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SUPERPOSITION MODEL ANALYSIS OF THE ZERO-FIELD SPLITTING PARAMETERS OF Fe^{3+}: $TlBX_2$ CRYSTALS – INSIGHT INTO LOCAL DISTORTIONS AND LOW SYMMETRY ASPECTS

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In this paper we report on our recent studies of the Fe^{3+} centers in single crystals of wide-band gap semiconductors $TlInS_2$, $TlGaS_2$, and $TlGaSe_2$. Superposition model (SPM) calculations were carried out to investigate the local environment around the Fe^{3+} centers. A novel approach based on the ascent in symmetry method is applied to the crystallographic data to quantify the structural approximation from triclinic to orthorhombic and to tetragonal site symmetry. Electron magnetic resonance (EMR) data are reconsidered to provide more meaningful interpretation of the zero-field splitting (ZFS) parameters obtained by fitting EMR spectra. The values of the experimental ZFS parameters are matched with the SPM obtained values to obtain better insight into the local distortions and low symmetry aspects. The SPM results indicate that Fe^{3+} ions substitute for the B^{3+} ions in $TlBX_2$ (B = In, Ga, X = S, Se) crystal here.

INTRODUCTION

The Fe^{3+} paramagnetic centers in the ternary thallium chalcogenides $TlBX_2$ (B = In, Ga, X = S, Se) have recently been intensively investigated (Mikailov, Rameev, Kazan, Yildiz, Mammadov & Aktas, 2005; Mikailov, Kazan, Rameev, Acikgoz & Aktas, 2006a; Mikailov, Kazan, Rameev, Kulibekov, Kerimova & Aktas, 2006b; Acikgoz, Kazan, Mikailov, Kerimova & Aktas, 2008a; Acikgoz, Kazan, Mikailov, Mammadov & Aktas, 2008b; Acikgoz, Kazan & Mikailov, 2009) in view of potential applications. Single $TlBX_2$ crystals belong to the class of ferroelectric wide-band gap semiconductors in which a complex sequence of structural phase transitions occurs with decreasing temperature (Mustafaeva, Asadov & Ismailov, 2009; Seyidov, Suleymanova & Salehli, 2009). Recently we have embarked on theoretical modeling of second- B_2^q (b_2^q) and fourth-rank ZFSPs B_4^q (b_4^q) zero-field splitting (ZFS) parameters (ZFSPs) and structural distortions in these systems (Gnutek, Acikgoz & Rudowicz, 2010; Acikgoz, Gnutek & Rudowicz, 2010a) using the superposition model (SPM) (Newman & Urban, 1975; Rudowicz, 1987a; Yeom, Chang, Choh & Rudowicz, 1994; Clare & Devine, 1980). In the previous studies, the SPM analysis was carried out for the ZFS parameters for Fe^{3+} ions in $TlInS_2$ (Gnutek *et al.*, 2010) and $TlGaS_2$ (Acikgoz *et al.*, 2010a) crystals. Following the procedure worked out in (Gnutek *et al.*, 2010), SPM and crystallographic data were employed to determine the ZFS parameters for Fe^{3+} ions at the two substitutional structurally different Ga sites (hereafter denoted 1 and 2) in $TlGaSe_2$ crystal. In this paper preliminary results of this study are provided. Comprehensive SPM results together with their analysis will be presented in the full paper (Acikgoz, Gnutek & Rudowicz, 2010b).

CRYSTAL STRUCTURE OF $TLGaSe_2$ SINGLE CRYSTALS

The single crystals of $TlGaSe_2$ have the monoclinic space group *C2/c* (No. 15, C_{2h}^6) at room temperature (Müller & Hahn, 1978; Henkel, Hochheimer, Carlone, Werner, Ves & Schnering, 1982; Delgado, Mora, Perez & Gonzalez, 2007). The atomic positions of $TlGaSe_2$ determined in (Henkel *et al.*, 1982) and (Delgado *et al.*, 2007) and the unit cell parameters (Müller *et al.*, 1978; Henkel *et al.*, 1982; Delgado *et al.*, 2007) are listed in (Acikgoz *et al.*, 2010b). Fe^{3+} ions doped into $TlGaSe_2$ crystal occupy one of the two crystallographically inequivalent sites Ga^{3+} sites denoted Ga(1) and Ga(2) (Mikailov *et al.*, 2005, Acikgoz *et al.*, 2008b; Acikgoz *et al.*, 2009). For SPM calculations, a modified crystallographic axis system (CAS*) is adopted as: $x||a$,

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$y||b||C_2$, and $z||c^*$ with the c^*-axis perpendicular to the plane (ab) (see Fig. 2 in (Gnutek *et al.*, 2010). The ligand bond length (R_i) and angular positions of ligands (θ_i, ϕ_i) for the Ga(1) and Ga(2) sites were calculated based on two sets of crystallographic data and used for the SPM modeling of the ZFS parameters for Fe^{3+} ions in $TlBX_2$ (Gnutek *et al.*, 2010; Acikgoz *et al.*, 2010a, 2010b).

SUPERPOSITION MODEL ANALYSIS

The Fe^{3+} ions doped into $TlGaSe_2$ crystal substitute at the Ga^{3+} sites (Mikailov *et al.*, 2005; Acikgoz *et al.*, 2008b; Acikgoz *et al.*, 2009). The spin Hamiltonian (Rudowicz, 1987b; Rudowicz & Misra, 2001) expressed in the extended Stevens (ES) operator O_k^q notation (Rudowicz, 1985) is employed:

$$\begin{aligned} H &= H_{Ze} + H_{ZFS} \\ &= \mu_B B \cdot g \cdot S + \sum B_k^q O_k^q \left(S_x, S_y, S_z\right) \\ &= \mu_B B \cdot g \cdot S + \sum f_k b_k^q O_k^q \left(S_x, S_y, S_z\right) \end{aligned} \quad (1)$$

Since the general SPM equations and details of the procedure were provided in (Gnutek *et al.*, 2010; Acikgoz *et al.*, 2010a), we only report here some preliminary results. Two sets of the model parameters are considered in (Gnutek *et al.*, 2010; Acikgoz *et al.*, 2010a; Acikgoz *et al.*, 2010b). For illustration, the ZFS parameters for one SPM parameter set are presented in Table 1.

Table 1. The triclinic ZFS parameters b_k^q (in 10^{-4} cm^{-1}) calculated using the SPM for the Fe^{3+} ions at the Ga sites (1) and (2) in $TlGaSe_2$; for selection of the SPM parameters, see, (Acikgoz *et al.*, 2010b).

Set	1	2		1	2		1	2
b_2^0	-817.3	-98.8	b_4^0	-3.59	-3.92			
b_2^1	-5288.4	-313.2	b_4^1	-0.86	1.83	b_4^3	-6.32	13.48
b_2^{-1}	4433.5	-1355.6	b_4^{-1}	0.42	2.40	b_4^{-3}	-3.61	-14.97
b_2^2	1197.7	1272.5	b_4^2	0.55	0.63	b_4^4	-19.16	-19.57
b_2^{-2}	1805.1	3538.0	b_4^{-2}	-3.16	4.91	b_4^{-4}	0.44	0.3
b_2^2 / b_2^0	-1.47	12.88	b_4^2 / b_4^0	-0.153	-0.161	b_4^4 / b_4^0	5.34	4.99

Since the EMR spectra indicate nearly orthorhombic site symmetry (Mikailov *et al.*, 2005), next we employ the orthorhombic approximation (Gnutek *et al.*, 2010) of the structural data for the two centers in $TlGaSe_2$. The details of the ascent in symmetry method may be found in (Gnutek *et al.*, 2010). In short, using the averages of the ligands spherical polar coordinates in Table 2, we obtained the 'orthorhombic-like' coordinates denoted as the set OR1 and OR2. Subsequently, these coordinates are used to obtain the best matched sets aOR1 and aOR2 by changing iteratively θ_i and then ϕ_i and comparing b_2^0 and b_2^2 in the approximated sets with the experimental ZFSPs (Mikailov *et al.*, 2005). For illustration one set of the best matched ZFSP sets and the corresponding structural parameters are listed in Table 3 and 2, respectively. Accordingly, the fourth-rank ZFSPs were calculated for each pertinent structural data set for Fe^{3+}: $TlBX_2$ (Gnutek *et al.*, 2010; Acikgoz *et al.*, 2010a; Acikgoz *et al.*, 2010b).

Table 2. The spherical polar coordinates of ligands in $TlGaS_2$ (R_i, θ_i, ϕ_i) for the local site symmetry approximated to orthorhombic.

OR1	$R = R_{av} = 0.24124$	$\theta = \theta_{av} = 55.56$	$\varphi = \varphi_{av} = 44.24$
OR2	$R = R_{av} = 0.24065$	$\theta = \theta_{av} = 54.85$	$\varphi = \varphi_{av} = 44.24$
aOR1	$R = 0.2410$	$\theta = 48.38$	$\varphi = 41.44$
aOR2	$R = 0.2400$	$\theta = 48.58$	$\varphi = 41.58$

Table 3. The ZFS parameters b_k^q (in 10^{-4} cm^{-1}) for Fe^{3+} ions at the two Ga sites in $TlGaSe_2$ calculated using the SPM for the local site symmetry approximated to orthorhombic and experimental results (Mikailov *et al.*, 2005).

Set	OR1	aOR1	OR2	aOR2	Exp.
b_2^0	-910	7272	-131	7277	7274
b_2^2	1217	4673	1237	4670	4672
b_4^0	-3.68	-4.18	-4.01	-4.43	–
b_4^2	0.55	3.53	0.61	3.58	–
b_4^4	-19.73	-12.93	-20.21	-13.91	–

Comprehensive SPM results together with their analysis will be presented in the full paper (Acikgoz *et al.*, 2010b).

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