

Local Lattice Structure Study of the Octahedral (CrO₆)⁹⁻ Clusters for Cr³⁺ Ion Doping in a Variety of Oxide Crystals by Simulating the Corresponding EPR and Optical Spectra

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On the basis of the 120 × 120 complete energy matrix, the local lattice structures of the octahedral (CrO₆)⁹⁻ clusters for Cr³⁺ ions doping in a variety of oxide crystals with *D*_{3d} or *C*_{3v} site symmetry have been studied by employing two distorted parameters, respectively. By simulating the calculated EPR and optical spectra data to the experimental results, the local lattice structure parameters are determined unambiguously. It is shown, by means of a series of calculations, that although the local lattice structures around the M (M = Al³⁺, Ga³⁺, Li⁺, Sc³⁺, etc.) ions in host crystals are obviously different, the local lattice structures of the octahedral (CrO₆)⁹⁻ clusters in a variety of oxide crystals doped with Cr³⁺ ions are similar and fluctuant in the vicinity of that of the Cr₂O₃. This may be ascribed to the fact that there is the similarly octahedral (CrO₆)⁹⁻ clusters in a variety of oxide crystals doped with Cr³⁺ and the Cr₂O₃ crystal. Our viewpoint is consistent with that of Gaudry et al. [*Phys. Rev. B* 2003, 67, 094108].

I. Introduction

To study the inter-relation between the molecular structure and the electronic structure of the transition metal ions in the complex molecules by employing an EPR mechanism is an interesting and important problem. Up to now, four theoretical methods have been employed to investigate the zero-field splitting of the transition metal ion doping in crystals. The first is ab initio calculations,^{1–4} the ZFS is generally reckoned using an electrostatic model of the crystal field, together with one or more of the splitting mechanisms. The second is the empirical superposition model by analyzing the spin Hamiltonian.^{5–6} The third and fourth methods are both developed on the basis of the empirical superposition model: one of them is the high-order perturbation^{7–8} and the other is the complete energy matrix.^{9–10} Especially, the complete energy matrices have recently been extensively applied to deal with the systems doped with transition metal ions. In this paper, we will study the total properties of the octahedral (CrO₆)⁹⁻ clusters for Cr³⁺ ion doping in a variety of oxide crystals with *D*_{3d} or *C*_{3v} site symmetry by employing the complete energy matrix.

Oxide crystals exist in any or every place of our surroundings and play an important role in our diet, environment, health, work, and so on. So there is a continuing interest in the study of the relational properties of oxide crystals from both the experiment and theory. Thus, it has been found that transition metals (Fe, Mn, and Cr) doped in oxide crystals have been shown to improve the relational properties of oxide crystals (such as domain structure, electro-optical coefficients, light absorption, refractive indices, etc.). So the study of the electric and magnetic structures of Cr³⁺ complexes is an interesting and important problem. It is well known that, as for a d³ configuration ion in a trigonal ligand field, only the EPR and optical spectra

TABLE 1: Host Structures and the Local Lattice Structures of the (CrO₆)⁹⁻ Clusters in the Oxide Crystals with *D*_{3d} Symmetry Doped with Cr³⁺ Ions, *Dq* in Units of cm⁻¹

compound	<i>T</i> (K)	<i>Dq</i>	<i>R</i> ₀ (Å)	θ ₀ (deg)	<i>R</i> (Å)	θ (deg)	refs
ZnAl ₂ O ₄	300	1876	1.915	49.94	1.956	52.528	20
MgAl ₂ O ₄	300	1850	1.928	50.66	1.961	52.570	20
ZnGa ₂ O ₄	77	1840	1.988	50.66	1.970	53.510	20
Y ₃ Ga ₅ O ₁₂	77	1650	1.995	51.7	2.015	53.844	21
Y ₃ Al ₅ O ₁₂	77	1640	1.937	52.5	2.019	54.750	21
Be ₃ Al ₂ Si ₆ O ₁₈	300	1620	1.906		2.020	57.344	22
KAl(MoO ₄)	300	1497	2.000	53.64	2.051	53.601	23
RbSc(MoO ₄)	300	1445	2.007	48.97	2.062	55.909	24–25
KSc(MoO ₄)	300	1435	2.010	51.37	2.066	55.826	24–25
RbIn(MoO ₄)	300	1400	2.020	48.99	2.074	56.030	23

can get satisfactory explanation simultaneously, the related properties of d³ complexes can be determined by employing two distorted parameters. In this paper, local lattice structures of the trigonal octahedral (CrO₆)⁹⁻ clusters for Cr³⁺ ions doping in a variety of oxide crystals with *D*_{3d} or *C*_{3v} site symmetry have been investigated by employing two distorted parameters, respectively. The calculated results show that although the local lattice structures around the M (M = Al³⁺, Ga³⁺, Li⁺, Sc³⁺ etc.) ions in host crystals are obviously different, the local lattice structures of the octahedral (CrO₆)⁹⁻ clusters in a variety of oxide crystals doped with Cr³⁺ ions are similar and fluctuant in the vicinity of that of the Cr₂O₃. The sensitive relation between the crystal field strength *Dq* and the average values \bar{R} of Cr–O bond length will be analyzed further.

II. Theoretical Method

By employing the |L, M_L, S, M_S> basic function of a d³ configuration ion at trigonal symmetry site, we have constructed the complete energy matrix of the Hamiltonian^{11–12}

$$\hat{H} = \hat{H}_{\text{ee}} + \hat{H}_{\text{LF}} + \hat{H}_{\text{SO}} + \hat{H}_{\text{ZE}}$$

$$= \sum_{i < j} e^2/r_{ij} + \sum_i V_i + \zeta \sum_i l_i \cdot s_i + \mu_{\beta} \sum_i (k \bar{1}_i + g_e \bar{s}_i) \cdot \bar{H} \quad (1)$$

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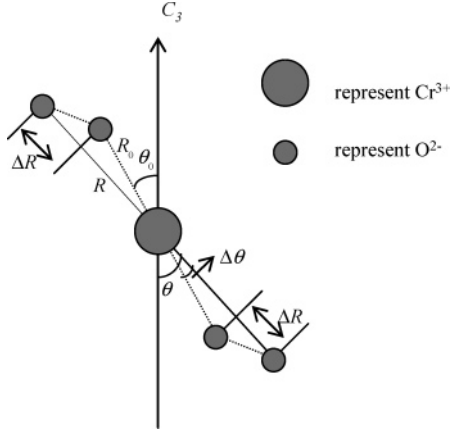


Figure 1. Local structure of octahedral Cr^{3+} centers in oxide crystals with D_{3d} symmetry. R_0 and θ_0 are the structure parameters of host crystals; R and θ are the impurity structure parameters. ΔR and $\Delta\theta$ represent the structure distortion.

TABLE 2: Racah Parameters B and C , the Spin–Orbit Coupling Coefficient ζ and the Orbit Reduction Factor k for Cr^{3+} Ion Doped in a Variety of Oxide Crystals with D_{3d} or C_{3v} Symmetry, with All Units in cm^{-1} Except for the Orbit Reduction Factor k

compound	B	C	ζ	k	refs
ZnAl_2O_4	700	3200	250	0.74	26
MgAl_2O_4	700	3200	250	0.58	26
ZnGa_2O_4	670	3230	250	0.76	27
$\text{Y}_3\text{Al}_5\text{O}_{12}$	650	3250	234	0.70	28
$\text{Y}_3\text{Ga}_5\text{O}_{12}$	570	3400	230	0.74	28
$\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}^a$	780	2960	225	0.70	29
$\text{KAl}(\text{MoO}_4)$	648	2917	227	0.66	30
$\text{RbSc}(\text{MoO}_4)$	681	2902	229	0.82	30
$\text{KSc}(\text{MoO}_4)$	681	2902	229	0.82	30
$\text{RbIn}(\text{MoO}_4)$	681	2902	229	0.81	30–31
Al_2O_3	650	3120	170	0.68	32–33
LiNbO_3	558	3204	195	0.82	34
LiTaO_3	667	3012	231	0.75	35
LiIO_3	668	2672	224	0.82	36–37

^a $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$; the Trees correction $\alpha = 70 \text{ cm}^{-1}$ is also employing in the calculation.

where \hat{H}_{ee} , \hat{H}_{LF} , \hat{H}_{SO} , and \hat{H}_{ZE} are, respectively, the electron–electron repulsion interaction, the ligand-field interaction, the spin–orbit coupling interaction, and the Zeeman interaction. ζ is the spin–orbit coupling coefficient, k is the orbit reduction factor and V_i is the ligand-field potential

$$V_i = \gamma_{00} Z_{00} + \gamma_{20} r_i^2 Z_{20}(\theta_i, \varphi_i) + \gamma_{40} r_i^4 Z_{40}(\theta_i, \varphi_i) + \gamma_{43}^c r_i^4 Z_{43}^c(\theta_i, \varphi_i) + \gamma_{43}^s r_i^4 Z_{43}^s(\theta_i, \varphi_i) \quad (2)$$

r_i , θ_i , and φ_i are the coordinates of the i th electron. According to the Hamiltonian (1), the 120×120 energy matrix for a d^3 configuration ion has been constructed. The matrix elements are functions of the Racah parameters B and C , the spin–orbit coupling coefficient ζ , and the ligand-field parameters that are of the forms for Cr^{3+} ions doping in a variety of oxide crystals with trigonal symmetry⁶

$$B_{20} = \frac{1}{2} \sum_{\tau} G_2(\tau)(3 \cos^2 \theta_{\tau} - 1),$$

$$B_{40} = \frac{1}{8} \sum_{\tau} G_4(\tau)(35 \cos^4 \theta_{\tau} - 30 \cos^2 \theta_{\tau} + 3),$$

TABLE 3: Comparison of Optical Spectra between the Theoretical and Experimental Values for Cr^{3+} Ions Doped in Oxide Crystals with D_{3d} Symmetry, where $A_4 = 36.35 \text{ a.u.}$ at Room Temperature and $A_4 = 36.53 \text{ a.u.}$ at Low Temperature (77 K), Respectively, with All Units in cm^{-1}

transitions	${}^4A_2 \rightarrow$	T (K)	2E	2T_1	4T_2	2T_2	4T_1
ZnAl_2O_4		300	14556	15098	18727	21573	26025
Expt ²⁶			14570	15837	20244	23340	26846
			14579		18756	23974	25832
MgAl_2O_4		300	14561	15106	18501	21555	25757
Expt ²⁶			14660	15824	19973	23273	26574
			14653	14812	18500	22100	25800
				15069		24100	
				15228			
ZnGa_2O_4		77	14613	15134	18427	21778	25308
Expt ²⁷			14549	15494	19186	22639	25749
			14589		18400	22000	23500
							25000
$\text{Y}_3\text{Ga}_5\text{O}_{12}$		77	14463	14879	16519	21463	22451
Expt ^{28,38–39}			14472	15108	17029	21995	22707
			14450	14793	16260	19305	22727
					16300		22730
					16500		
$\text{Y}_3\text{Al}_5\text{O}_{12}$		77	14555	15077	16425	21610	22915
Expt ^{28,40}			14544	15231	16732	21962	23138
			14564	15210	16400		23200
				15425	16700		
$\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$		300	14762	15322	15719	21537	23177
Expt ²⁹			14624	15951	16788	23243	24576
			14686	15140	15860	21037	23000
					16750		24000
$\text{KAl}(\text{MoO}_4)$		300	13436	13970	14992	19756	21292
Expt ³⁰				14288	15619	20507	21772
				13436	14972		21266
$\text{RbSc}(\text{MoO}_4)$		300	13585	14059	14460	20153	21185
				14394	14978	20817	21782
$\text{KSc}(\text{MoO}_4)$		300	13589	14070	14340	20135	21031
				14381	14823	20755	21589
$\text{RbIn}(\text{MoO}_4)$		300	13559	14024	14011	20052	20682
				14394	14570	20777	21359
Expt ³¹			13560	14395	14024		20053

$$B_{43}^c = \frac{\sqrt{35}}{4} \sum_{\tau} G_4(\tau) \cos \theta_{\tau} \sin^3 \theta_{\tau} \cos 3\phi_{\tau},$$

$$B_{43}^s = i \frac{\sqrt{35}}{4} \sum_{\tau} G_4(\tau) \cos \theta_{\tau} \sin^3 \theta_{\tau} \sin 3\phi_{\tau} \quad (3)$$

where

$$G_2(\tau) = -q_{\tau} e G^2(\tau), \quad G_4(\tau) = -q_{\tau} e G^4(\tau)$$

$$G^k(\tau) = \int_0^{R_{\tau}} R_{3d}^2(r) r^2 \frac{r^k}{R_{\tau}^{k+1}} dr + \int_{R_{\tau}}^{\infty} R_{3d}^2(r) r^2 \frac{R_{\tau}^k}{r^{k+1}} dr \quad (4)$$

In explicitly, the Zeeman term can be expressed by parallel or perpendicular component to the C_3 axis as follows:

$$H_{ZE}(\parallel) = \mu_{\beta} \sum_i (k l_{iz} + g_e s_{iz}) H_z$$

$$H_{ZE}(\perp) = \mu_{\beta} \sum_i (k l_{ix} + g_e s_{ix}) H_x \quad (5)$$

By using eq 5, the 120×120 complete energy matrix including the parallel and perpendicular components of Zeeman term for a d^3 configuration ion in a trigonal ligand field has been constructed.

TABLE 4: Zero-Field Splitting Parameters D and g Factors for Cr³⁺ Ions Doped in a Variety of Oxide Crystals with D_{3d} Symmetry as a Function of the Two Parameters ΔR and $\Delta\theta$ by Employing $A_4 = 36.35$ a.u. at Room Temperature and $A_4 = 36.53$ a.u. at Low Temperature (77 K), Respectively, $2D$ in Units of cm⁻¹

compound	T (K)	ΔR (Å)	$\Delta\theta$ (deg)	$2D$	$g_{ }$	g_{\perp}	$\Delta g (=g_{ } - g_{\perp})$
ZnAl ₂ O ₄	300	0.041	2.588	1.8553	1.9808	1.9739	0.0069
expt ⁴¹				1.8556	1.9807	1.9774	0.0033
MgAl ₂ O ₄	300	0.033	1.910	1.834	1.9851	1.9797	0.0054
expt ²⁶				1.830	1.9850	1.9830	0.0020
ZnGa ₂ O ₄	77	-0.018	2.850	1.048	1.9773	1.9733	0.0040
expt ²⁷				1.048	1.9774	1.9761	0.0013
Y ₃ Ga ₅ O ₁₂	77	0.020	2.144	0.6971	1.9766	1.9736	0.0030
expt ⁴²				0.697	1.9767	1.9757	0.0010
Y ₃ Al ₅ O ₁₂	77	0.082	1.675	0.4502	1.9766	1.9748	0.0018
expt ⁴³				0.4502	1.9765	1.9765	0.0000
Be ₃ Al ₂ Si ₆ O ₁₈	300	0.114	2.608	-1.780	1.9719	1.9786	-0.0067
expt ^{29,33}				-1.780	1.9730	1.9700	0.0030
KAl(MoO ₄)	300	0.051	-0.039	0.9598	1.9780	1.9742	0.0038
expt ⁴⁴				0.9596	1.9781	1.9727	0.0054
RbSc(MoO ₄)	300	0.055	6.939	-0.9634	1.9649	1.9694	-0.0045
expt ⁴⁵				-0.9632	1.9646	1.9683	-0.0037
KSc(MoO ₄)	300	0.056	4.456	-0.9029	1.9647	1.9690	-0.0043
expt ⁴⁶				-0.9030	1.9645	1.9693	-0.0048
RbIn(MoO ₄)	300	0.054	7.040	-1.078	1.9639	1.9690	-0.0051
expt ⁴⁷				-1.080	1.9640	1.9680	-0.0040

TABLE 5: Original Structures of the Oxide Crystals with C_{3v} Symmetry

compound	R_{10} (Å)	R_{20} (Å)	θ_{10} (deg)	θ_{20} (deg)	refs
Al ₂ O ₃	1.857	1.966	63.1	47.7	18
LiNbO ₃	1.889	2.112	61.65	47.99	48
LiTaO ₃	1.91	2.072	60.18	49.44	49
LiIO ₃	2.11	2.13	52.90	52.05	50

TABLE 6: Comparison of Optical Spectra between Theoretical and Experimental Values for Cr³⁺ Ions Doped in Oxide Crystals with C_{3v} Symmetry by Employing $A_4 = 36.35$ a.u. at Room Temperature and $A_4 = 36.53$ a.u. at Low Temperature (77 K), Respectively, with All Units in cm⁻¹

transitions	T (K)	2E	2T_1	4T_2	2T_2	4T_1
Al ₂ O ₃	77	14111	14570	18007	21441	24362
expt ³²⁻³³		14856	18273	21984	25607	
	300	14418	15168	18000	20993	24400
		14447	15190	18450	21068	25200
LiNbO ₃	77	13747	14009	15308	20394	20642
expt ³⁴		14384	15353	21136	21802	
	300	13790	14340	15300	20200	21000
LiTaO ₃		13897	14298	15288	20550	21591
	77	14637	15456	21256	22594	
expt ³⁵		13902	15291		21807	
	300	13972				
LiIO ₃		12758	13211	14313	19055	20986
	77		13635	14951	19878	21733
expt ³⁶⁻³⁷				13800		20200
			14400		20250	

The EPR spectra of Cr³⁺ ions in a trigonal ligand-field can be described by the spin Hamiltonian¹³

$$\hat{H}_S = g_{||}\mu_B H_z S_z + g_{\perp}\mu_B (H_x S_x + H_y S_y) + D[S_z^2 - (1/3)S(S+1)] \quad (6)$$

where, D is zero-field splitting parameter. From eq 1 the energy levels in the ground state 4A_2 without magnetic field are written as follows:

$$\begin{aligned} E(\pm 1/2) &= -D \\ E(\pm 3/2) &= D \end{aligned} \quad (7)$$

TABLE 7: Zero-Field Splitting Parameters D and g Factors for Cr³⁺ Ions Doped in a Variety of Oxide Crystals with C_{3v} Symmetry as a Function of the Two Parameters ΔR and ΔX by Employing $A_4 = 36.35$ a.u. at Room Temperature and $A_4 = 36.53$ a.u. at Low Temperature (77 K), Respectively, $2D$ in Units of cm⁻¹

compd	T (K)	ΔR (Å)	ΔX (Å)	$2D$	$g_{ }$	g_{\perp}	$\Delta g (=g_{ } - g_{\perp})$
Al ₂ O ₃	77	0.0419	0.02878	-0.3831	1.9858	1.9869	-0.0011
expt ⁵¹⁻⁵²				-0.383	1.9840	1.9867	-0.0027
LiNbO ₃	77	0.040	0.03583	-0.7730	1.9719	1.9753	-0.0034
expt ⁵³				-0.773	1.9720		
LiTaO ₃	300	0.0472	0.04665	-0.888	1.9696	1.9728	-0.0032
expt ⁴²				-0.888	1.9720		
LiIO ₃	77	-0.054	0.0359	-1.2198	1.9647	1.9704	-0.0057
expt ⁵⁴				-1.2198	1.9650	1.9710	-0.0060

TABLE 8: Local Lattice Structures of the (CrO₆)⁹⁻ Clusters in a Oxide Crystals with C_{3v} Symmetry Doped with Cr³⁺ Ions, Dq in Units of cm^{-1a}

compd	T (K)	Dq	R_1 (Å)	R_2 (Å)	θ_1 (deg)	θ_2 (deg)	\bar{R} (Å)	$\bar{\theta}_a$ (deg)
Al ₂ O ₃	77	1800	1.8989	2.0079	62.530	47.610	1.9534	55.070
LiNbO ₃	77	1530	1.9290	2.1520	61.690	48.230	2.0405	54.960
LiTaO ₃	300	1529	1.9572	2.1192	60.520	49.890	2.0382	55.205
LiIO ₃	77	1430	2.054	2.0740	56.723	55.730	2.0640	56.227
Cr ₂ O ₃			1.967	2.018	61.4	49.0	1.9925	55.20

^a $A_4 = 36.35$ a.u. at Room Temperature and $A_4 = 36.53$ a.u. at Low Temperature (77 K) are employed in the calculation, in units of cm⁻¹.

The corresponding ground-state zero-field splitting ΔE can be expressed as a function of the parameter D

$$\Delta E = E(\pm 3/2) - E(\pm 1/2) = 2D \quad (8)$$

Based on eqs 3 and 8, the relationship between the local lattice structures of the octahedral Cr³⁺ centers in oxide crystals with D_{3d} or C_{3v} site symmetry and its EPR parameters as well as the optical spectra can be investigated by means of the complete energy matrix, respectively.

III. Theoretical Calculations

1. Local Lattice Structures of the Octahedral (CrO₆)⁹⁻ Clusters for Cr³⁺ ion Doping in Oxide Crystals with D_{3d} Site Symmetry. Be₃Al₂Si₆O₁₈, ZnAl₂O₄, MgAl₂O₄, Y₃Al₅O₁₂,

TABLE 9: EPR Parameters D and g Factors and the Energy Transition ${}^4A_2 \rightarrow {}^4T_2$ for Cr^{3+} Ions Doped in Oxide Crystals with C_{3v} Symmetry as a Function of the Two Parameters ΔR and ΔX by Employing $A_4 = 36.12$ a.u., $2D$ in Units of cm^{-1}

compound	ΔR (Å)	ΔX (Å)	$2D$	g_{\parallel}	g_{\perp}	${}^4A_2 \rightarrow {}^4T_2$ (cm^{-1})
Al_2O_3	0.0374	0.02500	-0.3823	1.9858	1.9869	18003 18274
expt ^{32-33,51-52}			-0.3830	1.9840	1.9867	18000 18450
LiNbO_3	0.0354	0.03200	-0.7729	1.9719	1.9753	15308 15350
expt ^{34,53}			-0.7730	1.9720		15300
LiTaO_3	0.0445	0.0444	-0.887	1.9696	1.9728	15293 15459
expt ^{35,42}			-0.888	1.9720		15291
LiIO_3	-0.0584	0.03235	-1.2197	1.9647	1.9704	14304 14941
expt ^{36-37,54}			-1.2198	1.9650	1.9710	13800 14400

TABLE 10: EPR Parameters D and g Factors and the Energy Transition ${}^4A_2 \rightarrow {}^4T_2$ for Cr^{3+} Ions Doped in Oxide Crystals with D_{3d} Symmetry as a Function of the Two Parameters ΔR and $\Delta\theta$ by Employing $A_4 = 36.12$ a.u., $2D$ in Units of cm^{-1}

compound	ΔR (Å)	$\Delta\theta$ (deg)	$2D$	g_{\parallel}	g_{\perp}	${}^4A_2 \rightarrow {}^4T_2$ (cm^{-1})
ZnAl_2O_4	0.038	2.581	1.8557	1.9808	1.9739	18752 20269
expt ^{26,41}			1.8556	1.9807	1.9774	18756
MgAl_2O_4	0.0306	1.910	1.830	1.9851	1.9797	18499 19965
expt ²⁶			1.830	1.9850	1.9830	18500
ZnGa_2O_4	-0.0218	2.847	1.048	1.9773	1.9733	18397 19153
expt ²⁷			1.048	1.9774	1.9761	18400
$\text{Y}_3\text{Ga}_5\text{O}_{12}$	0.016	2.141	0.6973	1.9766	1.9736	16497
						17005
expt ^{28,38-39,42}			0.6970	1.9767	1.9757	16300 16500
$\text{Y}_3\text{Al}_5\text{O}_{12}$	0.078	1.673	0.4504	1.9766	1.9748	16403 16708
expt ^{28,40,43}			0.4502	1.9765	1.9765	16400 16700
$\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$	0.111	2.615	-1.780	1.9719	1.9786	15737 16805
expt ^{29,33}			-1.780	1.9730	1.9700	15860 16750
$\text{KAl}(\text{MoO}_4)$	0.049	-0.040	0.9594	1.9780	1.9742	14970 15595
expt ^{30,44}			0.9596	1.9781	1.9727	14972
$\text{RbSc}(\text{MoO}_4)$	0.0527	6.941	-0.9634	1.9649	1.9694	14449 14967
expt ⁴⁵			-0.9632	1.9646	1.9683	
$\text{KSc}(\text{MoO}_4)$	0.053	4.459	-0.9029	1.9647	1.9690	14354 14837
expt ⁴⁶			-0.9030	1.9645	1.9693	
$\text{RbIn}(\text{MoO}_4)$	0.050	7.050	-1.083	1.9639	1.9690	14022 14584
expt ^{31,47}			-1.080	1.9640	1.9680	14024

$\text{KAl}(\text{MoO}_4)$, ZnGa_2O_4 , $\text{Y}_3\text{Ga}_5\text{O}_{12}$, $\text{RbSc}(\text{MoO}_4)$, $\text{KSc}(\text{MoO}_4)$, and $\text{RbIn}(\text{MoO}_4)$ possess the D_{3d} point symmetry. When Cr^{3+} ions are doped in oxide crystals, the Cr^{3+} ion will replace the host ions (Al^{3+} , Ga^{3+} , Sc^{3+} , or In^{3+}). Cr^{3+} ion is surrounded by an oxygen octahedron which is distorted along the 3-fold axis. In the calculation, we choose the projection of one of the Cr–O bond in x – y plane along x axis. In this case, the B_{43}^s term is zero, and the ligand field parameters can be written as

$$\begin{aligned}
 B_{20} &= 3G_2(\tau)(3 \cos^2 \theta - 1) \\
 B_{40} &= (3/4)G_4(\tau)(35 \cos^4 \theta - 30 \cos^2 \theta + 3) \\
 B_{43}^c &= (3\sqrt{35}/2)G_4(\tau) \cos \theta \sin^3 \theta
 \end{aligned} \quad (9)$$

According to the van Vleck approximation for $G^k(\tau)$ integral,¹⁴ we may get the following relations:

$$G_2(\tau) = \frac{A_2}{R_\tau^3}, \quad G_4(\tau) = \frac{A_4}{R_\tau^5} \quad (10)$$

where $A_2 = -eq_\tau \langle r^2 \rangle$, $A_4 = -eq_\tau \langle r^4 \rangle$, and $A_2/A_4 = \langle r^2 \rangle / \langle r^4 \rangle$. The ratio of $\langle r^2 \rangle / \langle r^4 \rangle = 0.151227$ for Cr^{3+} may be obtained from the parametric radial wave function.¹⁵ The value of A_4 can be determined from the optical spectra and real local structure parameters of $(\text{CrO}_6)^{9-}$ in different crystals. Herein, both the obviously different symmetry systems Cr_2O_3 and $\text{MgO}:\text{Cr}^{3+}$ are

$$R_2 = R_{20} + \Delta R$$

taken in our analysis. We derive $A_4 = 36.12$ a.u. for $(\text{CrO}_6)^{9-}$ in MgO :¹⁶⁻¹⁷ Cr^{3+} and $A_4 = 36.35$ a.u. as well as $A_4 = 36.53$ a.u., respectively for the $(\text{CrO}_6)^{9-}$ cluster in Cr_2O_3 ¹⁸⁻¹⁹ at room temperature and the low temperature (77 K). Also, the influences of the different A_4 value from different symmetry systems Cr_2O_3 and $\text{MgO}:\text{Cr}^{3+}$ on the precision of the structure parameters are analyzed in the following. Correspondingly, the trigonal distortion can be described by means of two parameters ΔR and $\Delta\theta$, as plotted in Figure 1. Thus the impurity structural parameters R and θ can be expressed as

$$\begin{aligned}
 R &= R_0 + \Delta R \\
 \theta &= \theta_0 + \Delta\theta
 \end{aligned} \quad (11)$$

where, R_0 and θ_0 denote the M–O ($M = \text{Al}, \text{Ga}, \text{Sc}, \text{In}$) bond length and the angle between M–O bond and the C_3 axis, respectively, and the values are listed in Table 1 (see refs 20–25). As for the Racah parameters B and C , the spin–orbit coupling coefficient ζ , and the orbit reduction factors k , the classical values are taken that approved by many researchers,²⁶⁻³⁷ which are listed in Table 2. As for the orbit reduction factor k , the slightly adjusted value from the formula $k \approx N^2 = (\sqrt{B/B_0} + \sqrt{C/C_0})/2$ or the classical value $k = 0.7^{28,32-33}$ has been made in order to obtain the precise calculations of the g factors (g_{\parallel}, g_{\perp}). By diagonalizing the complete energy matrix with trigonal symmetry and employing the above parameters, the optical and EPR spectra of the octahedral $(\text{CrO}_6)^{9-}$ clusters for the Cr^{3+} ion doping in different oxide crystals with D_{3d} site symmetry are simulated by employing two distortion parameters ΔR and $\Delta\theta$, and the results are listed in Tables 1, 3, 4, and 10.

TABLE 11: Comparison of Theoretical Structure Parameters (or Average Values) to Different A₄ Values for Cr³⁺ Ions Doped in Oxide Crystals with D_{3d} (or C_{3v}) Symmetry

compound	R(\bar{R}) (Å)		$\Delta R'$ (Å)	θ ($\bar{\theta}$) (deg)		$\Delta\theta'$ (deg)
	A ₄ (a.u.)			A ₄ (a.u.)		
	(a) 36.35	36.12		(a)36.35	36.12	
	(b) 36.53			(b)36.53		
ZnAl ₂ O ₄	1.956(a)	1.9530	0.0030	52.528(a)	52.521	0.007
MgAl ₂ O ₄	1.961(a)	1.9586	0.0024	52.570(a)	52.570	0.000
ZnGa ₂ O ₄	1.970(b)	1.9662	0.0038	53.510(b)	53.507	0.003
Y ₃ Ga ₁₅ O ₁₂	2.015(b)	2.011	0.0040	53.844(b)	53.841	0.003
Y ₃ Al ₁₅ O ₁₂	2.019(b)	2.015	0.0040	54.175(b)	54.173	0.002
Be ₃ Al ₂ Si ₆ O ₁₈ ^a	2.020(a)	2.017	0.0030	57.344(a)	57.351	0.007
KAl(MoO ₄)	2.051(a)	2.049	0.0020	53.601(a)	53.600	0.001
RbSc(MoO ₄)	2.062(a)	2.0597	0.0033	55.909(a)	55.911	0.002
KSc(MoO ₄)	2.066(a)	2.063	0.0030	55.826(a)	55.829	0.003
RbIn(MoO ₄)	2.074(a)	2.070	0.0040	56.030(a)	56.040	0.010
Al ₂ O ₃	1.9534(b)	1.9489	0.0045	55.070(b)	55.067	0.003
LiNbO ₃	2.0405(b)	2.0359	0.0046	54.960(b)	54.960	0.000
LiTaO ₃	2.0382(a)	2.0355	0.0027	55.205(a)	55.203	0.002
LiIO ₃	2.0640(b)	2.0616	0.0024	56.227(b)	56.228	0.001

^a Be₃Al₂Si₆O₁₈, the Trees correction $\alpha = 70 \text{ cm}^{-1}$ is also employing in the calculation.

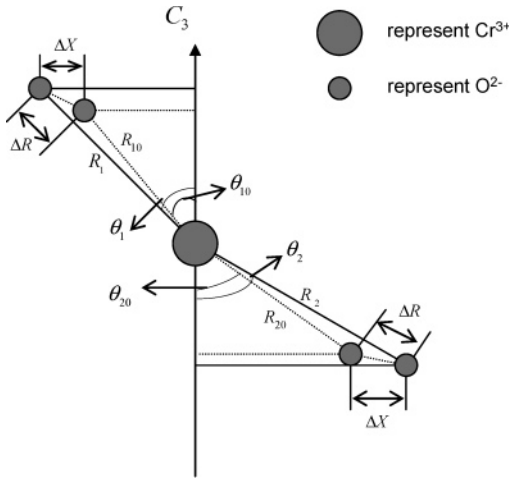


Figure 2. New model is used to describe the local structure of octahedral Cr³⁺ centers in oxide crystals with C_{3v} symmetry. R₁₀, R₂₀, θ_{10} , and θ_{20} are the structure parameters of the host crystals; R₁, R₂, θ_1 , and θ_2 are the impurity structure parameters. ΔR and ΔX denote the structure distortion.

2. Local Lattice Structures of the Octahedral (CrO₆)⁹⁻ Clusters for Cr³⁺ Ion Doping in Oxide Crystals with C_{3v} Site Symmetry. Al₂O₃, LiIO₃, LiTaO₃, and LiNbO₃ have the same point symmetry C_{3v}. When Cr³⁺ ions are doped in oxide crystals, the Cr³⁺ ion will replace the host ions (Al³⁺, Li⁺, Ta⁵⁺, or Nb⁵⁺). The Cr³⁺ ion is surrounded by six oxygen ions which form an octahedron with a distortion along one of the C₃ axes. Similarly, the ligand field parameters may be written as

$$B_{20} = (3/2)[G_2(p_1)(3 \cos^2 \theta_1 - 1) + G_2(p_2)(3 \cos^2 \theta_2 - 1)]$$

$$B_{40} = (3/8)[G_4(p_1)(35 \cos^4 \theta_1 - 30 \cos^2 \theta_1 + 3) + G_4(p_2)(35 \cos^4 \theta_2 - 30 \cos^2 \theta_2 + 3)]$$

$$B_{43}^c = (3\sqrt{35}/4)[G_4(p_1) \cos \theta_1 \sin^3 \theta_1 + G_4(p_2) \cos \theta_2 \sin^3 \theta_2] \quad (12)$$

where $G_2(p_i)$ and $G_4(p_i)$ are expressed as

$$G_2(p_i) = -qeG^2(p_i)$$

$$G_4(p_i) = -qeG^4(p_i) \quad (13)$$

$$G^k(p_i) = \int_0^{R_{pi}} R_{3d}^2(r)r^2 \frac{r^k}{R_{pi}^{k+1}} dr + \int_{R_{pi}}^{\infty} R_{3d}^2(r)r^2 \frac{R_{pi}^k}{r^{k+1}} dr \quad (14)$$

p_1 and p_2 represent the ligand ions in the up and down three-edge-pyramids in oxide crystals and θ_1 and θ_2 represent the corresponding angles between metal–ligand bonds and the C₃ axis. Since the bond lengths of two three-edge-pyramids in oxide crystals are not the same, we may predict that

$$G_2(p_1) \neq G_2(p_2)$$

$$G_4(p_1) \neq G_4(p_2) \quad (15)$$

Similarly, $G_2(P_i)$ and $G_4(P_i)$ can be written as

$$G_2(P_i) = \frac{A_2}{R_{pi}^3}, \quad G_4(P_i) = \frac{A_4}{R_{pi}^5} \quad (16)$$

where the definitions of the A₂ and A₄ are the same as the above, in order to explain the trigonal distortion of impurity structure with C_{3v} symmetry reasonably, a new model is proposed, as shown in Figure 2. So the local structure parameters R₁, R₂, θ_1 , and θ_2 for Cr³⁺ replacing the host ions in octahedral (CrO₆)⁹⁻ complexes can be expressed as a function of the ΔR and ΔX

$$R_1 = R_{10} + \Delta R, \quad R_2 = R_{20} + \Delta R$$

$$\theta_1 = \arcsin\left(\frac{R_{10} \sin(\theta_{10}) + \Delta X}{R_1}\right)$$

$$\theta_2 = \arcsin\left(\frac{R_{20} \sin(\theta_{20}) + \Delta X}{R_2}\right) \quad (17)$$

where R₀ and θ_0 denote the M–O (M = Al, Li, Nb, and Ta) bond length and the angle between M–O bond and the C₃ axis, respectively, and the values are listed in Table 5 [see refs 18 and 48–50]. As for the electrostatic parameters B and C, ζ and the orbit reduction factor k are also listed in Table 2. Using those parameters, the zero-field splitting parameter D, EPR g factors g_{||} and g_⊥, and optical spectra as a function of ΔR and ΔX are calculated by diagonalizing the complete energy matrix, and the results are listed in Tables 6–9.

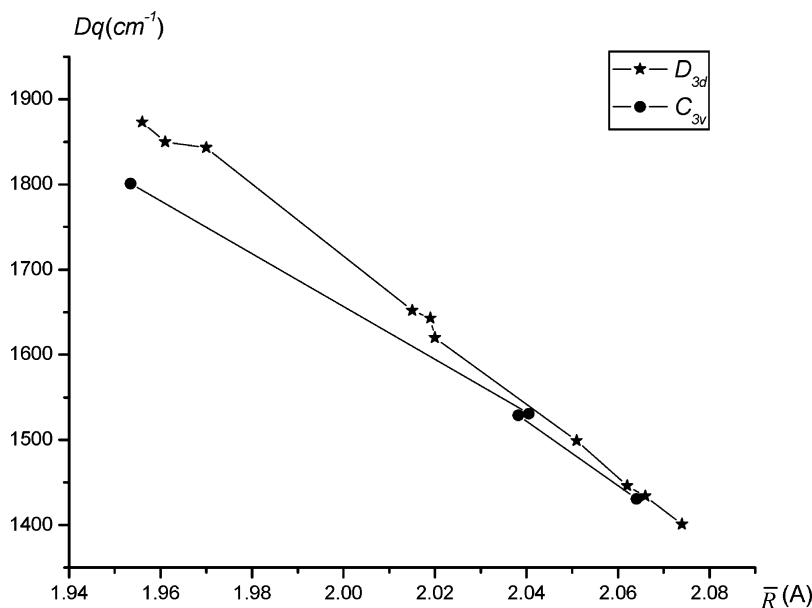


Figure 3. Theoretical values of Dq for $(\text{CrO}_6)^{9-}$ clusters plotted against the corresponding the average values \bar{R} of Cr–O bond length in oxide crystals with C_{3v} or D_{3d} symmetry.

From Tables 3, 4, 6, 7, 9, and 10, one can see that, when Cr^{3+} ion doping in a variety of oxide crystals with D_{3d} or C_{3v} site symmetry, the experimental findings of the zero-field splitting parameters, D , EPR g factors, g_{\parallel} and g_{\perp} , and optical spectra can be satisfactorily explained by corresponding distortion parameters, respectively. Moreover, it is indicated that the sign of the zero-field splitting D are consistent with that of the Δg . Correspondingly, the local structure parameters can also be determined, which are listed in Tables 1 and 8, respectively. According to Tables 1 and 8, the function of Dq vs \bar{R} is shown in Figure 3. It is shown that the average values of \bar{R} of Cr–O bond length decrease with the crystal field strength Dq rising except for the influence of the temperature in oxide crystals with C_{3v} or D_{3d} symmetry, which is consistent with the universal relation $Dq \propto 1/R^n$ ($n > 4$). It is further indicated that the calculated values of the Cr–O bond length for Cr^{3+} ion doping in a variety of oxide crystals with D_{3d} or C_{3v} site symmetry are reasonable.

From Tables 1, 8 and 11, we can see that the bond length of the octahedral $(\text{CrO}_6)^{9-}$ clusters and the angles between the M–O bond and C_3 axis are variational irregularly. However, although the local lattice structures around the M ($M = \text{Al}^{3+}$, Ga^{3+} , Li^+ , Sc^{3+} , etc.) ions in host crystals are obviously different, the local lattice structures of the octahedral $(\text{CrO}_6)^{9-}$ cluster in a variety of oxide crystals doped with Cr^{3+} ions are similar and fluctuant in the vicinity of that of the Cr_2O_3 . This may be ascribed to the fact that there is the similarly octahedral $(\text{CrO}_6)^{9-}$ clusters in a variety of oxide crystals doped with Cr^{3+} and the Cr_2O_3 crystal.

Moreover, from Table 11, both A_4 values derived from two different environments (Cr_2O_3 and $\text{MgO}:\text{Cr}^{3+}$) are applied to determine the local lattice structure of the octahedral $(\text{CrO}_6)^{9-}$ cluster, and the results show that the influences of the assumption A_4 on the precision of the structure parameters is very small and may be neglected. Furthermore, because the octahedral $(\text{CrO}_6)^{9-}$ cluster in the Cr_2O_3 crystal approaches the ideal $(\text{CrO}_6)^{9-}$ cluster, we suggest that the value of A_4 obtained from the Cr_2O_3 crystal should be employed in this calculation. In order to clarify the assumption in detail, careful experimental and theoretical investigations will be required to study a series of crystals in the future.

IV. Conclusions

Local lattice structures of Cr^{3+} complexes have been investigated on the basis of the complete energy matrix by studying the EPR and optical spectra simultaneously. The calculated results show that, although the local lattice structures around the M ($M = \text{Al}^{3+}$, Ga^{3+} , Li^+ , Sc^{3+} , etc.) ions in host crystals are obviously different, the local lattice structures of the octahedral $(\text{CrO}_6)^{9-}$ cluster in a variety of oxide crystals doped with Cr^{3+} ions fluctuate in the vicinity of that of the Cr_2O_3 . Moreover, the relation between crystal field strength Dq and the average values \bar{R} of Cr–O bond length derived from the calculated values is consistent with the universal relation $Dq \propto 1/R^n$ ($n > 4$), which further verifies that our results are reasonable.

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