

PAPER

EPR Study of Gd^{3+} local structure in ScF_3 crystal with negative thermal expansion coefficient

To cite this article: A Antuzevics *et al* 2015 *Phys. Scr.* **90** 115801

View the [article online](#) for updates and enhancements.

Related content

- [Temperature and hydrostatic pressure dependences of the \$b_2^+\$ spin-Hamiltonian parameter for \$Gd^{3+}\$ in fluoroperovskite single crystals](#)
T Rewaj, M Krupski, J Kuriata *et al.*
- [EPR study of a trigonally symmetric \$Gd^{3+}\$ centre in \$RbCaF_3\$](#)
H Takeuchi, H Ebisu and M Arakawa
- [Mn²⁺ ion as a probe of the spin transition](#)
Hervé Daubric, Janis Kliava, Philippe Guionneau *et al.*

Recent citations

- [Ultraviolet B emission from a \$Gd^{3+}\$ -doped \$BaAl_2O_4\$ powder phosphor](#)
Vijay Singh *et al*
- [Zero-field splitting in the isoelectronic aqueous \$Gd\(III\)\$ and \$Eu\(II\)\$ complexes from a first principles analysis.](#)
S. Khan *et al*

EPR Study of Gd^{3+} local structure in ScF_3 crystal with negative thermal expansion coefficient

A Antuzevics¹, U Rogulis¹, A Fedotovs¹, Dz Berzins¹, V N Voronov² and J Purans¹

¹Institute of Solid State Physics, University of Latvia, Kengaraga Str. 8, LV-1063 Riga, Latvia

²L. Kirensky Institute of Physics, Russian Academy of Sciences, Siberian Branch, 660036 Krasnoyarsk, Russia

E-mail: andris.antuzevics@gmail.com

Received 12 January 2015, revised 18 May 2015

Accepted for publication 18 September 2015

Published 9 October 2015



CrossMark

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 $(Sc_{0.85}Ga_{0.05}Fe_{0.10})F_3$ 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:

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

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 ScF_3 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 $S = 7/2$. 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 $g = 1.992 \pm 0.001$, $b_4 = (-3.96 \pm 0.02) \times 10^{-4} \text{ cm}^{-1}$ and $b_6 = (0.78 \pm 0.02) \times 10^{-4} \text{ cm}^{-1}$. 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 $g = 1.992 \pm 0.001$, $b_4 = (-2.73 \pm 0.02) \times 10^{-4} \text{ cm}^{-1}$ and $b_6 = (0.67 \pm 0.01) \times 10^{-4} \text{ cm}^{-1}$. 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.

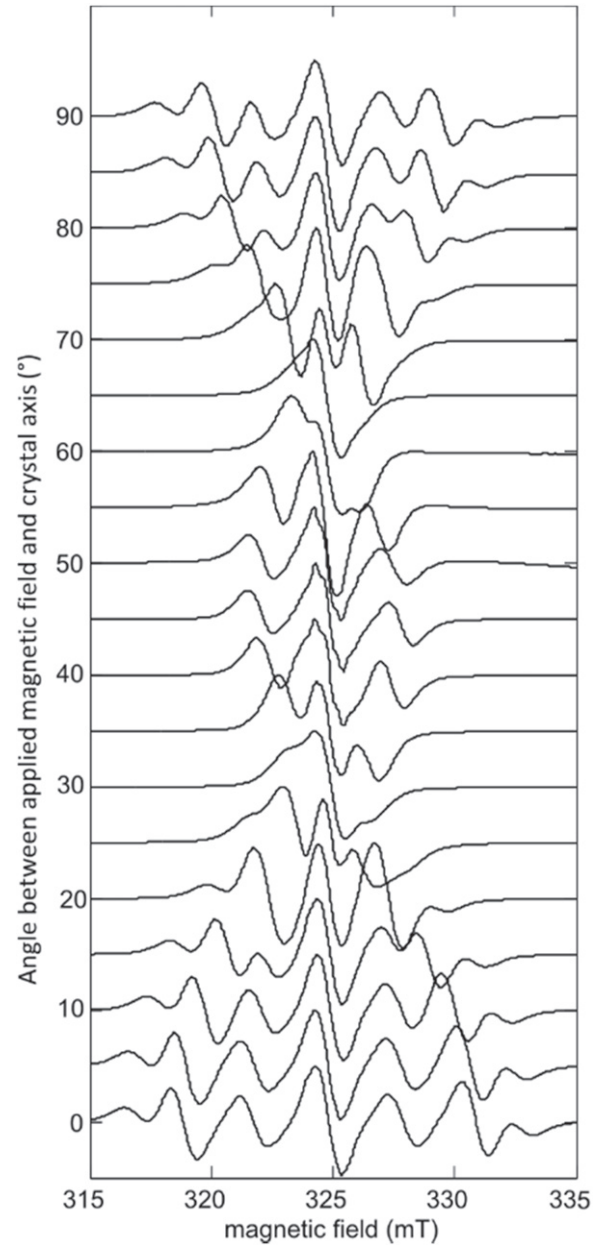


Figure 1. Experimental EPR spectra angular dependences of $\text{ScF}_3:\text{Gd}^{3+}$ at LNT.

4. Discussion

Gd^{3+} impurity ions have been found in many crystals at highly symmetric sites [22]. In ScF_3 crystal it replaces Sc^{3+} ion and does not require additional charge compensation. Gd^{3+} is an S-state ion with $4f^7$ 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 $^8S_{7/2}$ 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).

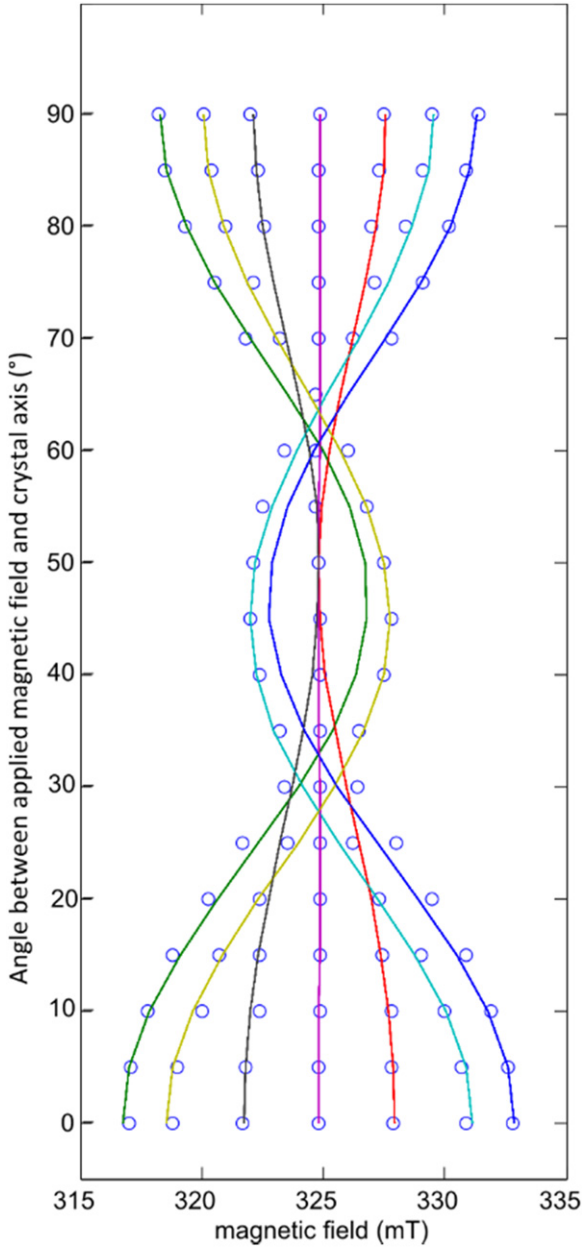


Figure 2. Experimental resonances (o) and calculated resonance field lines (-) at LNT.

ZFS parameter values on the other hand are dependent on the lattice constant R and the coordination number of paramagnetic ion and the type of neighbouring ligands [12, 13].

4.1. Superposition model analysis

Semi-empirical superposition model (SM) has been used extensively for Gd^{3+} ZFS parameter calculations in different crystals [12, 13, 24–28]. It states that crystal field at a paramagnetic centre can be calculated from the sum of contributions from neighbouring ligands. For quantitative calculations it is sufficient to know defect site geometry and interactions between magnetic ion and surrounding ligands [29]. These assumptions remain valid for ZFS spin-Hamiltonian

parameter calculations:

$$b_k^q = \sum_L \bar{b}_k(R_0) \left(\frac{R_0}{R_L} \right)^{t_k} G_k^q(\theta_L, \phi_L). \quad (2)$$

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

Previous SM study of Gd^{3+} in other cubic fluoride perovskites reveals that values of \bar{b}_4 depend mainly on the coordination number of impurity. In a sixfold fluorine coordination at RT the proposed SM parameter values are $\bar{b}_4 = -1.4 \times 10^{-4} \text{ cm}^{-1}$ and $t_4 = -8$ for a reference distance $R_0 = 2.227 \text{ \AA}$ [13]. In this work we take the reference distance as $R_0 = R_{Gd^{3+}} + R_{F^-} = 2.268 \text{ \AA}$ [30] and calculate fourth and sixth order \bar{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 $t_4 = -7 \pm 1$, $\bar{b}_4 = -1.6 \times 10^{-4} \text{ cm}^{-1}$ and $t_6 = -3 \pm 1$, $\bar{b}_6 = 1.2 \times 10^{-4} \text{ cm}^{-1}$. 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 β and K are volume thermal expansion and volume compressibility coefficients respectively. In [18] it was assumed that the local value of the ratio β/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 β 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

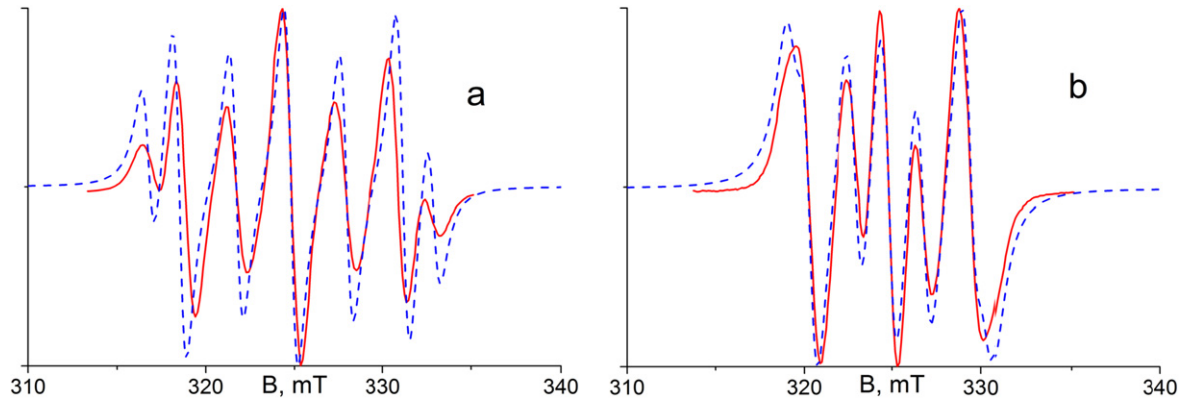


Figure 3. Experimental spectra (red lines) and simulations (blue dashed lines) at LNT (a) and RT (b) at B||[100].

Table 1. Experimental EPR parameters for Gd^{3+} centres in sixfold coordinated cubic fluoroperovskites. ZFS parameters are in units of 10^{-4} cm^{-1} .

Crystal	R (Å) [1, 23]	g	LNT		RT	
			$ b_4 $	$ b_6 $	$ b_4 $	$ b_6 $
ScF ₃ , pre-sent work	2.007	1.9920	3.96	0.78	2.73	0.67
ScF ₃ [10]		1.9919	3.90	0.80	4.70	1.70
RbCdF ₃ ^a [12]	2.199	1.9920			4.44	0.82
RbCaF ₃ ^a [12]	2.226	1.9920			4.92	0.83
CsCdF ₃ [12]	2.235	1.9920	5.99	0.92	4.82	0.86
CsCaF ₃ [12]	2.262	1.9920	6.74	0.97	5.49	0.89

^a At 77 K exists in D_{4h}^{18} structural phase, therefore, ZFS is not reported here.

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

ZFS parameter	Experimental	SM
$b_4, 10^{-4} \text{ cm}^{-1}$	-2.73 ± 0.02	-2.24 ± 0.29
$b_6, 10^{-4} \text{ cm}^{-1}$	0.67 ± 0.01	0.61 ± 0.09

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 $\beta = 0 \text{ K}^{-1}$ 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 $b_4(T)$, we will examine the temperature behaviour of Gd³⁺ centre local structure by estimating β from the equation (3).

The value of $(\partial b_4/\partial T)_p$ for ScF₃ is determined from the slope of $b_4(T)$ in figure 4 as $-56.4 \times 10^{-8} \text{ cm}^{-1} \text{ K}^{-1}$. The volume compressibility coefficient in ScF₃ is $K = -17.6 \times 10^{-6} \text{ MPa}^{-1}$ [1]. The $b_4(p)$ dependence is similar for all crystals studied in [18] so for our calculations we take the average value $(\partial b_4/\partial p)_T = 7.0 \times 10^{-8} \text{ cm}^{-1} \text{ MPa}^{-1}$. Assuming the phonon contribution as 68% to

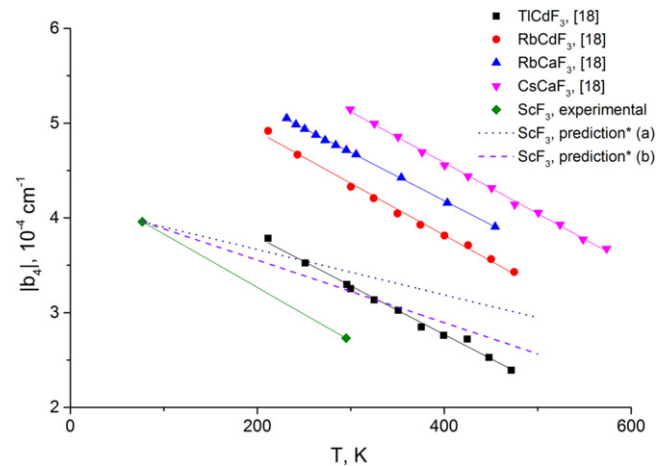


Figure 4. Temperature dependence of $|b_4|$ in fluoroperovskites. *The calculation of the slope for $b_4(T)$ was made from the equation (3) assuming the average static and vibrational contributions to $b_4(T)$ from [17] and (a) the crystallographic $\beta = -23 \times 10^{-6} \text{ K}^{-1}$ at 300 K [1], (b) the local structure thermal expansion coefficient $\beta = 0 \text{ K}^{-1}$ for the rigid corner-sharing GdF_{6/2} octahedra from the RUM model [31].

the total temperature dependence, we have calculated the value of $(\partial b_4/\partial T)_V$ as $-38.2 \times 10^{-8} \text{ cm}^{-1} \text{ K}^{-1}$.

Inserting these values in (3) we obtained $\beta = 46 \times 10^{-6} \text{ K}^{-1}$, which is in contradiction to the bulk value of $-23 \times 10^{-6} \text{ K}^{-1}$ 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 \bar{R} is larger than the crystallographic distance measured by diffraction because of the atom vibrations perpendicular to the bond [32].

$$\bar{R} = R + \frac{\langle \Delta u_{\perp}^2 \rangle}{2R} \quad (4)$$

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

explains our calculated positive value of β . We can conclude that the EPR parameters correlate with the average instantaneous distances between ions.

Our obtained value of β 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 crystallographic β these differences should not be so profound as in ScF₃ and the use of bulk value of β 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 ScF₃ crystal, the local structure of Gd³⁺ has a positive thermal expansion coefficient.

5. Summary

Simulation of the EPR spectra of Gd³⁺ impurity in ScF₃ with spin-Hamiltonian values $g = 1.992 \pm 0.001$ and fine structure parameters $b_4 = (-2.73 \pm 0.02) \times 10^{-4} \text{ cm}^{-1}$, $b_6 = (0.67 \pm 0.01) \times 10^{-4} \text{ cm}^{-1}$ at RT and $b_4 = (-3.96 \pm 0.02) \times 10^{-4} \text{ cm}^{-1}$, $b_6 = (0.78 \pm 0.02) \times 10^{-4} \text{ cm}^{-1}$ 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 $|b_4|$ and $|b_6|$ in ScF₃ is similar to other cubic fluoroperovskites. $b_4(T)$ analysis indicates that the local structure of Gd³⁺ centres expands positively in ScF₃.

Acknowledgments

We are grateful to Professor S Ovchinnikov for providing ScF₃ samples. This work was supported by L-KC-11-0005 project Nr.KC/2.1.2.1.1/10/01/006,5.3.

References

- [1] Greeve B K, Martin K L, Lee P L, Chupas P J, Chapman K W and Wilkinson A P 2010 *J. Am. Chem. Soc.* **132** 15496
- [2] Aleksandrov K S, Voronov V N, Vtyurin A N, Goryainov S N, Zamkova N G, Zinenko V I and Krylov A S 2002 *J. Exp. Theor. Phys.* **94** 977
- [3] Aleksandrov K S, Voronov V N, Vtyurin A N, Krylov A S, Molokeyev M S, Pavlovskii M S, Goryainov S V, Likhacheva A Y and Ancharov A I 2009 *Phys. Solid State* **51** 810
- [4] Aleksandrov K S, Voronov V N, Vtyurin A N, Krylov A S, Molokeyev M S, Oreshonkov A S, Goryainov S V, Likhacheva A Y and Ancharov A I 2011 *Phys. Solid State* **53** 564–9
- [5] Morelock C R, Greve B K, Gallington L C, Chapman K W and Wilkinson A P 2013 *J. Appl. Phys.* **114** 213501
- [6] Morelock C R, Gallington L C and Wilkinson A P 2014 *Chem. Mater.* **26** 1936–40
- [7] Hu L, Chen J, Fan L, Ren Y, Rong Y, Pan Z, Deng J, Yu R and Xing X 2014 *J. Am. Chem. Soc.* **136** 13566–9
- [8] Voronov V N, Petrakovskaya E A and Alexandrovich A A 2010 *Funct. Mater.* **17** 324–8
- [9] Voronov V N and Petrakovskaya E A 2013 *Fiz. Tverd. Tela* **55** 671–7
- [10] Starostina L S, Grechushnikov B N and Koryagin V F 1972 *Fiz. Tverd. Tela* **14** 3480–3
- [11] Kliava J and Purans J 1980 *J. Magn. Reson.* **40** 33–45
- [12] Arakawa M, Aoki H, Takeuchi H, Yosida T and Horai K 1982 *J. Phys. Soc. Japan* **51** 2459–63
- [13] Buzare L Y, Fayet-Bonnel M and Fayet J C 1981 *J. Phys. C: Solid State Phys.* **14** 67–81
- [14] Arakawa M, Ebisu S and Takeuchi H 1997 *J. Phys.: Condens. Matter.* **9** 5193
- [15] Buzare L Y, Fayet-Bonnel M and Fayet J C 1980 *J. Phys. C: Solid State Phys.* **13** 857–63
- [16] Arakawa M, Hirayama F, Ebisu H and Takeuchi H 2006 *J. Phys.: Condens. Matter.* **18** 7427
- [17] Arakawa M, Ebisu H, Yosida T and Horai K 1979 *J. Phys. Soc. Japan* **46** 1483–7
- [18] Rewaj T, Krupski M, Kuriata J and Buzare J Y 1992 *J. Phys.: Condens. Matter.* **4** 9909–18
- [19] Pastusiak W and Kuriata J 1999 *Physica B* **270** 6–10
- [20] Stoll S and Schweiger A 2006 *J. Magn. Reson.* **178** 42–55
- [21] Altschuler S A and Kozyrew B M 1974 *Electronic Paramagnetic Resonance in Compounds of Transition Elements* (New York: Wiley)
- [22] Buckmaster H A and Shing Y H 1972 *Phys. Stat. Sol. A* **12** 325–61
- [23] Jiang L Q, Guo J K, Liu H B, Zhu M, Zhou X, Wu P and Li C H 2006 *J. Phys. Chem. Solids* **67** 1531–6
- [24] Wu S, Zhang H, Lu G and Zhang Z 2007 *Pramana J. phys.* **69** 451–7
- [25] Yeung Y Y 1993 *J. Alloys Compd.* **193** 213–5
- [26] Misra S K, Mikolajczak P and Lewis N R 1981 *Phys. Rev. B* **24** 3729–35
- [27] Prokhorov A D, Prokhorov A A, Chernush L F, Minyakaev R, Dyakonov V P and Szymczak H 2014 *Phys. Status Solidi B* **251** 201–5
- [28] Yang W Q, Zhang Y, Zheng W C and Lin Y 2013 *J. Fluorine Chem.* **153** 7–11
- [29] Newman D J and Ng B 1989 *Prog. Phys.* **52** 699–763
- [30] Shannon R D 1976 *Acta Crystallogr.* **32** 751–67
- [31] Tao J Z and Sleight A W 2003 *J. Solid State Chem.* **173** 442–8
- [32] Formasini P, Abd el All N, Ahmed S I, Sanson A and Vaccari M 2009 *J. Phys.: Conf. Ser.* **190** 012025