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Theoretical investigations of the local structure distortion and the spin Hamiltonian parameters of Cr^{3+} ions at tetragonal charge-compensation defect CrF_5O site in Cr^{3+}: $KMgF_3$ crystals

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ABSTRACT

The local structure distortion and the spin Hamiltonian (SH) parameters, including the zero-field splitting (ZFS) parameter D and the Zeeman g-factors $g_{\parallel}$ and $g_{\perp}$, are theoretically investigated by means of complete diagonalization method (CDM) and the microscopic spin Hamiltonian theory for tetragonal charge compensation CrF_5O defect center in Cr^{3+}:$KMgF_3$ crystals. The superposition model (SPM) calculations are carried out to provide the crystal field (CF) parameters. This investigation reveals that the replacement of O^{2-} for F^- and its induced lattice relaxation $\Delta_1(O^{2-})$ combined with an inward relaxation of the nearest five fluorine $\Delta_2(F^-)$ give rise to a strong tetragonal crystal field, which in turn results in the large ZFS and large anisotropic g-factor Δg. The experimental SH parameters D and Δg can be reproduced well by assuming that O^{2-} moves towards the central ion Cr^{3+} by $\Delta_1(O^{2-})=0.172R_0$ and the five F^- ions towards the central ion Cr^{3+} by $\Delta_2(F^-)=0.022R_0$. Our approach takes into account the spin–orbit (SO) interaction as well as the spin–spin (SS), spin–other-orbit (SOO), and orbit–orbit (OO) interactions omitted in previous studies. This shows that although the SO interaction is the most important one, the contributions to the SH parameters from other three magnetic interactions are appreciable and should not be omitted, especially for the ZFS parameter D.

1. Introduction

The fluoroperovskites such as $KMgF_3$, $KZnF_3$, etc. doped with the transition metal (TM) ions Cr^{3+} have attracted much attention because of the application as tunable solid-state lasers operating at room temperature [1–4], which depend strongly on the presence of defects induced by the transition metal impurities. The impurity Cr^{3+} ions in the materials play a major role because they can be responsible for modifications of the optical properties of crystals required for particular laser applications. A perfect $KMgF_3$ crystal has cubic structure, the local symmetry around Mg^{2+} ion is O_h, Mg^{2+} ion is surrounded by six F^- ion. Trivalent Cr^{3+} ions replace divalent Mg^{2+} ions when they are doped into $KMgF_3$ crystals. However, a low-symmetry defect site in Cr^{3+}:$KMgF_3$ crystals will form owing to the charge compensation. In the case of Cr^{3+}:$KMgF_3$, a tetragonal defect site has been found by EPR experiment [5]. This tetragonal site is characteristic of a very large axial zero-field splitting (ZFS) parameter $D=-21.67\times10^{-2}\,cm^{-1}$ and the anisotropic Zeeman g-factor $\Delta g=g_{\parallel}-g_{\perp}=-9.5\times10^{-3}$ [5], interestingly, several times greater in magnitude than those ($D=-5.22\times10^{-2}\,cm^{-1}$ and $\Delta g=g_{\parallel}-g_{\perp}=-2.3\times10^{-3}$ [5]) for the tetragonal site Cr^{3+} in $KZnF_3$ crystals; it has been attributed to Cr^{3+} ions with O^{2-} ions on the tetragonal axis, i.e. the CrF_5O configuration [5]. Patel et al. investigated the ZFS parameter D of the tetragonal site Cr^{3+} in $KMgF_3$ crystals using the approximative perturbation formula they obtained $D=-43.0\times10^{-2}\,cm^{-1}$ [5] which is remarkably larger in magnitude than the experimental value $-21.67\times10^{-2}\,cm^{-1}$. In fact, Macfarlane [6] pointed out that Patel's perturbation formula was a wrong one. So far there is no satisfactory theoretical work, which can explain all of these experimental findings. For an understanding of the role of impurities on a microscopic scale, it is very necessary to know the defect nature and local structure distortion of the impurity centers. As is well known, the spin Hamiltonian (SH) parameters including the ZFS parameters and Zeeman g-factor for TM ions in crystals reflect even small variations very sensitively in the coordination of the paramagnetic centers [7–9]. Hence, the studies of these parameters can provide a great deal of microscopic insight concerning the crystal structure, structural disorder, phase transitions, pressure behavior as well as the observed magnetic, and spectroscopic properties [9–11].

To probe the local structure distortion and the SH parameters for Cr^{3+} ions in $KMgF_3$ crystal, in this work, the relationship

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between the SH parameters and the defect structure of Cr^{3+} centers in $KMgF_3$ crystal has been established on the basis of the superposition model [12]. By investigating the SH parameters including the zero-field splitting parameters D and anisotropic Zeeman g-factor Δg ($=g_{\parallel}-g_{\perp}$), the local structure distortion and the microscopic origins of the spin Hamiltonian parameters for the tetragonal Cr^{3+} centers in $KMgF_3$ crystal materials, taking into account the spin–spin (SS), the spin–other-orbit (SOO), and the orbit–orbit (OO) magnetic interactions besides the well-known spin–orbit (SO) magnetic interaction, have been investigated using complete diagonalization method (CDM). It will be shown that the replacement and the local structure distortion will give rise to the strong tetragonal crystal field (CF), which affects the ZFS parameter D and g-factor: Δg through the magnetic interactions including SO, SS, SOO, and OO ones.

2. Theoretical analysis

In order to gain a more reliable microscopic insight into the local structure distortion of the tetragonal charge compensation defect CrF_5O site in Cr^{3+}:$KMgF_3$ crystals, it requires us to develop more complete calculation methods, which would allow for the investigation of small perturbations so far neglected. This includes the spin–spin (SS), spin–other-spin (SOO), and orbit–orbit (OO) magnetic interactions [13–16], in addition to the spin–orbit (SO) magnetic interaction usually taken into account. Thus, in this work, the total Hamiltonian is taken as [17]

$$H = H_{ee}(B,C)+H_{CF}(B_{kq})+H_m(\xi_d,M_0,M_2), \tag{1}$$

where H_{ee} denotes the electrostatic interaction, H_{CF} the CF interaction, and H_m the magnetic interactions, which can be given as [17]

$$H_m = H_{SO}(\xi_d)+H_{SOO}(M_0,M_2)+H_{SS}(M_0,M_2) + H_{OO}(M_0,M_2), \tag{2}$$

where ξ_d is the spin–orbit interaction parameter whereas M_0 and M_2 are Marvin's radial integrals [16] used for representing the SS, SOO, and OO interactions. The CF Hamiltonian for $3d^3$ ions at tetragonal symmetry site can be explicitly expressed as

$$H_{CF} = B_{20}C_0^{(2)}+B_{40}C_0^{(4)}+B_{44}(C_4^{(4)}+C_{-4}^{(4)}), \tag{3}$$

where B_{Lq} are the CF parameters with $B_{L-q}=(-1)^q B_{Lq}^*$ and $C_q^{(k)}$ are normalized spherical harmonics. It can be seen from Eq. (3) that there are three independent CF parameters B_{20}, B_{40}, and B_{44} for the tetragonal symmetry.

Since Cr^{3+} in Cr^{3+}:$KMgF_3$ crystals is in $3d^3$ configuration, which has 120 microcosmic states. The matrix of Hamiltonian in Eq. (1) are of the dimension 120×120 and can be partitioned into four smaller matrices, i.e. 30×30 ($E'\alpha'$), 30×30($E'\beta'$), 30×30($E''\alpha''$), and 30×30($E''\beta''$) for the tetragonal symmetry crystal field. Details concerning the choice of the basis and calculation of the pertinent matrix elements have been published previously [18]. The Hamiltonian matrices obtained in this way are the functions of the Racah parameters B and C, the CF parameters B_{Lq} (in the Wybourne notation [16]), the SO constant ξ_d, and the SS, SOO, and OO parameters M_0, M_2. Provided the values of these microscopic parameters are available, diagonalization of the full Hamiltonian matrices yields the energy levels and eigenvectors. The ground state eigenvectors obtained in this way for tetragonal symmetry CF are admixtures of the excited LS states. The four ground state eigenvectors, which will be used in the calculations of g-factors, can be expressed as

$$|\psi_{1/2}\rangle = |E''\alpha''(^4F\downarrow{}^4A_{2g}\downarrow{}^4B_1)\rangle = \sum_{i=1}^{30} a_i|\varphi_{1i}\rangle \tag{4a}$$

$$|\psi_{-1/2}\rangle = |E''\beta''(^4F\downarrow{}^4A_{2g}\downarrow{}^4B_1)\rangle = \sum_{i=1}^{30} b_i|\varphi_{2i}\rangle \tag{4b}$$

$$|\psi_{+3/2}\rangle = |E'\beta'(^4F\downarrow{}^4A_{2g}\downarrow{}^4B_1)\rangle = \sum_{i=1}^{30} c_i|\varphi_{3i}\rangle \tag{4c}$$

$$|\psi_{-3/2}\rangle = |E'\alpha'(^4F\downarrow{}^4A_{2g}\downarrow{}^4B_1)\rangle = \sum_{i=1}^{30} d_i|\varphi_{4i}\rangle \tag{4d}$$

where we use the notation $|\Gamma_{C_{4v}^*}(^{2S+1}L\downarrow{}^{2S+1}\Gamma_{O_h}\downarrow{}^{2S+1}\Gamma_{C_{4v}})\rangle$ to label final states in Eqs. (4), since it shows explicitly the parentage of the states arising from the combined action of magnetic interactions and tetragonal crystal field [19].

The microscopic spin Hamiltonian theory [20–22] enables us to derive explicit expressions for the spin Hamiltonian parameters. The effective spin Hamiltonian for $3d^3$ ions at tetragonal symmetry sites, taking into account the ZFS and Zeeman terms, can be written as:

$$H_S = D\left[S_z^2-\tfrac{1}{3}S(S+1)\right]+\mu_B g_{\parallel}B_zS_z + \mu_B g_{\perp}(B_xS_x+B_yS_y) \tag{5}$$

with the z-axis along the [0 0 1] direction for the tetragonal symmetry.

According to the spin Hamiltonian theory, the ZFS parameter D and Zeeman g-factors: $g_{\parallel}$ and $g_{\perp}$ can be expressed as follows:

$$D = \tfrac{1}{2}\left[\varepsilon(|E'(^4F\downarrow{}^4A_{2g}\downarrow{}^4B_1)\rangle)-\varepsilon(|E''(^4F\downarrow{}^4A_{2g}\downarrow{}^4B_1)\rangle)\right] \tag{6}$$

$$g_{\parallel} = \tfrac{2}{3}\{k\langle\psi_{+3/2}|L_0^{(1)}|\psi_{+3/2}\rangle+g_e\langle\psi_{+3/2}|S_0^{(1)}|\psi_{+3/2}\rangle\}, \tag{7a}$$

$$g_{\perp} = \frac{\sqrt{2}}{\sqrt{3}}\Big\{k(\langle\psi_{+3/2}|L_{-1}^{(1)}|\psi_{+1/2}\rangle-\langle\psi_{+3/2}|L_{+1}^{(1)}|\psi_{+1/2}\rangle) + g_e(\langle\psi_{+3/2}|S_{-1}^{(1)}|\psi_{+1/2}\rangle-\langle\psi_{+3/2}|S_{+1}^{(1)}|\psi_{+1/2}\rangle)\Big\}, \tag{7b}$$

where k is the orbital reduction factor [23]. It is well established that the ground state $|\tilde{M}_s=\pm1/2\rangle$ of H_S in Eq. (5) in zero magnetic field corresponds to $D>0$, whereas $|\tilde{M}_s=\pm3/2\rangle$ to $D<0$. Correspondingly, Eq. (6) yields positive and negative D for the ground state $|\tilde{M}_s=\pm1/2\rangle$ and $|\tilde{M}_s=\pm3/2\rangle$, respectively.

For Cr^{3+} in $KMgF_3$:Cr^{3+} crystals, the Racah parameters $B=823\ cm^{-1}$ and $C=3005\ cm^{-1}$ have been obtained from optical spectra [4]. In our calculations, the spin–orbit coupling constant ξ_d is taken as $207\ cm^{-1}$ [24] and the SS, SOO, and OO parameters $M_0=0.2021\ cm^{-1}$ and $M_2=0.0159\ cm^{-1}$ for Cr^{3+} ions [25] are adopted. In order to evaluate the orbital reduction factor k, we use the relation $k\approx(\sqrt{B/B_0}+\sqrt{C/C_0})/2$ [26,27], where $B_0=920.48\ cm^{-1}$, $C_0=3330.71\ cm^{-1}$ are the Racah parameters of the free Cr^{3+} ion [27], we obtain $k\approx0.95$. Having fixed the parameters B, C, ξ_d, k, M_0, and M_2, the experimentally measured parameters, i.e. D, $g_{\parallel}$, and $g_{\perp}$ become only the functions of the CF parameters B_{20}, B_{40}, and B_{44} . This enables us to study the local structure distortion around Cr^{3+} defect centers.

In order to predict the theoretical values of the SH parameters D, $g_{\parallel}$, and $g_{\perp}$ based on the present method, the values of the CF parameters (B_{20}, B_{40}, B_{44}) must be known. The latter values can be obtained either experimentally from optical spectroscopy or predicted using appropriate local structure defect models. In Section 3 we consider such models.

3. The local structure defect model and CF parameters

A perfect $KMgF_3$ crystal has cubic structure, the local symmetry around Mg^{2+} ion is O_h, Mg^{2+} ion is surrounded by six F^- ion. Trivalent Cr^{3+} ions replace divalent Mg^{2+} ions when they are