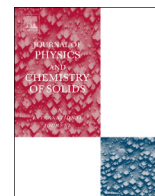




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ABSTRACT

Theoretical analysis of the EPR spectra of Cr³⁺ centers in Tl₂MgF₄ (Tl₂MgF₄ and Tl₂ZnF₄) fluorine compounds have been carried out for the first time. The correlation between the experimental data and theoretical values regarding zero-field splitting (ZFS) provides suitable structural models to understand the local structure around the Cr³⁺ centers in Tl₂MgF₄ and Tl₂ZnF₄. A clear compression of the MF₆ octahedron around tetragonal (TE) Cr³⁺ center has been shown in both crystals. The calculations for the monoclinic (MO) Cr³⁺ center reveal that the length of the four equatorial F-ligands (R_2) is about 1.5% longer than that of the octahedral ZnF₆ in undoped Tl₂ZnF₄ and the length of the axial F-ligands (R_1) is quite shorter (~9.5%) than R_2 . Also, it yields a quite large b_2^{-1} and declined angle (27.46°, ~30%) for z-axis. Our results indicate that the presence of the different structural formations may be considered around the orthorhombic (OR) Cr³⁺ center III and IV. It was suggested that the latter one can be attributed to an angular distortion relevant to the equatorial F-ligands along z||[110]-axis.

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1. Introduction

A₂BF₄-type layered perovskite-like crystals draw more attention of electron magnetic resonance (EMR) researchers due to their close relation to ABF₃-type cubic perovskite crystals. It was experimentally observed that both group of crystals have various paramagnetic centers when they are doped with transition metal (TM) ions. EPR investigations of TM ion doped A₂BF₄ crystals reveal more interesting results with various extra centers having some lower symmetry than those of ABF₃ crystals. Namely, in addition to the tetragonal (TE) and trigonal (TR) Cr³⁺ centers formed in ABF₃ crystals, some orthorhombic (OR) and monoclinic (MO) Cr³⁺ centers have been found being formed in A₂BF₄ crystals. In particular, previously published EPR data for Cr³⁺ in Tl₂MgF₄ (Tl₂MgF₄ and Tl₂ZnF₄) crystals have shown that the presence of four structurally different Cr³⁺ centers. In the paper [1], Arakawa et al. reported the results of their investigation on Cr³⁺ doped Tl₂ZnF₄. Aside from the previously observed centers (center I and IV) [2], they also observed two new centers: a MO center (center II) and another OR center (center III). A vacancy at the nearest Tl⁺ site was assigned to the Cr³⁺ center II at the site of Zn²⁺ ion as a result of the spin-Hamiltonian separation (SHS) analysis, which is based on separating the second-rank ZFSPs (fine structure terms) into an uniaxial term along the crystalline c-axis

and another uniaxial term along the crystalline b-axis [2].

It is known that paramagnetic impurity ions doped into A₂BF₄ fluorides substitute for host B²⁺ cations and form paramagnetic impurity centers. When the impurity ions is a divalent M²⁺ such as Mn²⁺ and Ni²⁺, there is no need for a charge compensator, however, when a trivalent impurity ion such as Cr³⁺ and Fe³⁺ substitute for host divalent cation ion this situation is associated with a charge compensator for local charge neutrality. Based on the local charge compensation around the divalent sites after Cr³⁺ substitution it is possible to consider some different formations for the TE and TR centers in ABF₃ crystals. One of them is the Cr³⁺-Li⁺ center, where Li⁺ ion at the nearest B²⁺ site compensates the excess monovalent positive charge on Cr³⁺ ion [3]. The other one is the Cr³⁺-V_A center, where a vacancy at the nearest A⁺ site occurs [4]. Even, through the creation of a B²⁺ vacancy at the nearest B²⁺ site, the formation of the Cr³⁺-V_B center was also reported with an overcompensation of the positive charge on Cr³⁺ by the B²⁺ vacancy [5]. Similar various structural formations were reported for Cr³⁺ doped A₂BF₄ crystals even with low symmetry centers.

For not only the confirmation of the experimental observations but also to better understand the structural mechanism around the TM ion centers, a theoretical analysis is required. Nevertheless, no theoretical investigation of Cr³⁺ centers in Tl₂MF₄ crystals has been done yet. Thus, in this study, we have investigated theoretically the Cr³⁺ centers in Tl₂MgF₄ and Tl₂ZnF₄ crystals by means of semi-empirical calculations using superposition model (SPM), see, e.g. the papers [6,7] for the successful applications of this

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model on Cr^{3+} ion doped systems. Based on the correlation between the crystallographic and EPR data we have carried out the modeling of the zero-field splitting (ZFS) parameters (ZFSPs) for all of the observed Cr^{3+} centers and have enabled to determine the local structure of $[\text{Cr}-\text{F}_6]^{3-}$ clusters through various modeling approaches.

2. Method for calculations

Experimental spectra of Cr^{3+} doped Tl_2MgF_4 and Tl_2ZnF_4 crystals can be analyzed by utilizing the spin Hamiltonian, suitable for the spin $S=3/2$ systems, consisting of the Zeeman electronic terms and the ZFS terms [8,9,10]:

$$H = H_{Ze} + H_{ZFS} = \mu_B \mathbf{B} \cdot \mathbf{g} \cdot \mathbf{S} + \sum B_k^q O_k^q = \mu_B \mathbf{B} \cdot \mathbf{g} \cdot \mathbf{S} + \sum f_k b_k^q O_k^q \quad (1)$$

where μ_B is the Bohr magneton, \mathbf{B} is the applied magnetic field, g is the spectroscopic splitting factor, S is the effective spin operator, and B_k^q (or b_k^q) are ZFSPs associated with the extended Stevens operators O_k^q , whereas $f_k=1/3$, and $1/60$ are the scaling factors for $k=2$, and 4, respectively [11,12].

Explicit form of the ZFS term in Eq. (1) can be written for each symmetry case [13–15]. ZFS of a d^3 configuration Cr^{3+} center with TE symmetry can be analyzed by the following explicit expression of the spin-Hamiltonian:

$$H_{ZFS} = \frac{1}{3} b_2^0 O_2^0 = \frac{1}{3} D \left(S_z^2 - \frac{1}{3} S(S+1) \right) \quad (2)$$

For the Cr^{3+} centers with MO symmetry, for which only one symmetry axis C_2 exists, can be represented by the following H_{ZFS} s:

$$H_{ZFS} = \frac{1}{3} (b_2^0 O_2^0 + b_2^{-1} O_2^0 + b_2^2 O_2^0) \quad (3a)$$

$$H_{ZFS} = \frac{1}{3} (b_2^0 O_2^0 + b_2^{-2} O_2^0 + b_2^2 O_2^0) \quad (3b)$$

$$H_{ZFS} = \frac{1}{3} (b_2^0 O_2^0 + b_2^1 O_2^0 + b_2^2 O_2^0) \quad (3c)$$

which differ with respect to the choice of the MO direction, i.e. $C_2 \parallel X$ -axis (Eq.(3a)), $C_2 \parallel Z$ -axis (Eq.(3b)), and $C_2 \parallel Y$ -axis (Eq.(3c)). On the other hand, for Cr^{3+} center with OR symmetry we can use H_{ZFS} as:

$$H_{ZFS} = \frac{1}{3} (b_2^0 O_2^0 + b_2^2 O_2^0) = \frac{1}{3} D \left(S_z^2 - \frac{1}{3} S(S+1) \right) + E (S_x^2 - S_y^2) \quad (4)$$

In general, following the general definitions for the SPM quantities outlined recently in [16,17], the ZFSPs can be expressed as

$$b_k^q = \sum_i \bar{b}_k(R_i) \cdot K_k^q(\theta_i, \phi_i) \quad (5)$$

where $K_k^q(\theta_i, \phi_i)$ are the coordination factors [18] as functions of the position angles θ_i and ϕ_i of ligands. The intrinsic parameters (IPs) $\bar{b}_k(R_i)$ are assumed to obey the following power law:

$$\bar{b}_k(R_i) = \bar{b}_k(R_0) \left(\frac{R_0}{R_i} \right)^{t_k} \quad (6)$$

where R_0 is the reference distance, R_i are the ligand distances in the ML_6 complex; $\bar{b}_k(R_0)$ is the intrinsic parameter, whereas t_k is the power law exponent which are treated as adjustable parameters. The $\bar{b}_k(R_0)$, t_k , and the reference distance R_0 can be

included into a combined set, which is known as SPM parameter set for SPM applications [19]. Only one data set [20] of the model parameters, i.e. $\bar{b}_k(R_0)$ and t_k with R_0 , suitable for the ligand system of the $\text{Cr}^{3+}-\text{F}^-$ bond configuration, exists in literature. These are: $\bar{b}_2(R_0) = (46770 \pm 800) \times 10^{-4} \text{ cm}^{-1}$ and $t_2 = -0.24 \pm 0.03$ with $R_0 = 0.2113 \text{ nm}$.

SPM provides the following general expressions for ZFSPs for the Cr^{3+} centers in 6-fold coordination in terms of IPs:

$$b_2^0 = D = \frac{\bar{b}_2(R_0)}{2} \sum_{i=1}^n \left(\frac{R_0}{R_i} \right)^{t_2} (3 \cos^2 \theta_i - 1) \quad (7)$$

$$b_2^{-1} = 3\bar{b}_2(R_0) \sum_{i=1}^n \left(\frac{R_0}{R_i} \right)^{t_2} \sin 2\theta_i \sin \phi_i \quad (8)$$

$$b_2^2 = 3E = \frac{3\bar{b}_2(R_0)}{2} \sum_{i=1}^n \left(\frac{R_0}{R_i} \right)^{t_2} \sin^2 \theta_i \cos 2\phi_i \quad (9)$$

Here we provide the expression for only ZFSP b_2^{-1} regarding the MO direction $C_2 \parallel X$ -axis. Indeed, as mentioned above, depending on the choice of the C_2 direction, we may have b_2^{-2} or b_2^1 instead of b_2^{-1} for choosing $C_2 \parallel Z$ -axis or $C_2 \parallel Y$ -axis, respectively.

3. Results and discussion

The presence of TE center I and OR center IV in Tl_2MgF_4 [2] whereas TE center I, MO center II, and OR centers III and IV in Tl_2ZnF_4 [1] crystals are known experimentally. The types of Cr^{3+} centers present in Tl_2MF_4 crystals and values of the previously determined experimental ZFSPs ($D=b_2^0$ and $3E=b_2^2$) for them are tabulated in Table 1. It should be noted that the values of the ZFSP $D=b_2^0$ in Tl_2MgF_4 and Tl_2ZnF_4 are rather higher than those in other A_2BF_4 crystals, even $D=b_2^0$ of the TE Cr^{3+} center is almost three times of that in K_2ZnF_4 ($-381.0 \times 10^{-4} \text{ cm}^{-1}$ [1]) and Rb_2ZnF_4 ($-369.0 \times 10^{-4} \text{ cm}^{-1}$ [21]). Furthermore, it is worth noting that the rhombicity ratio $\lambda=E/D$ measuring the deviation from axial symmetry for the OR and MO centers is much higher in these crystals. Even, it is 0.71 and 0.77 for OR center IV in Tl_2MgF_4 and Tl_2ZnF_4 , respectively. Normally, the ratio λ yields $0 \leq \lambda = E/D \leq 1/3$ [22].

In SPM analyses, it is pertinent to know metal-ligand (M–F) distances for an appropriate prediction of the local structure distortion around the Cr^{3+} centers. For Tl_2MF_4 crystals, there is no report about the host structure of Mg^{2+} and Zn^{2+} ions in terms of local structure parameters. However, it is known that the site of the binary cations Mg^{2+} and Zn^{2+} is exactly at the center of the unit-cell of Tl_2MgF_4 and Tl_2ZnF_4 crystals. The separation between two equatorial F-ligands (F–Mg/Zn–F distance: R_2) coincides with the unit-cell parameter a , which means $a/2$ equals to R_2 . The TE

Table 1

The values of the previously determined experimental ZFSPs [in 10^{-4} cm^{-1}] for various Cr^{3+} centers in Tl_2MF_4 crystals.

Compounds	Center	$D=b_2^0$	$3E=b_2^2$	Refs
Tl_2MgF_4	I (TE)	–1041.7	–	[2]
	IV (OR)	843.6	598.0	[2]
Tl_2ZnF_4	I (TE)	–866.1	–	[2]
	II (MO)	–1507.9	–706.1	[1]
	III (OR)	924.5	–156.0	[1]
	IV (OR)	684.6	529.0	[2]

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