

Spin–Spin and Spin–Other-Orbit Interactions of Spin-Hamiltonian Parameters for $3d^{2(8)}$ Ions in Al_2O_3 Crystals

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By considering weaker magnetic interactions (including spin–spin and spin–other-orbit interactions) in Hamiltonian, the spin-Hamiltonian parameters, including the zero-field splitting parameter D and g factors (g_{\parallel}, g_{\perp}) for $3d^{2(8)}$ ions in Al_2O_3 crystals have been investigated. The results show that the contributions to D , g_{\parallel} and g_{\perp} from the spin–orbit interaction are dominant. The contributions from weaker magnetic interactions to D decrease (increase) with increasing charge of impurity ions for $3d^2$ ($3d^8$) ions.

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1. Introduction

In past decades, a large number of theoretical and experimental investigations have been reported on the EMR spectra and spin-Hamiltonian parameters of iron group ions in Al_2O_3 [1–16]. In Al_2O_3 host crystal, Al^{3+} is located at octahedral trigonal symmetry site surrounded by six O^{2-} ions. When transition metal (TM) ions are doped into Al_2O_3 crystal for replacing Al^{3+} ions, impurity defect centers are created. The spin-Hamiltonian (SH) parameters, including the zero field splitting (ZFS) parameter D and g factors (g_{\parallel}, g_{\perp}), have been determined for V^{3+} and Cr^{4+} ($3d^2$) ions in Al_2O_3 crystals in [8, 14, 15], whereas for Ni^{2+} and Cu^{3+} ($3d^8$) ions in [3, 17]. The SH parameters of Ni^{2+} and Cu^{3+} ions in Al_2O_3 crystals were explained theoretically based on the spin–orbit (SO) mechanism in [1, 2]. With considering spin–spin (SS) and spin–other-orbit (SOO) interactions, Rudowicz et al. have studied V^{3+} ($3d^2$) and Ni^{2+} ($3d^8$) ions in some crystals [13, 18–20]. They found that, for $3d^2$ and $3d^8$ ions at trigonal symmetry sites, although the SO mechanism is the most important one, the SS and SOO interactions were found important. The SH parameters arise not only from the three individual microscopic mechanisms (SO, SS, and SOO) but are also from the combined SO–SS–SOO mechanism. In this paper, considering all four mechanisms, the SH parameters of V^{3+} , Cr^{4+} , Ni^{2+} and Cu^{3+} ions in Al_2O_3 crystals are studied, and the contributions from each mechanism are discussed.

2. Theory

By taking into account the SS and SOO interactions, the total Hamiltonian of a $3d^{2(8)}$ ion in trigonal crys-

tal field (CF) in intermediate scheme can be written as [13, 18–20]:

$$H = H_{ee}(B, C) + H_{SO}(\zeta) + H_{CF}(B_{kq}) + H_{SS}(M_0, M_2) + H_{SOO}(M_0, M_2). \quad (1)$$

Here, H_{ee} represents electrostatic interactions, B and C are the Racah parameters, H_{SO} represents SO interactions, ζ is the SO interaction parameter, H_{CF} represents the CF interaction, which for trigonal type I symmetry (D_3, D_{3d}, C_{3v}) is in the expanded form of the Wybourne notations [21–25]:

$$H_{CF} = B_{20}C_{20} + B_{40}C_{40} + \text{Re}B_{43}(C_{43} - C_{4-3}). \quad (2)$$

The CF parameters B_{kq} in Eq. (2) measure the strength of interaction between the open-shell electrons of paramagnetic ions and their surrounding crystalline environment [23, 26], and hence play a key role in the CF studies.

$C_q^{(k)}$ is the tensor operator defined by $C_q^{(k)} = \sqrt{\frac{4\pi}{2k+1}}Y_{kq}$, where Y_{kq} denotes the spherical harmonics. H_{SS} and H_{SOO} represent SS and SOO mechanisms, respectively. M_0 and M_2 are the Marvin radial integrals [27]. The method of calculations of the matrix elements of H_{ee} , H_{SO} , and H_{CF} has been described in [28], and those for H_{SS} and H_{SOO} in [13] and [29].

For $3d^2$ and $3d^8$ ions with the trigonal symmetry, the matrices of Hamiltonians in Eq. (1) are of the dimension 45×45 and can be partitioned into three 15×15 matrices. The ground term of the $3d^2$ and $3d^8$ configurations is 3F , which is split by octahedral CF into 3A_2 , 3T_2 , and 3T_1 states. For $3d^2$ configuration, 3T_1 is the cubic ground state, which is split into an orbital doublet and singlet due to C_{3v} symmetry. The orbital ground state of $3d^2$ configuration ions is split into a spin doublet $|E_{\pm 1}({}^3F \downarrow {}^3T_1 \downarrow {}^3A_2)\rangle$ and a spin singlet $|A_1({}^3F \downarrow {}^3T_1 \downarrow {}^3A_2)\rangle$ due to SO, SS, and SOO interactions [19]. For $3d^8$ configuration, 3A_2 is the cubic ground state, which is split into a spin doublet $|E_{\pm 1}({}^3F \downarrow {}^3A_2 \downarrow {}^3A_2)\rangle$ and a spin singlet

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$|A_1(^3F \downarrow ^3A_2 \downarrow ^3A_2)\rangle$ due to SO, SS, and SOO interactions [19]. The ground states are obtained by complete diagonalization of the Hamiltonian matrix. For convenience, we denote $|E_{\pm 1}(^3F \downarrow ^3T_1 \downarrow ^3A_2)\rangle$ or $|E_{\pm 1}(^3F \downarrow ^3A_2 \downarrow ^3A_2)\rangle$ as $|\psi_{\pm 1}\rangle$, and denote $|A_1(^3F \downarrow ^3T_1 \downarrow ^3A_2)\rangle$ as $|\psi_0\rangle$. Diagonalization of the full Hamiltonian matrices yields the energy levels and eigenvectors as functions of the Racah parameters B and C , CF parameters B_{kq} , SO coupling constant ζ , and the Marvin radial parameters M_0 and M_2 . The ground state eigenvectors will be used in calculating the g factors. For $3d^N$ ions at C_{3v} symmetry, the effective spin Hamiltonian, taking into account the ZFS and Zeeman terms [23, 30], can be written as [19] ($z||[111]$):

$$H_S = D \left[S_z^2 - \frac{1}{3}S(S+1) \right] + \mu_B g_{\parallel} B_z S_z + \mu_B g_{\perp} (B_x S_x + B_y S_y). \quad (3)$$

By means of the matrix element equivalence between the effective SH and actual physical Hamiltonian, the g fac-

tors g_{\parallel} and g_{\perp} for $3d^2$ and $3d^8$ ions at C_{3v} symmetry sites are expressed in terms of the quantities pertinent for the actual physical Hamiltonian as

$$g_{\parallel} = k \langle \psi_{+1} | L_z | \psi_{+1} \rangle + g_e \langle \psi_{+1} | S_z | \psi_{+1} \rangle, \quad (4)$$

$$g_{\perp} = \sqrt{2} (k \langle \psi_{+1} | L_x | \psi_0 \rangle + g_e \langle \psi_{+1} | S_x | \psi_0 \rangle), \quad (5)$$

where k represents the orbital reduction factor [18, 19], and $g_e = 2.0023$ [24].

The ZFS parameter D is given by [13, 19]:

$$D = \varepsilon (|E(^3F \downarrow ^3T_1 \downarrow ^3A_2)\rangle) - \varepsilon (|A_1(^3F \downarrow ^3T_1 \downarrow ^3A_2)\rangle) \quad (6)$$

for $3d^2$ and

$$D = \varepsilon (|E(^3F \downarrow ^3A_2 \downarrow ^3A_2)\rangle) - \varepsilon (|A_1(^3F \downarrow ^3A_2 \downarrow ^3A_2)\rangle) \quad (7)$$

for $3d^8$ ions, respectively. Equations (4)–(7) have been built-in the CDM/MSH program which we have recently developed [31].

Parameters used in calculations (units in cm^{-1} except k).

TABLE I

Impurities	B	C	B_{20}	B_{40}	$\text{Re}B_{43}$	ζ	k	M_0	M_2
V^{3+}	618.2	2502	1366.55	-22842.9	-28843.16	164	0.96	0.1644	0.0129
Cr^{4+}	426	1736	-1856.1	-25397.2	-38395.5	209	0.64	0.0983	0.0078
Ni^{2+}	800	3400	-983.55	-14486.4	-16529.7	565	0.87	0.2560	0.0200
Cu^{3+}	1030	4850	-557.31	-29380.8	-35501.5	600	0.68	0.2085	0.0164

TABLE II

The calculated SH parameters due to various mechanisms (see text) and ratio parameters (in brackets) for V^{3+} , Cr^{4+} , Ni^{2+} and Cu^{3+} ions in Al_2O_3 crystal.

X	Magnetic interactions considered	$Al_2O_3:V^{3+}$	$Al_2O_3:Cr^{4+}$	$Al_2O_3:Ni^{2+}$	$Al_2O_3:Cu^{3+}$
D	SO	8.75048 (108.67)	7.81984 (103.41)	-1.28514 (93.13)	-0.16427 (87.38)
	SS	0.13784 (1.71)	0.07571 (1.00)	-0.03308 (2.40)	-0.01653 (8.79)
	SOO	0.01564 (0.19)	0.00216 (0.03)	-0.00048 (0.03)	-0.00004 (0.02)
	SO - SS - SOO	-0.85186 (-10.58)	-0.33597 (-4.44)	-0.06128 (4.44)	-0.00716 (3.81)
	SO + SS + SOO	8.05210 (100.00)	7.56174 (100.00)	-1.37998 (100.00)	-0.18800 (100.00)
Exp.		8.06 ± 0.15 [32]	7.562 [8]	-1.380 [17]	-0.1880 [17]
Δg_{\parallel}	SO	-0.08966 (105.49)	-0.04328 (102.29)	0.19206 (98.32)	0.07516 (98.69)
	SS	0.00000 (0.00)	0.00000 (0.00)	0.00000 (0.00)	0.00000 (0.00)
	SOO	0.00199 (-2.34)	0.00060 (-1.42)	0.00356 (1.82)	0.00104 (1.37)
	SO - SS - SOO	0.00268 (-3.15)	0.00037 (-0.87)	-0.00027 (-0.14)	-0.00004 (-0.06)
	SO + SS + SOO	-0.08499 (100.00)	-0.04231 (100.00)	0.19535 (100.00)	0.07616 (100.00)
Exp.		-0.087 ± 0.002 [32]		0.1934 [17]	0.0765 [17]
Δg_{\perp}	SO	-0.28714 (103.65)	-0.12492 (101.71)	0.18175 (98.32)	0.07398 (98.69)
	SS	0.00000 (0.00)	0.00000 (0.00)	0.00000 (0.00)	0.00000 (0.00)
	SOO	0.01151 (-4.15)	0.00214 (-1.74)	0.00338 (1.83)	0.00103 (1.37)
	SO - SS - SOO	-0.00140 (0.50)	-0.00004 (0.03)	-0.00027 (-0.15)	-0.00005 (-0.07)
	SO + SS + SOO	-0.27703 (100.00)	-0.12282 (100.00)	0.18486 (100.00)	0.07496 (100.00)
Exp.		-0.2773 ± 0.001 [32]		0.1836 [17]	0.0749 [17]

3. Calculations and discussions

Petrosyan and Mirzakhanyan have obtained the Racah parameters and SO coupling parameter from optical spectra for Ni^{2+} and Cu^{3+} ions in Al_2O_3 crystals [17]. The Marvin radial parameters M_0 and M_2 can be obtained by the relations $M_0 = k^2 M_{0F}$ and $M_2 = k^2 M_{2F}$, here k is the orbital reduction factor [18, 19]. The parameters for V^{3+} , Cr^{4+} , Ni^{2+} , and Cu^{3+} in Al_2O_3 crystals used in calculations are listed in Table I.

In general, numerical calculations show that setting $\zeta = 0$ and $M_0 = M_2 = 0$ results in $D = 0$ and $g_{\parallel} = g_{\perp} = 2.0023$, i.e. $\Delta g_{\parallel} (= g_{\parallel} - g_e) = \Delta g_{\perp} (= g_{\perp} - g_e) = 0$, whereas considering the magnetic interactions and trigonal CF simultaneously yields $D \neq 0$, $\Delta g_{\parallel} \neq 0$ and $\Delta g_{\perp} \neq 0$ [18]. So, to study the relative contribution to SH parameters, we should calculate the departure of g factors from g_e rather than g factors themselves.

By using the parameters given above, we calculated the SH parameters of Ni^{2+} , Cu^{3+} , V^{3+} , and Cr^{4+} ions in Al_2O_3 crystal and the contribution to SH parameters from each mechanism. The results are shown in Table II; the experimental data are also listed for comparison.

Table II confirms that the contributions to SH parameters from SO mechanism are the most important ones [29, 31]. To illustrate the relative magnitude of various interaction mechanisms, the percentage ratio parameter can be defined as:

$$\gamma_M = \frac{X_M}{X_{\text{SO+SS+SOO}}} \times 100\%, \quad (8)$$

where X denotes D , Δg_{\parallel} or Δg_{\perp} , and the subscript ‘‘M’’ denotes each magnetic interaction mechanism. The values of γ_M are listed in Table II in brackets. One can see that, for $3d^2$ (V^{3+} and Cr^{4+}) ions, the sum of γ_{SS} , γ_{SOO} and $\gamma_{\text{SO-SS-SOO}}$ for D , Δg_{\parallel} or Δg_{\perp} is negative. This indicates that the contribution from weaker magnetic interactions are opposite to those from the SO mechanism. For $3d^8$ (Ni^{2+} and Cu^{3+}) ions, the sum of γ_{SS} , γ_{SOO} and $\gamma_{\text{SO-SS-SOO}}$ for D , Δg_{\parallel} or Δg_{\perp} is positive. This means that if we consider only the SO mechanism, the SH parameters will be overestimated for d^2 ions and underestimated for d^8 ions. We find also that the contributions from weaker magnetic interactions to the ZFS parameter D decrease (increase) with increasing charge of impurity ions for $3d^2(3d^8)$ configurations.

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