectra were recorded at $T = 4.2$ K on a home-built EPR spectrometer based on an E 110 Varian X-band equipment and on a standard E 12 Varian X-band spectrometer. Magnetic fields up to 1.2 T were available.
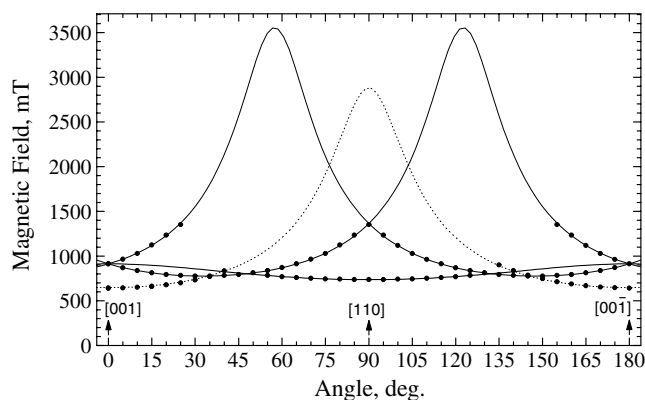
3. Results and discussion

3.1. EPR-results

The crystal has space-group symmetry D_{4h}^7 [6]. The host cation site is surrounded by five Cl$^-$ ions forming a square pyramid and by a square of four F$^-$ ions in a plane parallel to the pyramid
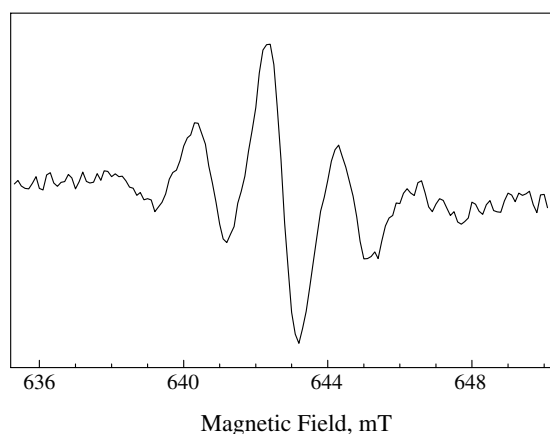
**Figure 2.** Superhyperfine structure of the EPR spectrum of axial Sm^{3+}(I) in BaFCl. **H** $\parallel$ c (=[001]). $T = 4.2$ K, $\nu = 9.235$ GHz.

Figure 3. The angular dependence of the EPR lines of the axial Sm^{3+}(I) (dashed curves) and of the monoclinic Sm^{3+}(II) (solid curves) in the (1$\bar{1}$0) plane. ●: experimental data points. The theoretical curves were obtained by using equation (1) together with the data of table 1.

basis but rotated by 45° with respect to the fourfold axis (see figure 1). The local point symmetry of the cation site is C$_{4v}$. Two different types of samarium EPR spectra were observed. One of them (Sm^{3+}(I)) had tetragonal symmetry whereas the other one (Sm^{3+}(II)) was monoclinic. No hyperfine structure was visible on any of the lines of the monoclinic spectrum, in part due to its low intensity. But the axial Sm^{3+} spectrum presented clear superhyperfine structure due to four equivalent ligands ($I = 1/2$) when the magnetic field **H** was parallel to c (figure 2). This latter spectrum was weaker than the monoclinic one. The angular dependence of the EPR lines in the (1$\bar{1}$0) and (001) planes is given in figures 3 and 4, respectively. These results demonstrate that the Sm^{3+}(I) indeed forms an axial paramagnetic centre (PC) whereas the Sm^{3+}(II) PC is monoclinic.

3.2. Analysis of the EPR spectra

The EPR spectra of both PC were parameterized by the standard spin Hamiltonian: $H = \beta_o \mathbf{H} g_{\text{eff}} \mathbf{S}$, where $S = 1/2$ and g_{eff} is the effective g tensor which has two (axial symmetry)
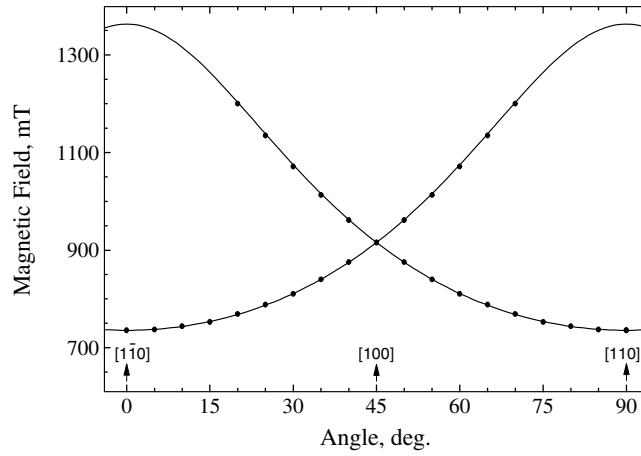
Figure 4. The angular dependence of the EPR lines of monoclinic Sm^{3+}(II) (solid curves) in the (001) plane. ●: experimental data points. The theoretical curves were obtained as given in the caption of figure 3.

Table 1. Experimental values of the g-factors of Sm^{3+} in BaFCl. The corresponding quantities for the axial Sm^{3+} PC in other crystals are given for comparison.

	Symmetry		$\tilde{g} = 1/3(g_x + g_y + g_z)$	Ground state
BaFCl	Monoclinic	$g_x = 0.903\ (3)$	0.650	Γ_7
		$g_y = 0.856\ (3)$		
		$g_z = 0.19\ (1)$		
		$\alpha = 57.4°\ (5)$		
	Axial	$g_\parallel = 1.027\ (3)$	0.496	Γ_6
		$g_\perp = 0.23\ (1)$		
$CaWO_4$ [3]	Axial	$g_\parallel = 0.440\ (5)$	0.577	Γ_6
		$g_\perp = 0.646\ (5)$		
$LiYF_4$ [4]	Axial	$g_\parallel = 0.410\ (5)$	0.566	Γ_6
		$g_\perp = 0.644\ (2)$		
KY_3F_{10} [5]	Axial	$g_\parallel = 0.714\ (2)$	0.311	Γ_6
		$g_\perp = 0.11\ (1)$		

and three (monoclinic symmetry) independent components. In the latter case the expression for g_{eff} is as follows (for an arbitrary orientation of the magnetic field **H** with respect to the crystallographic axes):

$$g_{eff} = \left[g_x^2 \cos^2 \varphi \sin^2 \vartheta + g_y^2 (\cos \alpha \sin \varphi \sin \vartheta - \sin \alpha \cos \vartheta)^2 \right.$$
$$\left. + g_z^2 (\sin \alpha \sin \varphi \sin \vartheta + \cos \alpha \cos \vartheta)^2 \right]^{1/2} \tag{1}$$

where α is the angle between the local z-axis of the g-tensor and the [001] direction. The plane defined by the two axes also contains g_y, whereas g_x is perpendicular to this one and is parallel to [1$\bar{1}$0]. Further, ϑ and φ are the polar angles between **H** and the c-axis related coordinate system of the crystal, but with φ being measured from the g_x-axis. This result was obtained for one out of the four possible orientations of the monoclinic plane (see figure 1). The solutions for the other three are obtained from (1) by successive rotations of the local axis system by 90° around c. The parameters of the spin-Hamiltonian were determined by a least square minimization process. They are given in table 1. For convenient comparison, the

corresponding parameters of the axial Sm^{3+} in the CaWO$_4$ [3], LiYF$_4$ [4] and KY$_3$F$_{10}$ [5] are also given in table 1. Preliminary EPR experiments performed on SrFCl:Sm^{3+} allowed us to identify one Sm^{3+} ion. It has very nearly the same EPR parameters as those of the monoclinic Sm$^{3+}_{\text{monocl}}$ PC in BaFCl. The analysis of the EPR data is in progress.

It is difficult to draw definite conclusions about ground states and structural models of the PCs from these EPR data and only probable ones may be proposed. The ground multiplet of Sm^{3+} is ^{6}H$_{5/2}$, which is split by a cubic crystal field into a doublet Γ_7 and a quartet Γ_8. Basically, the Sm^{3+} ion may either enter the host lattice by substituting for a host cation or by occupying an interstitial site between the host ion lattices. None of these possible sites offers a locally octahedral coordination for the impurity ion. However, the ground state in a cubic crystal field is the quartet Γ_8 [7]. In the situation of the tetragonal Sm^{3+} PC the crystal field splits Γ_8 into two Kramers doublets Γ_{t6} and Γ_{t7}. In the weakly tetragonal case (cubic field much stronger than the tetragonal one) the ground state is Γ_{t6} or Γ_{t7} and the wavefunctions can be described as follows in a first-order approximation:

$$\Gamma_{t6} \rightarrow |\pm 1/2\rangle, \qquad \Gamma_{t7} \rightarrow (|\pm 3/2\rangle + \sqrt{5}|\pm 5/2\rangle)/\sqrt{6}. \tag{2}$$

These functions lead to the following g factors: $g_\parallel = 0.286$, $g_\perp = 0.857$ for Γ_{t6}; $g_\parallel = 1.048$, $g_\perp = 0.476$ for Γ_{t7}. It should be noted that Sm^{3+} is characterized by very strong mixing of states from different J-values [1]. According to [3] the following wavefunctions and g-factors apply when the nearest excited ^{6}H$_{7/2}$ multiplet is further included:

$$\begin{aligned}
&\Gamma_{t6} \rightarrow a|5/2, \pm 1/2\rangle \pm b|7/2, \pm 1/2\rangle \pm c|7/2, \pm 7/2\rangle \\
&g_\parallel = \Lambda a^2 + \left(12\sqrt{10}/7\right)ab + \Lambda' b^2 - 7\Lambda' c^2 \\
&g_\perp = 3\Lambda a^2 - \left(6\sqrt{10}/7\right)ab - 4\Lambda' b^2 \\
&\Gamma_{t7} \rightarrow a'|5/2, \pm 5/2\rangle + b'|5/2, -3/2\rangle \pm c'|7/2, \pm 5/2\rangle + d'|7/2, -3/2\rangle \\
&g_\parallel = \Lambda\left(5a'^2 - 3b'^2 + \sqrt{5}a'c' + 10\sqrt{3}b'd'\right) + \Lambda'\left(85c'^2/13 - 3d'^2\right) \\
&g_\perp = \Lambda\left(2\sqrt{5}a'b' - \sqrt{15}a'd' - 15b'c' - 104\sqrt{3}c'd'/9\right)
\end{aligned} \tag{3}$$

where $\Lambda = 2/7$, $\Lambda' = 52/63$ are the Lande factors for $J = 5/2$ and $7/2$, respectively.

In this approximation the doublet Γ_{t7} has not been included because the available experimental data are insufficient to determine the wavefunctions of this level.

The functions

$$\Gamma_{t6} \rightarrow 0.9666|5/2, \pm 1/2\rangle \pm 0.1777|7/2, \pm 1/2\rangle \pm 0.1847|7/2, \pm 7/2\rangle \tag{4}$$

describe very well the experimental values of the g-factors ($g_\parallel^{\text{theor}} = 1.027$, $g_\perp^{\text{theor}} = 0.231$) and they closely coincide with the wavefunctions for the axial Sm^{3+} in CaWO$_4$ [3] and KMgF$_3$ [8] which were treated by the same approach. Additional information may be obtained by using the rule of correspondence between the average g-factor $\tilde{g} = 1/3(g_x + g_y + g_z)$ and the cubic g-factor g_{cub}. When Γ_{t6} is assumed to be the ground state, one obtains $g_{\text{cub}}(\Gamma_{t6}) = 0.476$. As one can see in table 1, there is very close correspondence between $\tilde{g}$ and $g_{\text{cub}}(\Gamma_{t6})$. Optical experiments are in progress to obtain an unambiguous determination of the ground state of the axial Sm^{3+} ion.

For the monoclinic PC Sm^{3+}(II), the situation is more intricate because the expressions for the wavefunctions and the g-factors are very bulky when the excited multiplet ^{6}H$_{7/2}$ is included. We only note that for both, the monoclinic and the axial samarium ion $\tilde{g}(\text{Sm}^{3+}_{\text{axial}})$ and $\tilde{g}(\text{Sm}^{3+}_{\text{monocl}})$ have values which are very close to $g_{\text{cub}} = 0.476$ (Γ_{t6}) and to $g_{\text{cub}} = 0.667$ (Γ_{t7}), respectively. Therefore, the axial and the monoclinic distortions of the cubic crystal field are small and the cubic part of the crystal field is in both cases dominant. It is thus possible to propose the following structural models for the two PCs. Sm^{3+}(I) most probably substitutes for

Ba^{2+} and the charge compensation is provided by an O^{2-} ion which substitutes for the nearest Cl^- ion on the *c*-axis. A small axial distortion of the cubic crystal field is further confirmed by the superhyperfine structure of the EPR line due to the four equivalent fluorine ions (figures 1 and 2). The $Sm^{3+}(II)$ too substitutes most probably for a Ba^{2+}. The compensation is realized by an O^{2-} ion which substitutes for one of the four nearest chlorine ions. This agrees with the almost exact coincidence of the value of the angle α (table 1) with the one between the Ba–Cl bond direction and the *c*-axis of the host crystal. The EPR spectra recorded with **H** parallel to (001) from a sample which had been oriented with the aid of x-rays allow us to exclude the possibility that the oxygen ion is substituting for a fluorine neighbour. Note that this substitution would lead to a stronger distortion of the cubic crystalline field.

4. Conclusions

The EPR results presented above allowed us to show that the two Sm^{3+} ions observed are stabilized by associated oxygen ions. This seems to be the first report on these PCs.

Acknowledgments

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