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Spin-Hamiltonian parameters and local structures of the tetragonal $(CrO_4)^{3-}$ clusters in Cr^{5+}-doped KDP-type crystals

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ABSTRACT

The spin-Hamiltonian parameters (*g* factors $g_{//}$, $g_{\perp}$ and hyperfine structure constants $A_{//}$, $A_{\perp}$) of tetragonal $(CrO_4)^{3-}$ clusters in Cr^{5+}-doped KDP-type crystals KH_2PO_4, KD_2PO_4, $NH_4H_2PO_4$, $ND_4D_2PO_4$, KH_2AsO_4, KD_2AsO_4 and NH_4AsO_4 are calculated from the high-order perturbation formulas based on the two-mechanism model for the elongated d^1 tetrahedral clusters in crystals with the ground state $|d_{x^2-y^2}\rangle$. In the model, the contributions to spin-Hamiltonian parameters from both the crystal field (CF) mechanism and the charge-transfer (CT) mechanism (the latter is neglected in the widely-applied CF theory) are included. On the basis of the calculated values and by taking account of the small admixture of the first excited state $|d_{z^2}\rangle$ to the ground state $|d_{x^2-y^2}\rangle$ due to the vibrational motion of ligands (this dynamic effect leads a twinkling elongated tetrahedron to become a compressed one), all the calculated spin-Hamiltonian parameters are in reasonable agreement with the experimental values. The difficulty in the explanation of spin-Hamiltonian parameters by using the conventional static contributions for these Cr^{5+}-doped KDP-type crystals are overcome, and the impurity-induced static local structures of $(CrO_4)^{3-}$ clusters (which are different from the corresponding ones in the host crystals) in KDP-type crystals are estimated. The results are discussed.

1. Introduction

KH_2PO_4 (KDP) is a well-known nonlinear optical (NLO) material and has been applied as laser frequency conversion, harmonic generation for higher pulse, low repetition rate lasers, electro-optical modulation, and Q-switching applications [1–4]. Because of the high laser damage threshold, KDP and deuterated KD_2PO_4 (DKDP) crystals are still the only NLO crystals used to laser radiation conversion in laser fusion systems [1,2]. So, the studies of pure and doped KDP-type crystals are of interest. The electron paramagnetic resonance (EPR) spectra of Cr^{5+}-doped KDP-type crystals KH_2PO_4, KD_2PO_4, $NH_4H_2PO_4$, $ND_4D_2PO_4$, KH_2AsO_4, KD_2AsO_4 and $NH_4H_2AsO_4$ were measured at room temperature paramagnetic phase of these crystals [5]. These measurements suggested that Cr^{5+} ions occupy the tetrahedral P^{5+} or As^{5+} sites to form the tetragonal $(CrO_4)^{3-}$ clusters in the KDP-type crystals, and their spin-Hamiltonian parameters (*g* factors $g_{//}$, $g_{\perp}$ and hyperfine structure constants $A_{//}$, $A_{\perp}$) were reported [5]. There are two unusual points related to these spin-Hamiltonian parameters: (i) The observed $g_{//} < g_{\perp}$ and $A_{//} > A_{\perp}$ (see Table 1) for all these Cr^{5+}-doped KDP-type crystals show that the ground state of Cr^{5+} ion must be mainly the $|d_{x^2-y^2}\rangle$, corresponding to the $(CrO_4)^{3-}$ tetrahedral clusters being tetragonally-elongated (i.e., $\alpha < \alpha_0$, where α is the angle between the metal–ligand distance *R* and C_4 axis, $\alpha_0 \approx 54.74°$ is the same angle in cubic tetrahedron). However, the $(PO_4)^{3-}$ or $(AsO_4)^{3-}$ clusters replaced by $(CrO_4)^{3-}$ clusters in the host KDP-type crystals are tetragonally-compressed (i.e., $\alpha_h > \alpha_0$ [6–10], see Table 2), suggesting that the ground state of Cr^{5+} ion is mainly the $|d_{z^2}\rangle$. The difference of tetragonal distortion property (elongation or compression) between the substitutional impurity clusters and the host clusters is due to the impurity-induced local lattice relaxation. In fact, similar difference can be found for other d^n impurity clusters in crystals. For example, in Cr^{5+}-doped YMO_4 (M = V, P) crystals, the observed *g* factors showed that the tetrahedral cluster changes from tetragonal elongation in the host crystal to tetragonal compression in the impurity center [11,12]. (ii) For d^1 tetrahedral clusters with the ground state $|d_{x^2-y^2}\rangle$, from the dominant second-order perturbation formulas in the conventional crystal-field (CF) theory, we have [13]

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Table 1
The spin-Hamiltonian parameters (g factors $g_{//}$, $g_{\perp}$, and hyperfine structure constants $A_{//}$, $A_{\perp}$, A_i are in units of 10^{-5} cm^{-1}) for the tetragonal $(CrO_4)^{3-}$ clusters in Cr^{5+}-doped KDP-type crystals.

	KH_2PO_4	KD_2PO_4	$NH_4H_2PO_4$	$ND_4D_2PO_4$	KH_2AsO_4	KD_2AsO_4	$NH_4H_2AsO_4$
$\Delta g_{//}^{CF}$	−0.1152	−0.1152	−0.1173	−0.1161	−0.1175	−0.1173	−0.1195
$\Delta g_{//}^{CT}$	0.0548	0.0548	0.0540	0.0545	0.0566	0.0567	0.0561
$g_{//}^{(elong.)}$	1.9419	1.9419	1.9390	1.9406	1.9414	1.9417	1.9388
$g_{//}$ (Calc.)	1.9560	1.9561	1.9560	1.9558	1.9559	1.9560	1.9561
$g_{//}$ (Expt. [5])	1.9560(5)	1.9561(5)	1.9560(5)	1.9558(5)	1.9559(5)	1.9560(5)	1.9561(5)
$\Delta g_{\perp}^{CF}$	−0.0273	−0.0273	−0.0279	−0.0275	−0.0275	−0.0274	−0.0280
$\Delta g_{\perp}^{CT}$	0.0107	0.0107	0.0105	0.0106	0.0110	0.0110	0.0109
$g_{\perp}^{(elong.)}$	1.9857	1.9857	1.9849	1.9854	1.9858	1.9860	1.9852
$g_{\perp}$ (Calc.)	1.9759	1.9758	1.9740	1.9752	1.9758	1.9760	1.9740
$g_{\perp}$ (Expt. [5])	1.9759(5)	1.9758(5)	1.9740(5)	1.9752(5)	1.9758(5)	1.9760(5)	1.9740(5)
$A_{//}^{(1)}$	365	361	370	360	375	361	372
$A_{//}^{(2)CF}$	50	50	52	52	49	49	50
$A_{//}^{(2)CT}$	−11	−11	−11	−11	−12	−12	−12
$A_{//}^{(elong.)}$	404	400	410	400	412	398	411
$A_{//}$(Calc.)	273	269	259	264	276	268	257
$A_{//}$(Expt.[5])	271(10)	266(5)	257(5)	262(5)	271(9)	267(5)	257(5)
$A_{\perp}^{(1)}$	18	14	22	14	42	29	37
$A_{\perp}^{(2)CF}$	8	8	9	9	8	8	9
$A_{//}^{(2)CT}$	−2	−2	−2	−2	−2	−2	−2
$A_{\perp}^{(elong.)}$	24	20	29	20	48	35	44
$A_{\perp}$(Calc.)	72	70	82	72	90	80	93
$A_{\perp}$(Expt.[5])	93(37)	93(37)	93(37)	93(37)	93(37)	93(37)	93(37)

Table 2
Structural data, group overlap integrals, cubic field parameters, covalence parameters, core polarization constants and admixture angles for the $(CrO_4)^{3-}$ clusters in Cr^{5+}-doped KDP-type crystals.

	KH_2PO_4	KD_2PO_4	$NH_4H_2PO_4$	$ND_4D_2PO_4$	KH_2AsO_4	KD_2AsO_4	$NH_4H_2AsO_4$
R_h (Å)	1.525 [6]	1.525 [6]	1.539 [7]	1.539 [8]	1.686 [9]	1.686 [9]	1.675 [10]
R (Å)	1.613	1.613	1.627	1.627	1.691	1.691	1.680
α_h (deg.)	54.91 [6]	55.23 [6]	55.74 [7]	55.48 [8]	54.93 [9]	54.92 [9]	55.49 [10]
α (deg.)	54.68	54.68	54.70	54.68	54.62	54.61	54.64
S_{dp} (σ)	−0.1399	−0.1399	−0.1364	−0.1364	−0.1205	−0.1205	−0.1232
S_{dp} (π)	0.0512	0.0512	0.0491	0.0491	0.0404	0.0404	0.0418
Dq (cm^{-1})	1350	1350	1300	1300	1250	1250	1250
f_{γ}	0.532	0.532	0.54	0.535	0.502	0.501	0.51
κ	0.33	0.32	0.34	0.32	0.395	0.36	0.38
θ (deg.)	31.5	31.6	33.9	32.4	32.4	31.6	34.2

$$g_{//} \approx g_e - \frac{8k\zeta}{E_1}, \qquad g_{\perp} \approx g_e - \frac{2k\zeta}{E_2} \tag{1}$$

In which $g_e \approx 2.0023$ is the free-electron g value. The CF energy levels [13].

$$E_1 = 10Dq, \qquad E_2 = 10Dq - 3Ds + 5Dt, \tag{2}$$

where Dq is the cubic field parameter, and Ds and Dt are the tetragonal field parameters. The difference between E_1 and E_2 is generally small because the tetrahedral distortion of d^1 tetrahedral clusters in crystals is often not too large. Thus, the ratio $\Delta g_{//}/\Delta g_{\perp} \approx 4$ (where $\Delta g_i \approx g_i - g_e$, $i = //$ or $\perp$). However, the observed ratios $\Delta g_{//}/\Delta g_{\perp}$ ($\approx$1.6 (2), see Table 1) for Cr^{5+}-doped KDP-type crystals are much smaller than 4. The large disparity of ratio $\Delta g_{//}/\Delta g_{\perp}$ suggests that there may be small admixture of the first excited state $|d_{z^2}\rangle$ to the ground state $|d_{x^2-y^2}\rangle$. However, the investigations of molecular energy scheme showed that the static tetrahedral (D_{2d}) CF cannot give rise to the admixture [11,14]. So, until now no theoretical explanations for these spin-Hamiltonian parameters in Cr^{5+}-doped KDP-type crystals have been made. It is noted that although the static effect cannot result in the above admixture, a dynamic effect due to the vibrational motion of ligands may lead to the admixture. For instance, for some tetragonally-compressed Cu^{2+} ($3d^9$, the complementary ion of $3d^1$) octahedral clusters in crystals with the ground state $|d_{z^2}\rangle$, a dynamic effect due to the vibrational motion of ligands (which can lead a twinkling compressed octahedron to become an elongated one) was suggested to explain the observed $g_{//} > g_e$ (note: from the high-order perturbation formula $g_{//} \approx g_e - \frac{3\zeta^2(g_e-k)}{E_1^2}$ [12,15], $g_{//}$ should be smaller slightly than g_e) [15–17]. Specially, in the above $(CrO_4)^{3-}$ tetrahedral clusters in YMO_4 crystals, the dynamic effect of vibrational motion of ligands leads a twinkling compressed $(CrO_4)^{3-}$ tetrahedron to be an elongated one [12]. This twinkling elongation can give rise to the small admixture between $|d_{x^2-y^2}\rangle$ and $|d_{z^2}\rangle$ states. Thus, the observed g_i ($i = //$ or $\perp$) factors are averaged in time for $g_i^{(comp.)}$ (corresponding the ground state $|d_{z^2}\rangle$) and $g_i^{(elong.)}$ (corresponding to the ground state $|d_{x^2-y^2}\rangle$), and the large derivations of $g_{//}$ from g_e for tetragonal $(CrO_4)^{3-}$ clusters in YMO_4 crystals are explained reasonably [12].

Similarly, in this paper, we study the spin-Hamiltonian parameters of the tetrahedral $(CrO_4)^{3-}$ clusters in Cr^{5+}-doped KDP-type crystals by considering the dynamic effect due to the vibrational motion of ligands. The effect leads a twinkling elongated $(CrO_4)^{3-}$ tetrahedron to be a compressed one. Thus, the ground state is the admixture of the main $|d_{x^2-y^2}\rangle$ state with the $|d_{z^2}\rangle$ state, i.e., [12,16,17]

$$|\varphi\rangle = \cos\theta|d_{x^2-y^2}\rangle + \sin\theta|d_{z^2}\rangle \tag{3}$$