Investigation of the EPR Parameters and Local Structures for the Tetragonal $\text{Ti}^{3+}\text{--O}^{2-}\text{--V}_M$ Centers in MgO and CaO Crystals

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The EPR parameters (g factors $g_{\parallel}$, $g_{\perp}$ and hyperfine structure constants $A_{\parallel}$, $A_{\perp}$) of the tetragonal $\text{Ti}^{3+}\text{--O}^{2-}\text{--V}_M$ centers in MgO and CaO crystals are calculated from the high-order perturbation formulae based on the cluster approach. The calculated results are in reasonable agreement with the observed values. The local structural parameters for the tetragonal Ti^{3+} centers in both crystals are also obtained from the calculation. These results are discussed.

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1. Introduction

MgO and CaO are the important matrices in the studies of the optical and EPR spectra of transition-metal ($3d^n$) ions in crystals [1–6]. For example, the EPR spectra of Ti^{3+} ($3d^1$) ions in MgO and CaO crystals were measured [6]. From the measurement, a tetragonal Ti^{3+} center ascribed to the defect model $\text{Ti}^{3+}\text{--O}^{2-}\text{--V}_M$ (where V_M denotes a neighboring cation vacancy along $\langle 001 \rangle$ axis owing to charge compensation) was found in both crystals and their EPR parameters (g factors $g_{\parallel}$, $g_{\perp}$ and hyperfine structure constants $A_{\parallel}$, $A_{\perp}$) were obtained [6]. By fitting the calculated g factors from the simple perturbation formulae based on the classical crystal-field theory to the observed values, Davies and Wertz [6] found the energy separations $E_1 \approx 10Dq \approx 30000 \text{ cm}^{-1}$, $E_2 \approx \delta \approx 5Dt - 3Ds \approx 3000 \text{ cm}^{-1}$ for $\text{MgO}:\text{Ti}^{3+}$ and $E_1 \approx 22000 \text{ cm}^{-1}$, $E_2 \approx 4800 \text{ cm}^{-1}$ for $\text{CaO}:\text{Ti}^{3+}$. As pointed out by them [6], these values of E_1 and E_2 are expected to be overestimated because in the classical crystal field theory, the covalence effect in $[\text{TiO}_6]^{9-}$ cluster and hence the covalence reduction effect in the spin-orbit coupling parameter are not considered. In addition, the local geometry (or the local structure) of this tetragonal Ti^{3+} impurity center in both crystals was not studied. Considering that in $\text{MgO}:\text{Ti}^{3+}$ and $\text{CaO}:\text{Ti}^{3+}$ crystals, the spin-orbit coupling parameter ζ_p^0 ($\approx 150 \text{ cm}^{-1}$ [7]) of the ligand O^{2-} is very close to that ($\zeta_d^0 \approx 154 \text{ cm}^{-1}$ [8]) of the central Ti^{3+} ion, the contributions to the EPR

parameters from the spin-orbit coupling parameter ζ_p^0 via covalence effect should be included. Thus, the high-order perturbation formulae of EPR parameters based on the cluster approach should be used in the calculation of EPR parameters of $\text{MgO}:\text{Ti}^{3+}$ and $\text{CaO}:\text{Ti}^{3+}$ crystals. In these formulae, the covalence effect and hence the contributions to EPR parameters from both the spin-orbit coupling parameters ζ_d^0 and ζ_p^0 are considered. In this paper, we calculate the EPR parameters of $\text{MgO}:\text{Ti}^{3+}$ and $\text{CaO}:\text{Ti}^{3+}$ by using the formulae based on cluster approach. The local structural data of the $\text{Ti}^{3+}\text{--O}^{2-}\text{--V}_M$ centers (and hence the local geometry of the Ti^{3+} centers) in both crystals are also estimated from the calculations. The results are discussed.

2. Calculation

For a $3d^n \text{MX}_6$ octahedral cluster, the one-electron basis function $|\psi_{\gamma}\rangle$ is the linear combination of the d orbital $|d_{\gamma}\rangle$ of $3d^n$ ion and the p orbital $|p_{\gamma}\rangle$ of the ligands,

$$|\psi_{\gamma}\rangle = N^{\frac{1}{2}}(|d_{\gamma}\rangle - \lambda_{\gamma}|p_{\gamma}\rangle) \quad (1)$$

where $\gamma = e_g$ or t_{2g} stands for the irreducible representation of O_h group. N_{γ} and λ_{γ} are the normalization factor and the orbital mixing coefficient, respectively. They can be related by the normalization relationship

$$N_{\gamma}(1 - 2\lambda_{\gamma}S_{dp}(\gamma) + (\lambda_{\gamma})^2) = 1, \quad (2)$$

in which $S_{dp}(\gamma)$ is the group overlap integral.

For the above tetragonal Ti^{3+} centers, the ground orbital state is ${}^2B_2(|d_{xy}\rangle)$. Thus, from the above basis function, the third-order perturbation formulae of $3d^1$ ion in tetragonal symmetry based on the cluster approach can be expressed as [9]:

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$$\begin{aligned}
g_{\parallel} &= g_s - 8k'\zeta'/E_1 - k\zeta^2/(E_2)^2 - 4k'\zeta\zeta'/(E_1E_2) \\
&\quad - g_s\zeta^2/(E_2)^2, \\
g_{\perp} &= g_s - 2k\zeta/E_2 + k\zeta^2/(E_2)^2 - 2k\zeta'^2/(E_1E_2) \\
&\quad + 2k'\zeta\zeta'/(E_1E_2) \\
&\quad - 2g_s\zeta'^2/(E_1)^2 - g_s\zeta^2/2(E_2)^2, \\
A_{\parallel} &= P(-\kappa - \frac{4}{7}) + P' \left[-8k'\zeta'/E_1 - \frac{6}{7}k\zeta/(E_2) \right. \\
&\quad - \frac{4}{7}k\zeta^2/(E_2)^2 - \frac{6}{7}k\zeta'^2/(E_1E_2) - \frac{22}{7}\zeta\zeta'/(E_1E_2) \\
&\quad \left. - \frac{6}{7}g_s\zeta'^2/(E_1)^2 - \frac{17}{14}g_s\zeta^2/(14E_2)^2 \right], \\
A_{\perp} &= P(\frac{2}{7} - \kappa) + P' \left[-\frac{11}{7}k\zeta/(E_2) \right. \\
&\quad + \frac{11}{14}k\zeta^2/(E_2)^2 - \frac{11}{7}k\zeta'^2/(E_1E_2) + \frac{11}{7}k'\zeta\zeta'/(E_1E_2) \\
&\quad \left. - \frac{11}{7}g_s\zeta'^2/(E_1)^2 - \frac{11}{28}g_s\zeta^2/(E_2)^2 \right], \quad (3)
\end{aligned}$$

with

$$\begin{aligned}
\zeta &= N_t(\zeta_d^0 + \lambda_t^2\zeta_p^0/2), \\
\zeta' &= (N_tN_e)^{\frac{1}{2}}(\zeta_d^0 - \lambda_t\lambda_e\zeta_p^0/2), \\
k &= N_t[1 - 2\lambda_tS_{dp}(t_{2g}) + \lambda_t^2/2], \\
k' &= (N_tN_e)(1 - \lambda_tS_{dp}(t_{2g}) + \lambda_eS_{dp}(e_g) - \lambda_t\lambda_e/2), \\
P &= N_tP_0, \quad P' = (N_tN_e)^{\frac{1}{2}}P_0, \quad (4)
\end{aligned}$$

where g_s (≈ 2.0023) is the free-electron value. κ is the core polarization constant. ζ_d^0 and ζ_p^0 are the spin-orbit coupling parameter of d electrons of free $3d^1$ ion and that of p electrons of free ligand ion, respectively. P_0 is the dipolar hyperfine structure constant of free $3d^1$ ion. For the $\text{MgO}:\text{Ti}^{3+}$ and $\text{CaO}:\text{Ti}^{3+}$ investigated, the ζ_d^0 and ζ_p^0 are given in Sect. 1 and $P_0(\text{Ti}^{3+}) \approx -25.7 \times 10^{-4} \text{ cm}^{-1}$ [10].

The group overlap integral $S_{dp}(\gamma)$ is dependent upon the impurity-ligand distance R_0 in the studied system. Since the size and/or nature of impurity ion are often different from those of the replaced host ion, we estimate reasonably the distance R_0 by the approximate formula [11, 12]:

$$R_0 \approx R_H + \frac{1}{2}(r_i - r_h), \quad (5)$$

in which r_i and r_h are the ionic radius of impurity and that of the replaced host ion, R_H is the corresponding distance in the host crystal. Thus, from $r_i(\text{Ti}^{3+}) \approx 0.76 \text{ \AA}$, $r_h(\text{Mg}^{2+}) \approx 0.66 \text{ \AA}$, $r_h(\text{Ca}^{2+}) \approx 0.99 \text{ \AA}$ [13], $R_H(\text{MgO}) \approx 2.1 \text{ \AA}$, and $R_H(\text{CaO}) \approx 2.4 \text{ \AA}$ [13], we obtain the $\text{Ti}^{3+}-\text{O}^{2-}$ distances R_0 in $\text{MgO}:\text{Ti}^{3+}$ and $\text{CaO}:\text{Ti}^{3+}$ crystals. They are shown in Table I. Thus, from the Slater-type SCF functions [14, 15] and the distances R_0 , the integrals $S_{dp}(\gamma)$ for both crystals are calculated and the results are also shown in Table I.

TABLE I

The structural data, group overlap integrals, molecular orbital coefficients, and core polarization constant for the tetragonal Ti^{3+} centers in $\text{MgO}:\text{Ti}^{3+}$ and $\text{CaO}:\text{Ti}^{3+}$ crystals.

	R_0 [Å]	ΔR [Å]	$S_{dp}(t_{2g})$	$S_{dp}(e_g)$	λ_γ	N_t	N_e	κ
MgO	2.15	0.233	0.0395	0.1101	0.484	0.8361	0.8868	0.6
CaO	2.285	0.490	0.0259	0.0802	0.375	0.8920	0.9255	0.6

The energy separations E_i in Eq. (3) can be written as $E_1 = E(^2B_1) - E(^2B_2) \approx 10Dq$,

$$E_2 = E(^2E) - E(^2B_2) \approx 5Dt - 3Ds, \quad (6)$$

where Dq , Ds , and Dt are the crystal-field parameters. For the studied $\text{Ti}^{3+}-\text{O}^{2-}-V_M$ center, since the effective charge of cation vacancy V_M is negative, the O^{2-} ion intervening in the Ti^{3+} and V_M is displaced towards the Ti^{3+} ion by an amount $\Delta R = R_0 - R_1$ (where R_1 is the distance between Ti^{3+} and the intervening O^{2-} ion. The distances between Ti^{3+} and the rest five O^{2-} ions are still R_0) owing to the electrostatic repulsive force between this O^{2-} and V_M . Therefore, for the tetragonal center, the crystal-field parameters in the superposition model [16] can be expressed as

$$\begin{aligned}
Dq &\approx \frac{1}{6} [5Dq(R_0) + Dq(R_1)] \approx \\
&\frac{1}{6} \left[\frac{20}{3}\bar{A}_4(R_0) + \frac{4}{3}\bar{A}_4(R_0) \left(\frac{R_0}{R_1} \right)^{t_4} \right], \\
Ds &\approx \frac{2}{7}\bar{A}_2(R_0) \left[1 - \left(\frac{R_0}{R_1} \right)^{t_2} \right], \\
Dt &= \frac{8}{21}\bar{A}_4(R_0) \left[1 - \left(\frac{R_0}{R_1} \right)^{t_4} \right], \quad (7)
\end{aligned}$$

in which t_2 (≈ 3 [17–19]) and t_4 (≈ 5 [17–19]) are the power-law exponents. $\bar{A}_2(R_0)$ and $\bar{A}_4(R_0)$ are the intrinsic parameters with the reference distance R_0 . $\bar{A}_4(R_0) = 3/4Dq_c(R_0)$ [16, 18, 19] for a cubic $3d^n$ octahedral cluster and $\bar{A}_2(R_0) \approx (9-12)\bar{A}_4(R_0)$ were obtained for $3d^n$ ions in many crystals [18–21]. We take the average value $\bar{A}_2(R_0) \approx 10.5\bar{A}_4(R_0)$ here. The cubic field parameter $Dq_c(R_0)$ can be obtained from the optical spectra of the system studied. Since no optical spectra of $\text{MgO}:\text{Ti}^{3+}$ and $\text{CaO}:\text{Ti}^{3+}$ were reported, we estimate reasonably the values of $Dq_c(R_0)$ from those of similar $[\text{TiO}_6]^{9-}$ clusters in other crystals. Since the parameter $Dq_c(R_0) \propto R_0^{-n}$ (where $n \approx 5 \pm 1.5$ [22–24]), from the $Dq_c(R_0) \approx 1910 \text{ cm}^{-1}$ [25] within the cubic approximation with the $\text{Ti}^{3+}-\text{O}^{2-}$ distance $R_0 \approx 2.037 \text{ \AA}$ in $\text{Al}_2\text{O}_3:\text{Ti}^{3+}$ (note: $\bar{R}_H \approx 1.912 \text{ \AA}$ [26] in $\text{Al}_2\text{O}_3:\text{Ti}^{3+}$ and $R_i(\text{Al}^{3+}) \approx 0.51 \text{ \AA}$ [13]) and the $\text{Ti}^{3+}-\text{O}^{2-}$ distance R_0 of $\text{MgO}:\text{Ti}^{3+}$ and $\text{CaO}:\text{Ti}^{3+}$ (see Table I), we obtained $Dq_c(R_0) \approx 1500$ and 1100 cm^{-1} for $\text{MgO}:\text{Ti}^{3+}$ and $\text{CaO}:\text{Ti}^{3+}$, respectively. Thus, we have $\bar{A}_4(R_0) \approx 1125 \text{ cm}^{-1}$ with $R_0 \approx 2.15 \text{ \AA}$ for $\text{MgO}:\text{Ti}^{3+}$, and $\bar{A}_4(R_0) \approx 825 \text{ cm}^{-1}$ with $R_0 \approx 2.285 \text{ \AA}$ for $\text{CaO}:\text{Ti}^{3+}$.

It is difficult to obtain the orbital mixing coefficients λ_γ , so we take them as the adjustable parameters. For simplicity, we assume $\lambda_\gamma \approx \lambda_t \approx \lambda_e$. Thus, in the above formulae, there are three adjustable parameters λ_γ , ΔR and κ (which is used only in the calculations of $A_\parallel$ and $A_\perp$). By fitting the calculated EPR parameters $g_\parallel$, $g_\perp$, $A_\parallel$ and $A_\perp$ from the above formulae to the experimental values, these adjustable parameters for Ti^{3+} ions in MgO and CaO can be obtained and are shown in Table I. Thus, the normalization factor N_γ (see Table I) in both crystals can be calculated by using Eq. (2) and so the parameters in Eq. (4) are therefore obtained. The calculated EPR parameters for both crystals are compared with the observed values in Table II.

TABLE II

The EPR parameters of the tetragonal Ti^{3+} center in MgO: Ti^{3+} and CaO: Ti^{3+} crystals. Upper values — calculated, lower values — experimental [6].

	$g_\parallel$	$g_\perp$	$A_\parallel [10^{-4} \text{ cm}^{-1}]$	$A_\perp [10^{-4} \text{ cm}^{-1}]$
MgO	1.9530	1.8987	27	9
	1.95304(10)	1.89878(10)	26.8(2)	10.0(5)
CaO	1.9426	1.9366	29	8
	1.9427 (1)	1.9380 (1)	27.4(1)	9.9(15)

3. Discussion

From Table II, it can be seen that by considering suitable local structures, the calculated EPR parameters $g_\parallel$, $g_\perp$, $A_\parallel$ and $A_\perp$ (from the third-order perturbation formulae based on cluster approach) for the tetragonal $Ti^{3+}-O^{2-}-V_M$ centers in MgO: Ti^{3+} and CaO: Ti^{3+} crystals are in agreement with the observed values. In the calculations, since the covalence effect is considered, the required energy separations are $E_1 \approx 16950 \text{ cm}^{-1}$ and $E_2 \approx 2510 \text{ cm}^{-1}$ for MgO: Ti^{3+} and $E_1 \approx 15300 \text{ cm}^{-1}$ and $E_2 \approx 4210 \text{ cm}^{-1}$ for CaO: Ti^{3+} . These values are indeed smaller than the corresponding values overestimated in Ref. [6] (see Introduction) and can be regarded as suitable. In addition, the direction of the displacement ΔR in both crystals is consistent with the expectation based on the electrostatic interaction between the intervening O^{2-} and Ti^{3+} ions. The $Ti^{3+}-O^{2-}$ distance R_0 in MgO: Ti^{3+} is smaller than that in CaO: Ti^{3+} and then the interaction between Ti^{3+} and O^{2-} ions in MgO: Ti^{3+} is stronger than that in CaO: Ti^{3+} . Therefore, it can be expected that the orbital mixing coefficient λ_γ in MgO: Ti^{3+} should be larger than that in CaO: Ti^{3+} and the displacement ΔR in MgO: Ti^{3+} is smaller than that in CaO: Ti^{3+} . The above calculated results (see Table I) confirm the two points. Therefore, they can be looked upon as reasonable.

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