Theoretical explanation of the spin-lattice coupling coefficients G_{11} and G_{44} for d^3 (V^{2+}, Cr^{3+}) ions in MgO crystals

Theoretical explanation of the spin–lattice coupling coefficients G_{11} and G_{44} for d³ (V²⁺, Cr³⁺) ions in MgO crystals

Zheng Wen-Chen†

China Center of Advanced Science and Technology (World Laboratory), PO Box 8730, Beijing, People's Republic of China

Abstract. In this paper the analytical expressions for spin–lattice coupling coefficients G_{11} and G_{44} in cubic symmetry for d³ ions are established from a uniform method suitable for all d^n ions and the high-order perturbation formulae of zero-field splitting for d³ ions in tetragonal and trigonal symmetries. According to these expressions, the coefficients G_{11} and G_{44} for MgO : V²⁺ and MgO : Cr³⁺ crystals have been calculated from the point-charge-dipole model and parameters obtained from optical spectra. It can be found that for the MgO : V²⁺ crystals, the calculated results are in excellent agreement with the experimental ones, but for the MgO : Cr³⁻ crystal, the results are greater than the observed values. The difference is attributed mainly to the distinctive local strains of the stressed crystals in the two cases.

1. Introduction

The spin–lattice coupling coefficients or dynamic spin Hamiltonian parameters G_{ij} are usually calculated from the derivatives of zero-field splittings or crystal-field components with respect to strain tensor elements [1–3]. The method is complex and it is sometimes easy to make mistakes, in particular when the complex high-order perturbation formulae of zero-field splitting are applied. However, in some special cases, the calculations can be simplified significantly. For example, we have put forward a uniform method for calculating the coefficients G_{11} and G_{44} in cubic symmetry for all d^n ions very easily from the derivatives of the zero-field splittings in tetragonal and trigonal symmetries with respect to the distinctive bonding angles, respectively, and used it to calculate the coefficients G_{11} and G_{44} for S-state ions [4]. In this paper, we will again use the method for d³ ions and hence obtain analytical expressions for the coefficients G_{11} and G_{44} for d³ ions from the high-order perturbation formulae given by Macfarlane [5]. The numerical calculations of the coefficients G_{11} and G_{44} for V²⁺ and Cr³⁺ ions in the uniaxially stressed MgO crystals are carried out using the point-charge-dipole model. It will be seen that for the MgO : V²⁺ crystal, the results are in good agreement with the experimental findings, but for the MgO : Cr³⁺ crystal, the calculated results are greater than the observed values. The difference can be explained from the fact that the local

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† Address for correspondence: Department of Material Science, Sichuan University, Chengdu 610064, People's Republic of China.

Table 1. The spin–lattice coupling coefficients G_{11} and G_{44} in MgO:V^{2+} and MgO:Cr^{3+} crystals (in units of cm^{-1} per unit strain).

V^{2-}		Cr^{3+}	
G_{11}	G_{44}	G_{11}	G_{44}
—	—	3.45[a]	2.16[a]
—	—	1.64[b]	2.81[b]
0.56[c]	3.13[c]	0.61[c]	4.96[c]
—	—	1.16[d]	1.14[d]
0.42[e]	3.04[e]	1.08[e]	4.86[e]
0.42[f]	3.0[f]	0.6[g]	4.2[g]

[a] Reference [7].
[b] Reference [8].
[c] Reference [9].
[d] Reference [10].
[e] Present work.
[f] Reference [11].
[g] Reference [6]. These values are calculated from the bulk elastic constants and are therefore smaller than the real values.

strains in the vicinity of the two impurity ions are not the same. In the case of the Cr^{3+} ion, the local strains are obviously smaller than the host ones and hence the real experimental values of G_{11} and G_{44} should be larger than those in the original literature [6]. Considering this point, our results can be regarded as more reasonable than those of the previous works [7–10] (see table 1).

2. Derivation of the analytical expressions for G_{11} and G_{44}

In our previous paper [4], a uniform method of calculating expressions for the coefficients G_{11} and G_{44} is given, i.e.,

$$G_{11} = -\frac{1}{3}\left(\frac{\partial D_{\text{tetra}}}{\partial \alpha}\right)_0 \qquad G_{44} = -\frac{\sqrt{2}}{6}\left(\frac{\partial D_{\text{tri}}}{\partial \beta}\right)_0 \tag{1}$$

where D_{tetra} and D_{tri} denote the zero-field splitting in tetragonal and trigonal fields, respectively. The suffix 0 denotes that the differentiation is evaluated in the case of cubic symmetry. α and β are related to the tetragonal and trigonal distortions due to stresses, respectively. Angle α is defined as

$$\tan \alpha = R_\perp / R_\parallel \tag{2}$$

where $R_\parallel$ and $R_\perp$ stand for the bonding lengths parallel to and perpendicular to the axis of fourfold rotation. β denotes the angle between the direction of metal–ligand pair and the C_3 axis.

Obviously, if the formulae for the splitting D in tetragonal and trigonal fields are given, the analytical expressions for the coefficients G_{11} and G_{44} can be obtained very easily. The method is simpler than the usual one of calculating directly from the strain tenson elements and is applicable to all d^n ions.

Now let us focus attention on the d^3 ions. From the strong-field coupling scheme, Macfarlane [5] gave the high-order perturbation formulae of the zero-field splitting in tetragonal and trigonal symmetries to be

$$D_{\text{tetra}} = \tfrac{1}{3}\xi_d^2\mu(1/D_1^2 - 1/D_3^2 - 9B/D_2D_3^2) + \tfrac{4}{9}\xi_d^2\delta(1/D_1^2 - 1/D_3^2 + 9B/D_2D_3^2) \tag{3}$$

$$D_{\text{tri}} = \tfrac{2}{9}\xi_d^2\upsilon(1/D_1^2 - 1/D_3^2) - \sqrt{2}\xi_d^2\upsilon'(2/3D_1D_4 + 1/D_2D_3 + 1/3D_3D_4 + 1/D_2D_4$$
$$+ 4\sqrt{2}B/D_1D_4D_5 + 4B/D_3D_4D_5 + 9B/2D_2^2D_3). \tag{4}$$

So, from (1), the analytical expressions of G_{11} and G_{44} are

$$G_{11} = \tfrac{1}{9}\xi_d^2(1/D_3^2 - 1/D_1^2 + 9B/D_2D_3^2)(\partial\mu/\partial\alpha)_0 + \tfrac{4}{27}\xi_d^2(1/D_3^2 - 1/D_1^2 - 9B/D_2D_3^2)$$
$$\times (\partial\delta/\partial\alpha)_0 \tag{5}$$

$$G_{44} = (\sqrt{2}\xi_d^2/27)(1/D_3^2 - 1/D_1^2)(\partial\upsilon/\partial\beta)_0 + \xi_d^2(2/9D_1D_4 + 1/3D_2D_3 + 1/9D_3D_4$$
$$+ 1/3D_2D_4 + 4\sqrt{2}B/3D_1D_4D_5 + 4B/3D_3D_4D_5 + 3B/2D_2^2D_3)$$
$$\times (\partial\upsilon'/\partial\beta)_0 \tag{6}$$

where ξ_d is the spin–orbit coupling coefficient, B the Racah parameter, D_i $(i = 1, \ldots, 5)$ the zero-order energy separations [5], and

$$(\partial\mu/\partial\alpha)_0 = \tfrac{48}{7}\, eq(1 + 3p/eR_0)\langle r^2\rangle/R_0^3 - \tfrac{200}{7}Dq \tag{7}$$

$$(\partial\delta/\partial\alpha)_0 = -\tfrac{36}{7}\, eq(1 + 3p/eR_0)\langle r^2\rangle/R_0^3 - \tfrac{200}{7}Dq \tag{8}$$

$$(\partial\upsilon/\partial\beta)_0 = \tfrac{48}{7}\, \sqrt{2}eq(1 + 3p/eR_0)\langle r^2\rangle/R_0^3 + \tfrac{60}{7}\, \sqrt{2}Dq \tag{9}$$

$$(\partial\upsilon'/\partial\beta)_0 = -\tfrac{12}{7}\, eq(1 + 3p/eR_0)\langle r^2\rangle/R_0^3 + \tfrac{30}{7}\, Dq. \tag{10}$$

The formulae (7)–(10) are calculated in accordance with the definitions of the tetragonal-field parameters μ, δ and trigonal-field parameters υ, υ', and from the point-charge-dipole model. q is the ligand charge and p the dipole.

3. Calculation for MgO : V^{2+}

For the V^{2+} ion, by using the empirical d orbital obtained from a great many experimental data of optical spectra for the crystals containing the V^{2+} ion [12], we can obtain

$$\langle r^2\rangle_0 = 2.565 \text{ au} \qquad \langle r^4\rangle_0 = 13.1132 \text{ au}$$
$$B_0 = 848.5 \text{ cm}^{-1} \qquad C_0 = 3101.9 \text{ cm}^{-1}. \tag{11}$$

For the spin–orbit coupling coefficient ξ_{d_0}, according to the experimental results [13], one can obtain $\xi_{d_0} = 167 \text{ cm}^{-1}$. By introducing the average covalency reduction factor N, we have

$$\langle r^k\rangle = N^2\langle r^k\rangle_0 \qquad B = N^4B_0 \qquad C = N^4C_0 \qquad \xi_d = N^2\xi_{d_0}. \tag{12}$$

From the optical absorption spectra of MgO : V^{2+} crystal [14], one can get

$$N = 0.911 \qquad p = 0.126eR_0. \tag{13}$$

The comparison of spectra between the theory and experiments is given in table 2.

Table 2. The optical spectra for $MgO:V^{2+}$ and $MgO:Cr^{3+}$ crystals (in units of cm^{-1}).

Transition	V²⁺		Cr³⁺	
	Theoretical frequency	Observed frequency	Theoretical frequency	Observed frequency
$^4A_2(F) \rightarrow {}^2E(1)$	10 653	11 498[a]	13 758	14 319[b] (14 325[c])
$^2T_1(1)$	11 211	11 860[a]	14 497	14 961[b] (15 019[b])
$^4T_2(F)$	13 200	13 200[a]	15 869	15 385[c] (16 300[b])
$^2T_2(1)$	16 071	16 760[a]	20 596	
$^4T_1(1)$	18 887	~19 000[a]	23 099	22 100[b]
$^2A_1(G)$	21 949		27 191	26 174[d]
$^2T_2(2)$	23 566		29 239	29 820[b]
$^2T_1(2)$	24 152		30 067	
$^2E(2)$	25 374		31 647	
$^4T_1(2)$	29 481	~30 000[a]	35 937	34 200[b]
$^2T_1(3)$	27 957		34 881	34 600[b]
$^2T_2(3)$	32 589		41 122	39 000[b]
$^2A_2(F)$	33 639		42 431	
$^2T_1(4)$	38 499		47 469	
$^2T_2(4)$	41 038		50 790	
$^2E(3)$	39 975		50 145	
$^2T_1(5)$	41 584		51 597	
$^2T_2(5)$	51 547		64 569	
$^2E(4)$	55 168		68 328	

[a] Reference [14].
[b] Reference [15].
[c] Reference [16].
[d] Reference [17].

Considering that the charge and size of V^{2+} ion are close to those of Mg^{2+} ion (ionic radius of Mg^{2+} is 0.86 Å and that of V^{2+} is 0.93 Å [18]), the structural parameter $R_0 = 2.1$ Å for a MgO crystal is a good approximation for the $V^{2+}-O^{2-}$ distance. Substituting these data (N, p, R_0) into the above formulae, we obtain

$$G_{11} = 0.42 \text{ cm}^{-1}/\text{unit strain} \qquad G_{44} = 3.04 \text{ cm}^{-1}/\text{unit strain}. \tag{14}$$

Obviously, the results show good agreement with the experimental findings (see table 1).

4. Calculation for $MgO:Cr^{3+}$

Following the same procedure as for the V^{2+} ion, according to the empirical d orbital of Cr^{3+} ion obtained from the optical spectra data of many crystals containing Cr^{3+} ions [19], we have

$$\langle r^2 \rangle_0 = 2.4843 \text{ au} \qquad \langle r^4 \rangle_0 = 16.4276 \text{ au}$$
$$B_0 = 920.48 \text{ cm}^{-1} \qquad C_0 = 3330.71 \text{ cm}^{-1} \qquad \xi_{d_0} = 240 \text{ cm}^{-1}. \tag{15}$$

The factor N is introduced as in the case of V^{2+} ion. From the optical spectra of $MgO:Cr^{3+}$ crystals [15–17], one can find $N = 0.954$, $p = 0.086\,eR_0$. The comparison of spectra between the theory and experiments is also given in table 2. It should be noted that these

values are calculated in accordance with the assumption that the distance of Cr^{3+}–O^{2-} is equal to 2.1 Å, the value of Mg^{2+}–O^{2-} distance in a MgO crystal. In fact, because the charge of the Cr^{3+} ion is obviously greater than that of Mg^{2+} and its ionic radius (0.775 Å [18]) is smaller, an inward displacement of all ligands surrounding the Cr^{3+} ion should arise when the Cr^{3+} ion replaces the Mg^{2+} ion in a MgO crystal. However, for the displacement, the different authors gave the different values [10, 20, 21] and no commonly accepted result is drawn. So, in this paper, we still use the assumption that $R_0 =$ 2.1 Å, the value of structural parameter in a MgO crystal. Substituting these values of N, p, R_0 into the above formulae, we obtain:

$$G_{11} = 1.08 \text{ cm}^{-1}/\text{unit strain} \qquad G_{44} = 4.86 \text{ cm}^{-1}/\text{unit strain}. \qquad (16)$$

The results are compared with the experiments in table 1.

5. Discussion

From the above calculated results, it can be seen that for the spin–lattice coupling coefficients G_{11} and G_{44}, the values for the MgO : V^{2+} crystal are in excellent agreement with the experimental ones, but for the MgO : Cr^{3+} crystal, the values are greater than those of experiments. The difference does not mean that the method is more suitable to V^{2+} ion than to Cr^{3+} ion, but is mainly due to the distinctive local strains in the vicinity of the two impurity ions. In fact, for V^{2+} ion, because it has the same charge and similar ionic radius as the Mg^{2+} ion, the local strains should be very close to the bulk ones of a MgO crystal. But for the Cr^{3+} ion, the charge is evidently greater than that of the Mg^{2+} ion, hence the crystal should be 'harder' in the vicinity of the impurity, which will lead to the reductions of local strains and 'elastic constants' s_{ij}. This point has been supported by the work of Sangster [21], in which he showed that in a MgO crystal, for divalent impurities, the local strains are close to those in the bulk crystal but when the impurity carries extra charge, large and symmetry-dependent reductions arise. So, for the MgO : V^{2+} crystal, the observed values of coefficients G_{11} and G_{44} obtained from the bulk elastic constants s_{ij} of the MgO crystal can be regarded as reasonable, and hence it leads to the agreement between the calculated and observed values. However, for MgO : Cr^{3+} crystals, because the local 'elastic constants' are smaller than the bulk ones of the MgO crystal, according to the formulae [9, 22]

$$\mathrm{d}D_{\text{tetra}}/\mathrm{d}P = -\tfrac{3}{2}G_{11}(s_{11} - s_{12}) \qquad \mathrm{d}D_{\text{tri}}/\mathrm{d}P = -G_{44}s_{44} \qquad (17)$$

the experimental values of coefficients G_{11} and G_{44} based on the local elastic constants should be greater than those calculated from the bulk ones and may be closer to our calculated results. So, when the local strains are taken into account, the discrepancies between theoretical and experimental values of the coefficients G_{11} and G_{44} for the MgO : Cr^{3+} crystal can be resolved. In addition, the approximations of the simple point-charge-dipole model and the uncertainties of the optical experiments for the MgO : Cr^{3+} crystal are also the sources of error. In conclusion, because the spin–lattice coupling coefficients G_{11} and G_{44} as well as optical spectra can be explained from our method for MgO : V^{2+} and MgO : Cr^{3+} crystals in a unified way, the method and expressions can be regarded as reasonable and should be effective in other similar cases.

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