EPR Study of Gd$^{3+}$ local structure in ScF$_3$ crystal with negative thermal expansion coefficient

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Received 12 January 2015, revised 18 May 2015
Accepted for publication 18 September 2015
Published 9 October 2015

Abstract
Zero field splitting (ZFS) of Gd$^{3+}$ impurity in ScF$_3$ is studied by electron paramagnetic resonance at 77 and 295 K. ZFS parameter $b_4$ values obtained from angular dependence simulations show that regardless of negative thermal expansion in ScF$_3$ temperature dependence of $|b_4|$ is similar to other cubic fluoroperovskites. Our analysis of ZFS parameters indicates that the local structure of Gd$^{3+}$ centres expands positively with temperature.

Keywords: electron paramagnetic resonance, Gd$^{3+}$, ScF$_3$, negative thermal expansion

(Some figures may appear in colour only in the online journal)

1. Introduction

Extensive experimental and theoretical studies have been reported on scandium trifluoride (ScF$_3$) structure due to its distinct property of negative thermal expansion (NTE) over a temperature range of 10–1100 K [1].

ScF$_3$ crystals are perovskite compounds with the structural formula ABX$_3$, where one of the cation positions is vacant. Unlike many other fluorides of this class, at atmospheric pressure ScF$_3$ has a cubic Pm-3m structure, where each Sc$^{3+}$ ion is surrounded by six F$^-$ ions. At increased pressure a phase transition from cubic to rhombohedral R-3c occurs [2–4].

It is possible to control thermal expansion in ScF$_3$ by forming solid solutions where Sc$^{3+}$ ions are substituted by Y$^{3+}$ or Ti$^{3+}$, however this can lead to a cubic-to-rhombohedral phase transition [5, 6]. A recent study has succeeded in achieving zero thermal expansion in cubic (Sc$_{0.85}$Ga$_{0.10}$Fe$_{0.10}$)F$_3$ over a wide temperature range, which is promising for practical applications [7].

Electron paramagnetic resonance (EPR) study of ScF$_3$ suggests that cationic vacancies in the cubic structure increase sensitivity to different impurities. EPR spectra angular dependences show that the local symmetry of Ga and Fe defect centres is lower than the cubic one. Splitting of each transition into seven components in iron doped ScF$_3$ is caused by the superhyperfine interaction with six fluorine ions [8, 9].

It has been determined that S-state ions, such as Mn$^{2+}$ and Gd$^{3+}$, replace Sc$^{3+}$ ion isomorphically in the crystal lattice therefore, the defect site remains cubic [10, 11]. Comprehensive studies for cubic Gd$^{3+}$ centres in fluoroperovskites have been made to determine ZFS parameters in various coordinations and phases [12–18]. Temperature studies of ZFS indicate that spin-phonon interactions cause 68% of the total temperature change in $b_4(T)$ and the remaining is caused by the thermal expansion of the lattice [18]. Theoretical studies have confirmed that phonon contributions should be more pronounced in crystals with six-fold coordination in comparison with the eight-fold one [19]. In this work we obtain more precise ZFS values for Gd$^{3+}$ centre in ScF$_3$ to study the temperature behaviour of paramagnetic centre local structure in crystal with NTE coefficient.

2. Experimental

The EPR spectra first derivative angular dependences were obtained at room (295 K RT) and liquid nitrogen (77 K LNT)
temperatures using a standard X-band spectrometer (RE 13-06) with 9.05 GHz microwave frequency. The crystal was glued to a sample-holder and rotated around one of its main axis perpendicularly to the applied magnetic field.

The spectra fitting was done with Easyspin software [20]. The spin-Hamiltonian used for calculations was:

\[
H = H_x + H_{CF} = g\beta SB + \frac{b_4}{60}(O_4^0 + 5O_4^1) + \frac{b_6}{1260}(O_6^0 - 21O_6^4). \tag{1}
\]

Formula (1) describes energy levels in a cubic symmetry crystal field with parameters \(b_4\) and \(b_6\). Spin operators \(O_{m}^{n}\) are explained in [21].

3. Results

The experimental EPR measurements of ScF₃ at LNT are presented in figure 1. Angular dependences are identical under a 90° rotation and exhibit symmetry around 45° position between the applied magnetic field and crystal axis. This verifies the cubic model (equation (1)) used for spectra simulations. EPR spectrum consists of seven lines characteristic for the paramagnetic centre with \(S = \frac{7}{2}\). Super-hyperfine structure (SHFS) splitting due to a coupling to 6 neighbouring fluorine ions of each line into 7 components has not been observed. It was determined from spectra simulations that the rotation axis was tilted 13° from the crystal main axis.

Resonance field position map for LNT is shown in figure 2. In the region where only three resonance positions could be determined the equivalent experimental spectra are not as smooth and symmetric. Experimental resonances are shown with circles and solid lines represent fitted theoretical curves with \(g = 1.992 \pm 0.001\), \(b_4 = (-3.96 \pm 0.02) \times 10^{-4}\) cm\(^{-1}\) and \(b_6 = (0.78 \pm 0.02) \times 10^{-4}\) cm\(^{-1}\). Average deviation for each experimental resonance from calculation is 0.25 mT. Signs are adopted according to research made in other cubic fluoroperovskites [12–18].

At RT measurements only five lines could be distinguished (figure 3(b)). The best fit of RT angular dependences was achieved with \(g = 1.992 \pm 0.001\), \(b_4 = (-2.73 \pm 0.02) \times 10^{-4}\) cm\(^{-1}\) and \(b_6 = (0.67 \pm 0.01) \times 10^{-4}\) cm\(^{-1}\). Average deviation for each experimental resonance from calculation is 0.12 mT.

As a result we have shown that ZFS is larger at lower temperatures and also have obtained more precise \(b_4\) and \(b_6\) parameter values. Spectra simulations with our ZFS parameters are shown in figure 3 with linewidths 1.4 and 1.8 mT for LNT and RT respectively. The shape of the simulated spectra could be improved by taking into account the SHFS interaction with six surrounding fluorine ions.

4. Discussion

Gd\(^{3+}\) impurity ions have been found in many crystals at highly symmetric sites [22]. In ScF₃ crystal it replaces Sc\(^{3+}\) ion and does not require additional charge compensation. Gd\(^{3+}\) is an S-state ion with 4\(^{f}\) electronic configuration. Resulting orbital angular momentum of electrons is zero therefore, microscopic mechanisms of ZFS are complicated [21].

In an EPR experiment, applied magnetic field splits the ground multiplet \(^{5}S_{7/2}\) into eight singlet states and seven transitions may occur. A characteristic feature of Gd\(^{3+}\) fine structure in other cubic fluorides is \(g\) value of approximately 1.992 (table 1).
assumptions remain valid for ZFS spin-Hamiltonian parameter calculations:

\[ b^{0}_Q = \sum_{L} b_{k}(R_0) \left( \frac{R_0}{R_L} \right)^{1/6} G_{k}^{4}(\theta_{L}, \phi_{L}). \quad (2) \]

\( R_0 \) is a fixed reference distance, \( R_L \) describes paramagnetic ion-ligand distance and \( G_{k}^{4} \) are spherical harmonic functions tabulated in [29]. SM is used to predict \( b^{0}_Q \) for crystals with different \( R_L \) values but first, SM parameter values \( b_k \) and \( t_k \) must be determined.

Previous SM study of Gd\(^{3+}\) in other cubic fluoride perovskites reveals that values of \( b_k \) depend mainly on the coordination number of impurity. In a sixfold fluorine coordination at RT the proposed SM parameter values are \( b_4 = -1.4 \times 10^{-4} \text{ cm}^{-1} \) and \( t_4 = -8 \) for a reference distance \( R_0 = 2.227 \text{ Å} \) [13]. In this work we take the reference distance as \( R_0 = R_{Gd^{3+}} + R_{F^{-}} = 2.268 \text{ Å} \) [30] and calculate fourth and sixth order \( b_k \) and \( t_k \) values by fitting the experimental ZFS results in RbCdF\(_3\), RbCaF\(_3\), CsCaF\(_3\) and CsCdF\(_3\) shown in table 1. \( R_L \) distances are taken from table 1. As a result we obtain \( t_4 = -7 \pm 1 \), \( b_4 = -1.6 \times 10^{-4} \text{ cm}^{-1} \) and \( t_6 = -3 \pm 1 \), \( b_6 = 1.2 \times 10^{-4} \text{ cm}^{-1} \). Fourth order SM parameter values are in good agreement with [13]. To our knowledge the sixth order SM parameters have been acquired here for the first time for sixfold coordinated Gd\(^{3+}\) centres in cubic fluoroperovskites. Using the determined SM parameters we make a theoretical estimation of ZFS in ScF\(_3\):Gd\(^{3+}\), which is shown in table 2.

4.2. Temperature dependence of \( b_4 \)

In ScF\(_3\) the parameter \( |b_4| \) increases on cooling similarly as in other crystals of this class. Therefore, thermal expansion alone cannot explain the temperature dependence of ZFS. A comprehensive study to separate thermal expansion and spin-phonon contributions to the temperature dependence of \( b_4 \) by [18] found out that the latter constitute 68% of the total dependence observed. If the remaining 32% are caused by thermal expansion of the lattice and ScF\(_3\) has a NTE coefficient, then the observed temperature dependence should differ from crystals with positive thermal expansion. However, as is shown in figure 4, this is not the case.

The thermodynamic relation used in [18] to separate different contributions to \( b_4(T) \) is:

\[ \left( \frac{\partial b_4}{\partial T} \right)_{v} = \left( \frac{\partial b_4}{\partial T} \right)_{p} - \left( \frac{\beta}{K} \right) \left( \frac{\partial b_4}{\partial p} \right)_{T} \quad (3) \]

where \( \beta \) and \( K \) are volume thermal expansion and volume compressibility coefficients respectively. In [18] it was assumed that the local value of the ratio \( \beta/K \) does not differ from the bulk value. We can see that such assumption is not valid for ScF\(_3\), because a negative value of \( \beta \) does not reproduce the experimental slope for \( b_4(T) \) (dotted line in figure 4).

In many materials the rigid unit mode (RUM) model is successful in explaining the origin of NTE which assumes that shrinking of the crystal lattice arises from rocking motions of rigid corner-sharing polyhedra [31]. The RUM

Figure 2. Experimental resonances (○) and calculated resonance field lines (∙) at LNT.
approximation in ScF₃:Gd³⁺ means that the first coordination sphere of a Gd³⁺ centre is rigid and has near zero thermal expansion coefficient. Calculation with β = 0 K⁻¹ gives a better agreement with our experimental ZFS values (dashed line in figure 4), however we can see that our experimental ZFS parameter values predict a positive value of β, so in order to reproduce the experimental slope for b₄(T), we will examine the temperature behaviour of Gd³⁺ centre local structure by estimating β from the equation (3).

The value of (∂b₄/∂T)ₚ for ScF₃ is determined from the slope of b₄(T) in figure 4 as −56.4 × 10⁻⁸ cm⁻¹ K⁻¹. The volume compressibility coefficient in ScF₃ is K = −17.6 × 10⁻⁶ MPa⁻¹ [1]. The b₄(p) dependence is similar for all crystals studied in [18] so for our calculations we take the average value (∂b₄/∂p)ₚ = 7.0 × 10⁻⁸ cm⁻¹ MPa⁻¹. Assuming the phonon contribution as 68% to the total temperature dependence, we have calculated the value of (∂b₄/∂T)ₚ as −38.2 × 10⁻⁸ cm⁻¹ K⁻¹.

Inserting these values in (3) we obtained β = 46 × 10⁻⁶ K⁻¹, which is in contradiction to the bulk value of −23 × 10⁻⁶ K⁻¹ at 300 K [1]. It means that in EPR experiment we detect the local structure of Gd³⁺ centre with different temperature behaviour than the bulk structure of ScF₃.

EXAFS studies have shown that the average instantaneous distance ˙R is larger than the crystallographic distance measured by diffraction because of the atom vibrations perpendicular to the bond [32].

\[ \dot{R} = R + \frac{\langle \Delta u^2 \rangle}{2R} \]

where R is the equilibrium interatomic distance (lattice constant) and Δuₚ — perpendicular displacement from the equilibrium position. The average instantaneous distance ˙R between neighbouring atoms in materials with NTE always has a positive thermal expansion coefficient value [32], which

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Experimental</th>
<th>SM</th>
</tr>
</thead>
<tbody>
<tr>
<td>ScF₃, present work</td>
<td>2.007 1.9920 3.96 0.78 2.73 0.67</td>
<td>ScF₃ [10] 1.9919 3.90 0.80 4.70 1.70</td>
</tr>
<tr>
<td>RbCdF₃⁺ [12]</td>
<td>2.199 1.9920 4.44 0.82</td>
<td>RbCdF₃⁺ [12] 2.266 1.9920 4.92 0.83</td>
</tr>
<tr>
<td>CsCdF₃ [12]</td>
<td>2.235 1.9920 5.99 0.92</td>
<td>CsCdF₃ [12] 2.262 1.9920 6.74 0.97</td>
</tr>
<tr>
<td>CsCaF₃ [12]</td>
<td>2.262 1.9920 6.40 0.97</td>
<td>CsCaF₃ [12] 2.300 1.9920 7.21 0.99</td>
</tr>
</tbody>
</table>

* At 77 K exists in D₆h structural phase, therefore, ZFS is not reported here.

**Table 2.** Experimental results and SM estimation of ZFS in ScF₃: Gd³⁺ at RT.

- The calculation of the slope for b₄(T) was made from the equation (3) assuming the average static and vibrational contributions to b₄(T) from [17] and (a) the crystallographic β = −23 × 10⁻⁶ K⁻¹ at 300 K [1], (b) the local structure thermal expansion coefficient β = 0 K⁻¹ for the rigid corner-sharing GdF₆/₂ octahedra from the RUM model [31].

**Figure 3.** Experimental spectra (red lines) and simulations (blue dashed lines) at LNT (a) and RT (b) at B[100].

**Figure 4.** Temperature dependence of b₄ in fluoroperovskites. The calculation of the slope for b₄(T) was made from the equation (3) assuming the average static and vibrational contributions to b₄(T) from [17] and (a) the crystallographic β = −23 × 10⁻⁶ K⁻¹ at 300 K [1], (b) the local structure thermal expansion coefficient β = 0 K⁻¹ for the rigid corner-sharing GdF₆/₂ octahedra from the RUM model [31].
explains our calculated positive value of $\beta$. We can conclude that the EPR parameters correlate with the average instantaneous distances between ions.

Our obtained value of $\beta$ should be treated cautiously because in this study the phonon induced lattice vibrations are effectively included in the interatomic distance (equation (4)), however, the model used in [18] separates the lattice vibration and thermal expansion effects. Although the temperature behaviour of the average effective distances and the lattice constant differs, we expect that in crystals with positive $\beta$ these differences should not be so profound as in ScF$_3$ and the use of bulk value of $\beta$ in model (3) is reasonable. Nevertheless, from our experiment we can see that ZFS parameter values have a better correlation with instantaneous interatomic distances and that regardless of NTE in the bulk ScF$_3$ crystal, the local structure of Gd$^{3+}$ has a positive thermal expansion coefficient.

5. Summary

Simulation of the EPR spectra of Gd$^{3+}$ impurity in ScF$_3$ with spin-Hamiltonian values $g = 1.992 \pm 0.001$ and fine structure parameters $b_4 = (-2.73 \pm 0.02) \times 10^{-4}$ cm$^{-1}$, $b_6 = (0.67 \pm 0.01) \times 10^{-4}$ cm$^{-1}$ at RT and $b_4 = (-3.96 \pm 0.02) \times 10^{-4}$ cm$^{-1}$, $b_6 = (0.78 \pm 0.02) \times 10^{-4}$ cm$^{-1}$ at LNT reproduce experimental spectra with high precision. SM calculations at RT provide a qualitatively good agreement with the experiment.

We have shown that regardless of NTE the temperature dependence of $|b_d|$ and $|b_6|$ in ScF$_3$ is similar to other cubic fluoroperovskites. $b_6(T)$ analysis indicates that the local structure of Gd$^{3+}$ centres expands positively in ScF$_3$.

Acknowledgments

We are grateful to Professor S Ovchinnikov for providing ScF$_3$ samples. This work was supported by L-KC-11-0005 project Nr.KC/2.1.2.1.1/10/01/006,5.3.

References