Investigations of the Spin Hamiltonian Parameters and the Local Structures of the Substitutional V^{4+} Centres in Rutile-Type MO_2 (M = Sn, Ti, Ge)

Shao-Yi Wu[a,b], Li-Hua Wei[a], Zhi-Hong Zhang[a], Xue-Feng Wang[a], and Ji-Zi Lin[a]

[a] Department of Applied Physics, University of Electronic Science and Technology of China, Chengdu 610054, P. R. China
[b] International Centre for Materials Physics, Chinese Academy of Sciences, Shenyang 110016, P. R. China

Reprint requests to S-Y. W.; E-mail: shaoyi_wu@163.com

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The spin Hamiltonian parameters and the local structures of the substitutional V^{4+} centres in rutile-type MO_2 (M = Sn, Ti and Ge) are theoretically investigated from the perturbation formulas of these parameters for a $3d^1$ ion in a rhombically compressed octahedron. The oxygen octahedra around V^{4+} are found to transform from the original elongation on the host M^{4+} site to compression in the impurity centres due to the Jahn-Teller effect. The calculated spin Hamiltonian parameters based on the above local structures show good agreement with the experimental data.

Key words: Defect Structures; Electron Paramagnetic Resonance; Crystal- and Ligand-Fields; V^{4+}; Rutile.

1. Introduction

Rutile-type MO_2 (M = Sn, Ti, Ge) are useful materials due to their unique optical [1 – 5], magnetic [6 – 9], dielectric [10, 11] and catalytic [12 – 16] properties when doped with some transition-metal elements. These properties are sensitively correlated with the local structures around the impurity ions in the hosts, which can be investigated with the aid of electron paramagnetic resonance (EPR) technique. For example, EPR analyses observed the rhombic substitutional V^{4+} centres in MO_2, and the spin Hamiltonian parameters g_i $(i = x, y, z)$ and the hyperfine structure constants A_i were also measured decades ago [17 – 19].

In order to interpret the above EPR results, theoretical calculations were performed based on the simple second-order perturbation formulas of the g factors (the hyperfine structure constants were not quantitatively treated) [20]. Nevertheless, the contributions from ligand orbital and spin-orbit coupling interactions were ignored in their treatments. In fact, the covalency effect or admixtures between the central metal and ligand orbitals can be significant in these systems due to the high valence state of V^{4+}. Meanwhile, the calculations of the g factors were not correlated with the impurity local structures, which would be normally different from those of the host M^{4+} site in pure crystals arising from size mismatching substitution. In addition, the local lattice deformations around V^{4+} due to the Jahn-Teller effect were not taken into account. As a result, the calculated g factors (particularly for SnO_2 and GeO_2) of [20] were not in good agreement with the experimental data. Since information about the local structures of impurities in rutile-type crystals would be helpful to understand the optical and magnetic properties of these systems, investigations of the spin Hamiltonian parameters and the local structures of the rhombic V^{4+} centres in MO_2 are of specific significance. In this work, the spin Hamiltonian parameters and the local structures of $MO_2 : V^{4+}$ are quantitatively studied from the high-order perturbation formulas of these parameters for a $3d^1$ ion in a rhombically compressed octahedron, by including reasonable local lattice distortion around V^{4+} due to the Jahn-Teller effect and the ligand orbital and spin-orbit coupling contributions.

2. Calculation

The impurity V^{4+} in MO_2 can occupy substitutionally the host tetravalent M^{4+} site and conserve the original rhombic (D_{2h}) point symmetry [21]. The oxygen octahedron is elongated in these systems, characterized

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Table 1. The host M^{4+}-O^{2-} bond lengths (in Å) and angles (in degree) [21] for the M^{4+} site, the group overlap (and A) integrals, molecular orbital coefficients N_γ and λ_γ (and λ_s), spin-orbit coupling coefficients (in cm^{-1}) and the orbital reduction factors for V^{4+} in MO_2.

Host	$R_\parallel$	$R_\perp$	$\bar{R}$	θ	S_{dpt}	S_{dpe}	S_{ds}	A	N_t
SnO_2	2.056	2.052	2.0533	78.18	0.0368	0.1023	0.0823	1.3362	0.737
TiO_2	1.988	1.944	1.9586	80.88	0.0495	0.1272	0.1025	1.2752	0.729
GeO_2	1.91	1.87	1.8833	79.8	0.0625	0.1501	0.1211	1.2261	0.731

Host	N_e	λ_t	λ_e	λ_s	ζ	ζ'	k	k'
SnO_2	0.789	0.635	0.518	0.417	205	170	0.886	0.502
TiO_2	0.796	0.661	0.542	0.437	205	168	0.888	0.485
GeO_2	0.811	0.673	0.554	0.447	206	169	0.896	0.485

by two longer bond lengths $R_\parallel$ and four shorter lengths $R_\perp$ with the planar bond angle θ different from the ideal value 90° for a regular octahedron (see Table 1). Usually, local structures around the impurity V^{4+} can be dissimilar to those in the pure crystal. For example, the parallel and perpendicular V^{4+}-O^{2-} bonds may suffer modifications (contraction or relaxation) due to the Jahn-Teller effect [22–24] and the size mismatching substitution. The above modifications can change the oxygen octahedron from the original elongation on M^{4+} site to compression in the impurity centres, with the parallel bond lengths smaller than the perpendicular ones. This sort of Jahn-Teller compression of ligand octahedron is supported by the studies for similar $[VO_6]^{8-}$ and $[CrO_6]^{7-}$ clusters in $SrTiO_3:V^{4+}$ and $SrTiO_3:Cr^{5+}$ [25–27] and $[NiO_6]^{9-}$ cluster in $LaSrAlO_4:Ni^{3+}$ [22].

For a V^{4+} ($3d^1$) ion in a rhombically compressed octahedron, its higher orbital doublet ^2E_g of original cubic case would split into two orbital singlets, $^2A_{1g}$ ($|z^2\rangle$) and $^2A'_{1g}$ ($|xy\rangle$), while the original lower orbital triplet $^2T_{2g}$ would be separated into three orbital singlets, $^2B_{2g}$ ($|xz\rangle$), $^2B_{3g}$ ($|yz\rangle$) and $^2B_{1g}$ ($|x^2-y^2\rangle$), with the latter lying lowest [28]. Note that in the above notations $|xy\rangle$ and $|x^2-y^2\rangle$ are interchanged, due to a rotation of the frame of axes in the XY plane.

Applying the perturbation procedure similar to [29, 30] and including the ligand orbital and spin-orbit coupling contributions, the high-order perturbation formulas of the spin Hamiltonian parameters for $3d^1$ ions in a rhombically compressed octahedron can be expressed as follows:

$$\begin{aligned}
g_x &= g_s - 2k'\zeta'/E_1 + k\zeta^2[1/(2E_1{}^2) - 1/(2E_2{}^2)] \\
&\quad + 2k'\zeta'\zeta[1/(E_2E_3) - 1/E_3{}^2], \\
g_y &= g_s - 2k'\zeta'/E_2 - k\zeta^2[1/(2E_1{}^2) - 1/(2E_2{}^2)] \\
&\quad + 2k'\zeta'\zeta[1/(E_1E_3) - 1/E_3{}^2], \\
g_z &= g_s - 8k'\zeta'/E_3 - (1/2)k\zeta^2(1/E_1 + 1/E_2)^2 \\
&\quad + 2k'\zeta'^2/E_3{}^2, \\
A_x &= P[-\kappa + 2N^2/7 + 11(g_x - g_s)/14], \\
A_y &= P[-(\kappa + \kappa') + 2N^2/7 + 11(g_y - g_s)/14], \\
A_z &= P[-(\kappa - \kappa') - 4N^2/7 + (g_z - g_s) \\
&\quad + 3(g_x - g_s)/14 + 3(g_y - g_s)/14],
\end{aligned} \tag{1}$$

where g_s (= 2.0023) is the spin-only value. P is the dipolar hyperfine structure parameter of the free $3d^1$ ion. κ and κ' are, respectively, the core polarization constants of the isotropic and anisotropic parts [27]. N is the average covalency factor, characteristic of the covalency effect of the studied systems. The denominators E_i ($i = 1-3$) stand for the energy separations between the excited $^2B_{2g}$, $^2B_{3g}$ and $^2A'_{1g}$ and the ground $^2B_{1g}$ states [29] and can be obtained from the strong cubic field approach: $E_1 = -3Ds + 5Dt + 3D_\xi - 4D_\eta$, $E_2 = -3Ds + 5Dt - 3D_\xi + 4D_\eta$ and $E_3 = 10Dq$, where Dq is the cubic field parameter, and Ds, Dt, D_ξ and D_η are the rhombic ones.

Based on the cluster approach, the spin-orbit coupling coefficients ζ, ζ' and the orbital reduction factors k, k' in (1) may be written as

$$\begin{aligned}
\zeta &= N_t(\zeta_d + \lambda_t{}^2\zeta_p/2), \\
\zeta' &= (N_tN_e)^{1/2}(\zeta_d - \lambda_t\lambda_e\zeta_p/2), \\
k &= N_t(1 + \lambda_t{}^2/2), \\
k' &= (N_tN_e)^{1/2}[1 - \lambda_t(\lambda_e + \lambda_sA)/2],
\end{aligned} \tag{2}$$

where ζ_d and ζ_p are the spin-orbit coupling coefficients of the free $3d^1$ and ligand ions, respectively. A denotes the integral $R\langle ns|\frac{\partial}{\partial y}|np_y\rangle$, where R is the metal-ligand distance in the studied system. N_γ and λ_γ (or λ_s) are, respectively, the normalization factors and the orbital mixing coefficients for the cubic irreducible representations γ (= e_g and t_{2g}). They are determined from the normalization conditions

$$\begin{aligned} &N_t(1-2\lambda_t S_{dpt}+\lambda_t^2)=1,\\ &N_e(1-2\lambda_e S_{dpe}-2\lambda_s S_{ds}+\lambda_e^2+\lambda_s^2)=1, \end{aligned} \tag{3}$$

and the approximate relationships

$$\begin{aligned} N^2 &= N_t^2[1+\lambda_t^2 S_{dpt}^2-2\lambda_t S_{dpt}],\\ N^2 &= N_e^2[1+\lambda_e^2 S_{dpe}^2+\lambda_s^2 S_{ds}^2\\ &\qquad -2\lambda_e S_{dpe}-2\lambda_s S_{ds}]. \end{aligned} \tag{4}$$

Here $S_{dp\gamma}$ (and S_{ds}) are the group overlap integrals. In general, the mixing coefficients increase with increasing the group overlap integrals, and one can approximately adopt the proportional relationship between the mixing coefficients and the related group overlap integrals, i. e., $\lambda_e/S_{dpe} \approx \lambda_s/S_{ds}$ within the same irreducible representation e_g.

From the point-charge model [31, 32] and the geometrical relationship of the studied impurity centres, the cubic and rhombic field parameters can be determined as follows:

$$\begin{aligned} Dq &= -eq\langle r^4\rangle/(6\bar{R}^5),\\ Ds &= 2eq\langle r^2\rangle(1/R'^3_{\parallel}-1/R'^3_{\perp})/7,\\ Dt &= eq\langle r^4\rangle[4/R'^5_{\parallel}+(7\cos 2\theta'+3)/R'^5_{\perp}]/42,\\ D_\xi &= 2eq\langle r^2\rangle\cos\theta'/(7R'^3_{\perp}),\\ D_\eta &= 5eq\langle r^4\rangle\cos\theta'/(42R'^5_{\perp}), \end{aligned} \tag{5}$$

where q (= $-2e$) is the effective charge of the oxygen ligand. In view of the covalency effect between the central ion and the ligand orbitals [31], the expectation values $\langle r^n\rangle$ ($n = 2,4$) of the $3d^1$ radial wavefunction in crystals can be reasonably expressed in terms of the corresponding free-ion values in TiO_2 [27] and the average covalency factor N:

$$\begin{aligned} \langle r^2\rangle &\approx 3.3222\,N\ \text{(a.u.)},\\ \langle r^4\rangle &\approx 21.0698\,N\ \text{(a.u.)}. \end{aligned} \tag{6}$$

In (5), $\bar{R}$ denotes the average metal-ligand bond length for the host M^{4+} site in MO_2, i. e., $\bar{R} = (R_{\parallel}+2R_{\perp})/3$. For convenience, the impurity-ligand bond lengths in the impurity centres can be written in terms of the average distance $\bar{R}$, the local compression parameter ρ and the rhombic distortion angle $\delta\theta$: $R'_{\parallel} \approx \bar{R}(1-2\rho)$, $R'_{\perp} \approx \bar{R}(1+\rho)$ and $\theta' \approx 90° + \delta\theta$.

From the distances $\bar{R}$ and the Slater-type SCF functions [33, 34], the integrals S_{dpt}, S_{dpe}, S_{ds} and A are calculated and shown in Table 1. The average covalency factors are taken as $N \approx 0.72$, 0.71 and 0.70 for SnO_2, TiO_2 and GeO_2, respectively, in view that the covalency increases slightly with decreasing the distance $\bar{R}$ in crystals [35]. Thus the values of the molecular orbital coefficients N_γ and λ_γ are calculated from (3) and (4) and shown in Table 1. Then the parameters ζ, ζ', k and k' can be determined from (2) and the spin-orbit coupling coefficient $\zeta_d \approx 248\ \text{cm}^{-1}$ for V^{4+} [36] and $\zeta_p \approx 151\ \text{cm}^{-1}$ for O^{2-} [37]. These values are also collected in Table 1.

Thus in the formulas of the g factors in (1), there are only two unknown local structural parameters, ρ and $\delta\theta$. By fitting the calculated g factors to the experimental data, we have

$$\begin{aligned} &\rho \approx 0.025, 0.020, 0.029,\\ &\delta\theta \approx -2.70°, -0.81°, -2.11° \end{aligned} \tag{7}$$

for SnO_2, TiO_2 and GeO_2, respectively. In the formulas of the hyperfine structure constants, the isotropic core polarization constant is approximately taken as $\kappa \approx 0.3$, the typical value for $3d^n$ ions in crystals [36]. Substituting these data and the free-ion value P ($\approx 170 \cdot 10^{-4}\ \text{cm}^{-1}$ [38]) into (1) and fitting the calculated A factors to the observed values, the anisotropic core polarization constant can be obtained, i. e.,

$$\kappa' \approx 0.07, 0.04, 0.08 \tag{8}$$

for SnO_2, TiO_2 and GeO_2, respectively. The corresponding spin Hamiltonian parameters (Cal.^{d}) are shown in Table 2. For comparison, the theoretical results (Cal.^{a}) based on the conventional second-order perturbation formulas of the g factors by neglecting the local lattice distortion and the ligand contributions in the previous treatments [20] are also given in Table 2. Meanwhile, the calculated results (Cal.^{b}) based on inclusion of the ligand contributions but neglecting the local lattice distortion are listed in Table 2 (note: the perturbation formulas [39] of the spin Hamiltonian parameters for $3d^1$ ions in rhombically elongated octahedra are adopted based on the host structural parameters $R_{\parallel}$, $R_{\perp}$ and θ for the ground state $^2B_{2g}$ here). In addition, the results (Cal.^{c}) based on inclusion of the local structural parameters in (7) and neglecting the ligand contributions (i. e., taking $\lambda_i = 0$, $\zeta_p = 0$ and then $\zeta = \zeta' = N\zeta_d$ and $k = k' = N$) are collected in Table 2.

Table 2. The spin Hamiltonian parameters for the substitutional V^{4+} centres in MO_2.

Host		g_x	g_y	g_z	A_x (10^{-4} cm^{-1})	A_y (10^{-4} cm^{-1})	A_z (10^{-4} cm^{-1})
SnO_2	Cal.[a]	1.946	1.893	1.965	–	–	–
	Cal.[b]	1.9192	1.9501	1.9403	34	40	134
	Cal.[c]	1.9073	1.8527	1.9105	26	49	138
	Cal.[d]	1.9394	1.9029	1.9416	21	40	140
	Expt. [17]	1.939	1.903	1.943	21.1	41.8	140.1
TiO_2	Cal.[a]	1.911	1.915	1.959	–	–	–
	Cal.[b]	1.9187	1.9408	1.9444	35	43	141
	Cal.[c]	1.8704	1.8678	1.9266	40	46	130
	Cal.[d]	1.9152	1.9135	1.9526	32	38	136
	Expt. [18]	1.915	1.9135	1.9565	31.5	43	142
GeO_2	Cal.[a]	1.905	1.939	1.956	–	–	–
	Cal.[b]	1.9354	1.952	1.9551	25	35	131
	Cal.[c]	1.9196	1.8819	1.9434	25	46	130
	Cal.[d]	1.9467	1.9211	1.9627	20	38	140
	Expt. [19]	1.9467	1.9211	1.9632	18.48	37.27	134.6

[a] Calculations based on the simple second-order perturbation formulas and the host structural parameters ($R_\parallel$, $R_\perp$ and θ) neglecting the ligand contributions in [20].

[b] Calculations based on the formulas [36] for $3d^1$ ions in elongated octahedra and the host structural parameters and inclusion of the ligand contributions in this work.

[c] Calculations based on (1) and inclusion of the local structural parameters [ρ and $\delta\theta$ in (7)] and neglecting the ligand contributions in this work.

[d] Calculations based on (1) and inclusion of both the local structural parameters and the ligand contributions in this work.

3. Discussion

Table 2 reveals that the calculated spin Hamiltonian parameters based on the local structural parameters ρ and $\delta\theta$ and the ligand contributions are in better agreement with the experimental data than those in the absence of the above contributions. In addition, the present study also shows some improvements in the g factors as compared with those of [20].

1) The local structural parameters in (7) for the V^{4+} centres obtained by analyzing the EPR data are quite different from the host values ($\rho_H \approx -0.0006$, -0.0075, -0.0071 and $\delta\theta_H \approx -11.82°$, $-9.12°$, $-10.2°$ for M = Sn, Ti and Ge, respectively) in pure MO_2. Particularly, the ligand octahedra around metal ions are transformed from slight elongation (negative compression parameter ρ_H) in the hosts to compression (positive compression parameter ρ) in the V^{4+} centres, and the rhombic distortion angles are also significantly reduced around the impurity. Since the ionic radius (≈ 0.63 Å [40]) of V^{4+} is slightly different from those of the host ions (≈ 0.71, 0.68 and 0.53 Å for Sn^{4+}, Ti^{4+} and Ge^{4+}, respectively [40]), the size effect induced by the substitution may modify the local environment around the impurity. More important, the $[VO_6]^{8-}$ clusters may suffer the Jahn-Teller effect via vibration interactions. For example, contraction and relaxation of the parallel and perpendicular impurity-ligand bonds can lead to compression of the ligand octahedra, and bending of the planar bonds can result in much smaller angles $\delta\theta$ as compared with those in the hosts. As a result, the ligand octahedra around the V^{4+} centres exhibit dominant axial compression distortion, with additional minor rhombic deformation. Such Jahn-Teller compression of the ligand octahedra is also found for ions isoelectronic to V^{4+} for example for Cr^{5+} in $SrTiO_3$ [25–27]. In addition, the Jahn-Teller effect for the low spin Ni^{3+} (equivalent to one 3d hole) in $LaSrAlO_4$ also tends to compress the oxygen octahedron [22]. From Table 2, the theoretical results (Cal.[a]) of [20] and those (Cal.[b]) of this work in the absence of local lattice distortions (i. e., the host structural parameters for the elongated oxygen octahedra are adopted for the ground state $^2B_{2g}$) are not as good as those (Cal.[d]) including the above distortions [i. e., the local structural parameters for the compressed octahedra in (7) are adopted for the ground state $^2B_{1g}$]. In view of these points, the local compression of the ligand octahedron around V^{4+} can be understood.

2) The observed g factors [17–19] of the V^{4+} centres indicate the moderate axial anisotropies Δg [$= g_z - (g_x + g_y)/2 \approx 0.022$, 0.0423 and 0.0293 for SnO_2, TiO_2 and GeO_2, respectively] and the non-axial anisotropies δg ($= g_x - g_y \approx 0.036$, 0.0015 and 0.0256). The above experimental findings are largely consistent with the local compression parameters ρ

(≈ 0.025, 0.020, 0.029) and rhombic distortion angles $\delta\theta$ ($\approx -2.70°$, $-0.81°$, $-2.11°$) obtained by analyzing their EPR data. Similar relationships for the hyperfine structure constants are approximately held. In addition, the anisotropic core polarization constant κ' ($\approx 0.04 \sim 0.08$), much smaller than the isotropic one ($\kappa \approx 0.3$), can also be regarded as reasonable.

3) The results (Cal.^{d}) based on inclusion of the ligand contributions are better than those (Cal.^{a}) of [20] and those (Cal.^{c}) of the present work based on neglecting the above contributions. In fact, neglecting the ligand contributions may lead to a larger spin-orbit coupling coefficient and the orbital reduction factor and thus to smaller g factors. Furthermore, the above discrepancy cannot be removed by adjusting the values of ρ and $\Delta\theta$. In consideration of the high valence state of V^{4+}, strong covalency (or admixture) between the metal and ligand orbitals can be expected. This point may be illustrated by the small covalency factors N ($\approx 0.7 < 1$) and the significant mixing coefficients ($\approx 0.4 \sim 0.6$) obtained here (see Table 1). Additionally, the agreements between theory and experiment for the hyperfine structure constants based on neglecting the ligand contributions are also worse than those including these contributions. Therefore, it seems that the formulas of the spin Hamiltonian parameters containing the ligand contributions in this work would be more applicable than the simple ones in the absence of the above contributions [20] for the EPR analyses of V^{4+} centres in MO_2 systems.

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