

Theoretical Studies of the EPR g Factors and the Hyperfine Structure Constants of Cr^{3+} in MgS and SrS

Shao-Yi Wu^a, Xiu-Ying Gao, and Wei-Zi Yan

Department of Applied Physics, University of Electronic Science and Technology of China, Chengdu 610054, P. R. China

^a International Centre for Materials Physics, Chinese Academy of Sciences, Shenyang 110016, P. R. China

Reprint requests to S.-Y. W. E-mail: wushaoyi@netease.com

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The EPR g factors and the hyperfine structure constant A factors for Cr^{3+} in MgS and SrS are theoretically studied by using the two-spin-orbit (S.O.)-coupling-coefficient formulas for a $3d^3$ ion in octahedra based on the cluster approach. In these formulas, both the contributions due to the S.O. coupling coefficient of the central $3d^3$ ion and that of ligands are taken into account. Based on these studies, the g and A factors of Cr^{3+} in both MgS and SrS are satisfactorily explained. The results are discussed.

Key words: EPR; Crystal- and Ligand-fields; Cr^{3+} ; MgS; SrS.

1. Introduction

The electroluminescence of SrS doped with transition-metal or rare-earth ions has extensively been investigated [1–5]. MgS is a useful material in astronomical search due to its far infrared spectra arising from the vibration of MgS on dust grains [6–8]. The properties of both materials may be sensitive to the local behaviour or properties of transition-metal or rare-earth impurity ions. Since electron paramagnetic resonance (EPR) is a powerful tool to study the local structures and properties of paramagnetic impurity ions in materials, EPR experiments were carried out on Cr^{3+} in MgS and SrS, and the g factors and the hyperfine structure constant A factors were measured [9, 10]. However, the above experimental results have not been theoretically interpreted. Since information about the electronic states of Cr^{3+} in the above crystals may be of some use to understand the properties of the doped materials, theoretical investigations on g and A factors for the octahedral Cr^{3+} centers in MgS and SrS of this work are significant. In this paper, we study theoretically the g and A factors of octahedral Cr^{3+} centers in both crystals by using the two-spin-orbit (S.O.)-coupling-coefficient formulas for g and A factors of $3d^3$ ions in octahedra, based on the cluster approach. In these formulas, both the contributions arising from

the S.O. coupling coefficient of the central $3d^3$ ion and that of ligands are included. The results are discussed.

2. Calculations

In general, for a transition-metal (e. g., Cr^{3+}) ion in crystals where the S. O. coupling coefficient of the ligands is much larger than that of the central ion, or the covalency of the impurity-ligand bond is strong (e. g., the Cr^{3+} - S^{2-} bond in this work), the conventional single-S.O.-coupling-coefficient formulas [11] are not suitable in studies of the g factors, due to neglecting of the S.O. coupling coefficient of ligands, and admixture of the p orbitals of ligands to the d orbitals of the central ion [12]. So, two-S.O.-coupling-coefficient formulas for g and A factors based on the cluster approach should be applied to these systems by considering both the contributions due to the S.O. coupling coefficient of the central ion and that of ligands, as stated by many authors [12–14].

From a molecular orbital (MO) model for octahedral $3d^n$ clusters in crystals, the one-electron basis functions can be expressed as [12]

$$|\gamma\rangle = N_\gamma^{1/2}(|d_\gamma\rangle - \lambda_\gamma|p_\gamma\rangle), \quad (1)$$

where $\gamma = t_{2g}$ and e_g stand for the irreducible representations of the O_h group. $|d_\gamma\rangle$ and $|p_\gamma\rangle$ are, respectively,

Table 1. Group overlap integrals, MO coefficients, orbital reduction factors, S.O. coupling coefficients (in cm⁻¹) and dipole hyperfine structure parameters (in 10⁻⁴ cm⁻¹) for Cr³⁺ in MgS and SrS.

	$S_{dp}(t_{2g})$	$S_{dp}(e_g)$	N_t	N_e	λ_t	λ_e	k	k'	ζ	ζ'	P
MgS	0.014	0.046	0.718	0.733	0.642	0.651	0.865	0.574	250	143	-28.8
SrS	0.004	0.017	0.728	0.743	0.626	0.636	0.870	0.589	251	147	-29.2

the d orbitals of the central 3dⁿ ion and the p orbitals of the ligands. The MO coefficients N_γ and λ_γ are, respectively, the normalization factors and the orbital mixing coefficients, which can be determined from the approximate relations [12]

$$f_\gamma = N_\gamma^2 [1 + \lambda_\gamma^2 S_{dp}^2(\gamma) - 2\lambda_\gamma S_{dp}(\gamma)], \quad (2)$$

and the normalization conditions [12]

$$N_\gamma(1 - 2\lambda_\gamma S_{dp}(\gamma) + \lambda_\gamma^2) = 1, \quad (3)$$

where $S_{dp}(\gamma)$ are the group overlap integrals. The covalency parameter $f_\gamma [\approx (B/B_0 + C/C_0)/2]$ is the ratio of the Racah parameters for a 3dⁿ ion in a crystal to those of a free ion.

Thus, according to the cluster approach [12, 14], the S. O. coupling coefficients ζ , ζ' , the orbital reduction factors k , k' and the dipolar hyperfine structure parameters P and P' (which are related to the A factor) for the octahedral 3dⁿ clusters can be expressed as

$$\begin{aligned} \zeta &= N_t(\zeta_d^0 + \lambda_t^2 \zeta_p^0/2), \\ \zeta' &= (N_t N_e)^{1/2}(\zeta_d^0 - \lambda_t \lambda_e \zeta_p^0/2), \\ k &= N_t(1 + \lambda_t^2/2), \\ k' &= (N_t N_e)^{1/2}(1 - \lambda_t \lambda_e/2), \\ P &= N_t P_0, \quad P' = (N_t N_e)^{1/2} P_0, \end{aligned} \quad (4)$$

where ζ_d^0 and ζ_p^0 are the S. O. coupling coefficient of d electrons of a free 3dⁿ ion and that of p electrons of a free ligand ion, respectively. P_0 is the dipolar hyperfine structure parameter of the free 3dⁿ ion. From (4), one can find that the contributions due to the S.O. coupling coefficient as well as the p orbitals of ligands are taken into account, based on the cluster approach.

In order to investigate the EPR parameters of an octahedral 3d³ cluster, the two- S. O.-coupling- coefficient formulas for g and A factors based on the cluster approach can be written as

$$\begin{aligned} g &= g_s - 8\zeta'k'/(3E_1) - 2\zeta(2k'\zeta - k\zeta') \\ &\quad + 2g_s\zeta'/(9E_1^2) + 4\zeta'^2(k - 2g_s)/9E_3^2 \end{aligned}$$

$$\begin{aligned} &- \zeta^2(k + g_s)/(3E_2^2) - 4\zeta\zeta'k'[1/(3E_1E_2) \\ &\quad + 1/(9E_1E_3) + 1/(3E_2E_3)], \\ A &= P\{-8\zeta'k'/(3E_1) - 2\zeta(2k'\zeta - k\zeta') \\ &\quad + 2g_s\zeta'/(9E_1^2) + 4\zeta'^2(k - 2g_s)/9E_3^2 \\ &\quad - \zeta^2(k + g_s)/(3E_2^2) - 4\zeta\zeta'k'[1/(3E_1E_2) \\ &\quad + 1/(9E_1E_3) + 1/(3E_2E_3)] - \kappa\}, \end{aligned} \quad (5)$$

where $g_s (= 2.0023)$ is the spin-only value. The energy denominators E_i ($i = 1 \sim 3$) can be expressed as follows [12]:

$$\begin{aligned} E_1 &\approx 10Dq, \quad E_2 \approx 15B + 5C, \\ E_3 &\approx 10Dq + 9B + 3C, \end{aligned} \quad (6)$$

where Dq is the cubic field parameter and κ the core polarization constant.

Now we apply the above formulas to the g and A factors for Cr³⁺ in MgS and SrS. For MgS and SrS, the metal-ligand distances R are 2.6017 Å and 3.0099 Å [15], respectively. From the Slater-type SCF wavefunctions [16, 17] and the distances R , the group overlap integrals $S_{dp}(\gamma)$ for both systems are calculated and shown in Table 1.

According to [10], the optical spectra of SrS:Cr³⁺ yield $Dq \approx 1100$ cm⁻¹. The Racah parameter B (≈ 447 cm⁻¹) was obtained from the optical spectra of the similar octahedral [CrS₆]⁹⁻ cluster in NaCrS₂ [18], where the Cr³⁺-S²⁻ distance is about 2.808 Å [15]. Considering that the Racah parameters B and C decrease slightly with decreasing distance R [19] and that the cubic field parameter $Dq \propto R^{-n}$ ($n \approx 3.5 \sim 6.5$ [20]), we can estimate

$$Dq \approx 1540 \text{ cm}^{-1}, \quad B \approx 442 \text{ cm}^{-1}, \quad C \approx 1768 \text{ cm}^{-1} \quad (7)$$

for MgS:Cr³⁺, and

$$Dq \approx 1100 \text{ cm}^{-1}, \quad B \approx 455 \text{ cm}^{-1}, \quad C \approx 1820 \text{ cm}^{-1} \quad (8)$$

for SrS:Cr³⁺. By using the free ion values $B_0 \approx 920$ cm⁻¹ and $C_0 \approx 3331$ cm⁻¹ [21] for Cr³⁺, the covalency parameters f_γ for both crystals

Table 2. EPR g factors and the hyperfine structure constant A factors for Cr^{3+} in MgS and SrS.

	g			$A(10^{-4} \text{ cm}^{-1})$		
	Cal. ^a	Cal. ^b	Expt.	Cal. ^a	Cal. ^b	Expt.
MgS	1.9778	1.9875	1.9874 [9]	15.7	15.3	15.3 [9]
SrS	1.9670	1.9808	1.9795 (2) [10]	16.8	16.2	16.4 (1) [10]

^a Theoretical results based on the conventional single-S.O.-coupling-coefficient formulas. ^b Theoretical results based on the two -S.O.-coupling-coefficient formulas.

are calculated, i.e., $f_{\gamma}(\text{MgS}:\text{Cr}^{3+}) \approx 0.506$ and $f_{\gamma}(\text{SrS}:\text{Cr}^{3+}) \approx 0.520$. Thus the MO coefficients N_{γ} and λ_{γ} are obtained for both crystals from (2) and (3), and given in Table 1. From the free ion values $\zeta_d^0(\text{Cr}^{3+}) \approx 273 \text{ cm}^{-1}$ [22], $P_0(^5\text{Cr}^{3+}) \approx -39.7 \times 10^{-4} \text{ cm}^{-1}$ [23] and $\zeta_p^0(\text{S}^{2-}) \approx 365 \text{ cm}^{-1}$ [24], the parameters k , k' , ζ , ζ' and P are calculated from (4) and also shown in Table 1.

The core polarization constant in the formula of A factor can be expressed as [25]

$$\kappa \approx -2\chi / (3\langle r^{-3} \rangle), \quad (9)$$

where χ is characteristic of the density of unpaired spins at the nucleus of the central metal ion, and $\langle r^{-3} \rangle$ is the expectation value of the inverse cube of the radial wavefunction of the 3d orbital [25]. By using the values $\langle r^{-3} \rangle \approx 3.959 \text{ a.u.}$ [25] for Cr^{3+} and $\chi \approx -2.2 \text{ a.u.}$ [23] for $\text{MgS}:\text{Cr}^{3+}$, we have $\kappa \approx 0.371$. Since the value of χ for $\text{SrS}:\text{Cr}^{3+}$ is not reported, we can reasonably estimate it from the proportional relationship $\chi(\text{MgS}:\text{Cr}^{3+})/\chi(\text{SrS}:\text{Cr}^{3+}) \approx \chi(\text{MgO}:\text{Cr}^{3+})/\chi(\text{CaO}:\text{Cr}^{3+})$ and the values $\chi(\text{MgO}:\text{Cr}^{3+}) \approx -2.27 \text{ a.u.}$ and $\chi(\text{CaO}:\text{Cr}^{3+}) \approx -2.35 \text{ a.u.}$ Thus, we have $\chi \approx -2.3 \text{ a.u.}$, and so $\kappa \approx 0.387$ for $\text{SrS}:\text{Cr}^{3+}$.

Substituting all the parameters into (5), the g and A factors for Cr^{3+} in MgS and SrS crystals are calculated and shown in Table 2. For comparisons, the theoretical results based on the conventional single-S.O.-coupling-coefficient formulas (i.e., taking $\zeta_p^0 = 0$, $\lambda_t = \lambda_e = 0$ and $N_t = N_e = f_{\gamma}^{1/2}$) are also calculated and compared with the observed values in Table 2.

3. Discussions

(1) From Table 2 one can find that the theoretical g and A factors for both crystals, based on the two-S.O.-coupling-coefficient formulas, agree with the experimental data, while the calculated results based on

the conventional single-S.O.-coupling-coefficient formulas are inconsistent with the observed values. So, for the systems with strong covalency such as Cr^{3+} in MgS and SrS (where the covalency parameter $f_{\gamma} \sim 0.5 \ll 1$) of this work, the two-S.O.-coupling-coefficient formulas are more reasonable than the conventional single-S.O.-coupling-coefficient formulas in theoretical studies of the EPR parameters g and A . In addition, the smaller g shift $\Delta g (= g - g_s)$ and the smaller A value of $\text{MgS}:\text{Cr}^{3+}$ compared with those of $\text{SrS}:\text{Cr}^{3+}$ are also in accordance with the smaller $\text{Cr}^{3+}\text{-S}^{2-}$ distance and hence stronger covalency of the former.

(2) The observed isotropic g and A factors reveal the cubic symmetry of the Cr^{3+} centers in both crystals. According to the investigations based on the shell-model interionic potential method, a transition-metal ion (e.g., Fe^{2+} , Co^{2+} and Ni^{2+}) in SrO may take an off-center displacement along certain symmetry (e.g., [111], [100] or [110]) directions due to its smaller ionic radius compared with that ($\approx 1.12 \text{ \AA}$ [26]) of the replaced Sr^{2+} [27, 28]. As a result, the local symmetry is reduced from the ideal cubic cation site to low symmetry (e.g., trigonal, tetragonal or rhombic) of the impurity center. These off-center displacements were indeed verified by experiments [29]. However, for Cr^{3+} in SrS of this work {where the size ($\approx 0.63 \text{ \AA}$ [26]) of the impurity ion is also much smaller than that of the host cation}, the impurity Cr^{3+} seems to be intensively confined to the regular Sr^{2+} site because of considerable covalency, and then the cubic symmetry of the host Sr^{2+} site is conserved in the impurity centers. In addition, charge compensation arising from the extra charge of the impurity Cr^{3+} may be far enough from the impurity centers in both crystals, and so its influence on the local symmetry should be negligible.

(3) The above theoretical formulas and methods can also be applied to other $3d^3$ ions (e.g., V^{2+} , Mn^{4+}) in sulfides. The investigations on the g and A factors of the Cr^{3+} centers in this work would be helpful to study chemical bonding and charge transfer of metal-sulfur systems.

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