Investigations of the EPR *g* Factors of $NaCrS_2$ and $NaCrSe_2$

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Z. Naturforsch. **60a,** 369 – 372 (2005); received January 4, 2005

The EPR *g* factors of Cr^{3+} in $NaCrS_2$ and $NaCrSe_2$ crystals are calculated from the high-order perturbation formulas based on the one-spin-orbit (SO)-coupling-parameter (i. e., the SO-coupling-parameter of the central $3d^n$ ion) as well as the two-SO-coupling-parameter (i. e., the SO-coupling-parameter of the $3d^n$ ion and that of ligands) models for $3d^n$ ions in cubic octahedral sites. The calculated results (in particular for $NaCrSe_2$) based on the two-SO-coupling-parameter model are closer to the observed values than those based on the one-SO-coupling-parameter model, suggesting that for calculations of the *g* factor of $3d^n$ ions in covalent crystals the two-SO-coupling-parameter model is preferable to the one-SO-coupling-parameter model. The reasonableness of the calculated results from the two-SO-coupling-parameter model is discussed.

Key words: Electron Paramagnetic Resonance; Crystal- and Ligand-field Theory; Spin-orbit Coupling; Cr^{3+}; $NaCrS_2$; $NaCrSe_2$.

1. Introduction

When a $3d^n$ ion enters a crystal, the *g* factor should shift from the free-ion value g_e (≈ 2.0023) [1 – 3]. The change of *g* factor is due to the interactions of excited states with the ground state via spin-orbit (SO)-coupling [1 – 3]. In the conventional crystal-field theory [1 – 5], for simplicity, only the contribution to the *g* factor due to the SO-coupling of central $3d^n$ ion is considered. The method is therefore called one-SO-coupling-parameter model. The model is only suitable for $3d^n$ ions in the ionic crystals, where the interaction between the SO-coupling-parameter of a $3d^n$ ion and that of a ligands via covalence effects can be neglected. However, since both the SO-coupling-parameter of ligands and the covalence of $3d^n$ clusters in crystals increase with increasing atomic number of the ligand ion [6], the contribution to the *g* factor from the SO-coupling-parameter of ligands via the covalence effect should be taken into account. Thus, the two-SO-coupling-parameter model based on the cluster approach was developed [7 – 12]. In this model, the contributions to *g* factors from both the SO-coupling-parameter of a $3d^n$ ion and that of ligands are included, and so it is suitable for a $3d^n$ ion in covalence crystals. Many studies of *g* factors for $3d^n$ ions in MX_6 (where $X = Cl^-$, Br^-, I^-, the VIIA group ligands) [7 – 9] and in ML_4 (where $L = S^{2-}$, Se^{2-}, Te^{2-}, the VIA group ligands) [11 – 12] have been made to analyze the relative importance of the contributions to *g* factors from the SO-coupling-parameter of ligands and the covalence of $3d^n$ clusters. However, for $3d^n$ ions in ML_6, the octahedral clusters with VIA group ligand ions, fewer studies exist. Isotropic *g* factors of the magnetic semiconductors $NaCrS_2$ and $NaCrSe_2$ were reported [13]. Cr^{3+} ions in both crystals occupy octahedral sites, and $(CrL_6)^{9-}$ (L = S, Se) clusters are formed in these crystals [14]. They are suitable examples for the study. In this paper, we study the *g* factors for both crystals by means of high-order perturbation formulas based on two- and also one-SO-coupling-parameter models.

2. Calculation

According to the two-SO-coupling-parameter model [7 – 9], the admixture of SO-coupling-parameters between the d electrons of $3d^n$ ions and the p electrons of ligands via the covalence effect will be considered. So, the zero-order wave functions should be combined with the one-electron wave function of the molecular orbitals which are a linear combination of d orbitals $|d_\gamma\rangle$ of $3d^n$ ions and p orbitals $|p_\gamma\rangle$ of ligand ions. Thus, for $3d^n$ ions in octahedral clusters, the molecular orbitals can be expressed as [7 – 9]

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

in which the subscript $\gamma = t_{2g}$ or e_g stands for the irreducible representation of O_h symmetry. N_γ and λ_γ are the normalization factors and the orbital mixing coefficients, respectively. Thus, two SO-coupling-parameters ζ and ζ', which describe, respectively, the SO-coupling between two t_{2g} terms and that between t_{2g} and e_g terms, can be written as [7 – 9]

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

where ζ_d^0 and ζ_p^0 are, respectively, the SO-coupling-parameters of the $3d^n$ ion and the ligand ion in the free state.

By use of the molecular orbitals and Macfarlane's perturbation-loop method [4, 5], the high-order perturbation formula of the g factor based on the two-SO-coupling-parameter model for a $3d^3$ ion in octahedral clusters can be expressed as [8]

$$\begin{aligned} g = 0.0023 &- 8k'\zeta'/(3E_1) \\ &- 2\zeta(2k'\zeta - k\zeta' + 2g_e\zeta')/9E_1^2) \\ &+ 4(k - 2g_e)\zeta'^2/9E_3^2 - 2\zeta^2(k + g_e)/(3E_2^2) \\ &- 4\zeta\zeta'k'/(3E_1E_2) + 4\zeta\zeta'k'/(9E_1E_2) \\ &+ 4\zeta\zeta'k'/(3E_2E_3), \end{aligned} \qquad (3)$$

where the zero-order energy denominations E_i are [4, 5]

$$\begin{aligned} E_1 &= \Delta = 10Dq, \quad E_2 = 15B + 5C, \\ E_3 &= \Delta + 9B + 3C. \end{aligned} \qquad (4)$$

The orbital reduction factors k and k' are given as

$$\begin{aligned} k &= N_t(1 - 2\lambda_t S_{dp}(t_{2g}) + \lambda_t^2/2), \\ k' &= N_t^{1/2}N_e^{1/2}(1 - \lambda_t S_{dp}(t_{2g}) - \lambda_e S_{dp}(e_g) - \lambda_t\lambda_e/2) \end{aligned} \qquad (5)$$

[note: since $S_{dp}(\gamma)$ is small, in [8 – 10] the terms including $S_{dp}(\gamma)$ in (5) are neglected].

In the above formulas, the molecular orbital coefficients N_γ and λ_γ are estimated from the normalization relationship

$$N_\gamma[1 - 2\lambda_\gamma S_{dp}(\gamma) + \lambda_\gamma^2] = 1 \qquad (6)$$

and the approximate conditions [7 – 9]

$$\beta \approx N_\gamma^2[1 - 2\lambda_\gamma S_{dp}(\gamma) + \lambda_\gamma^2 S_{dp}(\gamma)], \qquad (7)$$

in which $\beta \approx (B/B_0 + C/C_0)/2$ is the ratio of the Racah parameters for a $3d^n$ ion in the crystal to those for the free ion. $S_{dp}(\gamma)$ is the group overlap integral. In the above formulas, if we take $\lambda_\gamma = 0$ and $N_\gamma = \beta^{1/2}$, the admixtures of the orbitals of ligands to those of $3d^n$ ions are not considered. The above formulas based on the two-SO-coupling-parameter model become those based on the one-SO-coupling-parameter model.

The Racah parameters and cubic field parameter Dq for the studied system can be obtained from its optical spectra. For $NaCrS_2$ crystal, from its optical spectra [15] we have

$$\begin{aligned} &B \approx 440\ \text{cm}^{-1}, \quad C \approx 2080\ \text{cm}^{-1}, \\ &Dq \approx 1400\ \text{cm}^{-1}. \end{aligned} \qquad (8)$$

For the free Cr^{3+} ion, $B_0 \approx 1030$ cm^{-1} and $C_0 \approx 3850$ cm^{-1} [1]; thus we have $\beta = 0.484$ for $NaCrS_2$. For $NaCrSe_2$ crystal, to our knowledge no optical spectra were reported. We estimate reasonably the optical spectra parameters as follows: According to the linear trends aiding the interpretation and prediction of optical spectra of $3d^n$ ions [16], we have

$$\frac{P(\text{NaCrS}_2)}{P(\text{NaCrSe}_2)} \approx \frac{P(\text{ZnS} : \text{V}^{2+})}{P(\text{ZnSe} : \text{V}^{2+})}, \qquad (9)$$

where $P = Dq$ or β. Thus, from the optical spectral parameters of the isoelectronic $3d^n$ ion V^{2+} in ZnS and ZnSe [17] (note: the optical spectra of Cr^{3+} ion in ZnS and ZnSe were not reported completely), we have $Dq(\text{ZnS} : \text{V}^{2+}) \approx 500$ cm^{-1}, $Dq(\text{ZnSe} : \text{V}^{2+}) \approx 460$ cm^{-1}, $\beta(\text{ZnS} : \text{V}^{2+}) \approx 0.65$, $\beta(\text{ZnSe} : \text{V}^{2+}) \approx 0.59$. Thus, we obtain for $NaCrSe_2$

$$Dq \approx 1288\ \text{cm}^{-1}, \quad \beta \approx 0.439. \qquad (10)$$

Since the $NaCrSe_2$ crystal has the stronger covalence and larger metal-ligand distance than $NaCrS_2$, the smaller values of Dq and β in $NaCrSe_2$ than those in $NaCrS_2$ can be understood.

The group overlap integrals $S_{dp}(\gamma)$ are calculated with the Slater-type SCF functions [18, 19] and the metal-ligand distance R. For $NaCrS_2$, $R \approx 2.44$ Å [14, 15], we obtain $S_{dp}(e_g) \approx 0.0776$ and $S_{dp}(t_{2g}) \approx 0.0301$; and for $NaCrSe_2$, $R \approx 2.56$ Å [14], we obtain $S_{dp}(e_g) \approx 0.0757$ and $S_{dp}(t_{2g}) \approx 0.0279$.

Table 1. The molecular orbital coefficients, the SO-coupling-parameters and the orbital reduction factors in $NaCrS_2$ and $NaCrSe_2$ crystals.

	N_t	N_e	λ_t	λ_e	ζ (cm^{-1})	ζ' (cm^{-1})	k	K'
$NaCrS_2$	0.7102	0.7357	0.6697	0.6819	252.0	137.1	0.8408	0.5050
$NaCrSe_2$	0.6763	0.7026	0.7203	0.7307	475.7	−112.8	0.8246	0.4559

Table 2. The g factors of the Cr^{3+} ion in $NaCrS_2$ and $NaCrSe_2$ crystals.

	$g(\zeta_d)$[a]	$g(\zeta_d,\zeta_p)$[b]	g (expt.)
$NaCrS_2$	1.977	1.988	1.980 [13], 1.986(1) [21], 1.988(1) [21]
$NaCrSe_2$	1.977	2.011	1.997[13]

[a] Calculated from the one-SO-coupling-parameter model.

[b] Calculated from the two-SO-coupling-parameter model.

Substituting the values of $S_{dp}(\gamma)$ and β into (6) and (7), the molecular orbital coefficients N_γ and λ_γ for $NaCrS_2$ and $NaCrSe_2$ can be calculated. They are shown in Table 1. Thus, from the SO-coupling-parameters $\zeta_d^0(Cr^{3+}) \approx 273$ cm^{-1} [1], $\zeta_p^0(S^{2-}) \approx 365$ cm^{-1}, $\zeta_p^0(Se^{2-}) \approx 1659$ cm^{-1} [20] and by use of (2) and (5), the SO-coupling-parameters ζ, ζ' and orbital reduction factors k, k' are calculated. They are also shown in Table 1.

Applying all these parameters to (3), the g factors for $NaCrS_2$ and $NaCrSe_2$ crystals were calculated. The results are compared with the experimental values in Table 2. We also have calculated the g factors for both crystals with the perturbation formulas based on the one-SO-coupling-parameter model for comparing them with those obtained from the two-SO-coupling-parameter model. The results are also collected in Table 2.

3. Discussion

The calculated $g(\zeta_d)$ from the one-SO-coupling-parameter model for $NaCrS_2$ is close to that for $NaCrSe_2$, but the calculated $g(\zeta_d,\zeta_p)$ from the two-SO-coupling-parameter model for $NaCrS_2$ is smaller than that for $NaCrSe_2$. The experimental results [13] support the calculated values $g(\zeta_d,\zeta_p)$ (see Table 2), and so this model is preferable to the one-SO-coupling-parameter model. In addition, the calculated $g(\zeta_d,\zeta_p)$ for both crystals is greater than the calculated $g(\zeta_d)$. The difference $\Delta g = g(\zeta_d,\zeta_p) - g(\zeta_d)$ is caused by the contribution from the SO-coupling-parameter of the ligands. The greater the SO-coupling-parameter of the ligands, the greater its contribution to the g factor and hence the greater the difference Δg. So, in our calculations the larger Δg and hence the larger $g(\zeta_d,\zeta_p)$ for $NaCrSe_2$ than those for $NaCrS_2$ are reasonable in physics. It appears that for $3d^n$ clusters having a large SO-coupling-parameter of ligands, the studies of the g factor should apply the two-SO-coupling-parameter model.

The calculated $g(\zeta_d,\zeta_p)$ for both crystals are larger than the observed values given in [13] (see Table 2). In our opinion, the calculated $g(\zeta_d,\zeta_p)$ are more reasonable. The causes are as follows: 1) As pointed out in [13], the observed g factors in [13] have an inherent experimental error near 15% due to an inaccuracy in the assignment of the line positions. 2) $NaCrS_2$ and $NaCrSe_2$ have trigonal symmetry [14], the mean $\bar{g}[=\frac{1}{3}(g_\parallel + 2g_\perp)]$ is very close to the g value in cubic approximation. From the studies of EPR lineshifts caused by dipolar fields in $NaCrS_2$, Elliston [21] obtained at room temperature $\bar{g} \approx 1.986(3)$ by subtracting the computed dipolar shifts from the observed shifts at 36 GHz. The $\bar{g}$ value agrees with $\bar{g} \approx 1.988(1)$ determined by measuring the EPR lineshifts at 9.5 GHz, which should reduce the dipolar shifts but not the $\bar{g}$ values. These observed $\bar{g}$ values agree well with the calculated $g(\zeta_d,\zeta_p)$ and so the $g(\zeta_d,\zeta_p)$ for $NaCrS_2$ is reasonable. For the $NaCrSe_2$ crystal, no similar EPR lineshift experiments were reported. Considering that the calculated $g(\zeta_d,\zeta_p)$ for $NaCrS_2$ is larger than the observed value given in [13], for a similar $NaCrSe_2$ crystal, the larger calculated $g(\zeta_d,\zeta_p)$ than the observed value given in [13] can be regarded as more reasonable. This point remains to be further checked by experimental studies, in particular, the experiment of EPR lineshifts as made for $CrNaS_2$.

Acknowledgements

This project was supported by the National Natural Science Foundation of China (Grant No. 10274054) and the Scientific Foundation of Civil Aviation Flying Institute of China.

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