



Trends in  
**Applied Sciences  
Research**

ISSN 1819-3579



Academic  
Journals Inc.

[www.academicjournals.com](http://www.academicjournals.com)

## Investigations on the Gyromagnetic Factors for the Layered Triangular Antiferromagnets $VX_2$ ( $X = Cl, Br, I$ )

<sup>1,2</sup>Shao-Yi Wu, <sup>1</sup>Xiu-Ying Gao, <sup>1</sup>Qiang Fu and <sup>1</sup>Ji-Zi Lin

<sup>1</sup>Department of Applied Physics, University of Electronic Science and Technology of China, Chengdu 610054, Peoples's Republic of China

<sup>2</sup>International Center for Materials Physics, Chinese Academy of Sciences, Shenyang 110016, Peoples's Republic of China

---

**Abstract:** The gyromagnetic factors  $g_{||}$  and  $g_{\perp}$  for the layered trigonal antiferromagnets  $VX_2$  ( $X = Cl, Br, I$ ) are theoretically investigated by using the perturbation formulas of the  $g$  factors for a  $3d^3$  ion in trigonal symmetry based on the cluster approach. In these formulas, the contributions from the  $s$ -orbitals of the ligands which were often ignored in the previous treatments are taken into account here. The related trigonal field parameters  $V$  and  $V'$  are determined from the superposition model and the structural data of the systems. The calculated  $g$  factors are in good agreement with the observed values, particularly the results for  $VI_2$  show some improvement compared with those in the absence of the ligand  $s$ -orbital contributions.

**Key words:** Electron paramagnetic resonance, Crystal-and ligand-fields,  $VX_2$  ( $X = Cl, Br, I$ )

---

### Introduction

The layered trigonal antiferromagnets  $VX_2$  ( $X = Cl, Br, I$ ) have the crystal structure of  $CdI_2$  with space group  $P\bar{3}mL$ , where the halide anions form hexagonal close-packed layers and the cations occupy half the octahedral holes. Recently,  $VX_2$  have attracted extensive interest due to the properties of quantum fluctuations (Bondarenko *et al.*, 1996; Rastelli and Tassi, 1996; Watabe *et al.*, 1995), critical behaviours (Kawamura, 1988) and Raman scattering (Guntherodt *et al.*, 1979; Bauhofer *et al.*, 1980). In addition, Electron Paramagnetic Resonance (EPR) experiments have been carried out on these systems and the anisotropic  $g$  factors  $g_{||}$  and  $g_{\perp}$  were measured at 300 K (Yamada *et al.*, 1984).

In order to interpret these EPR experimental results, inspiring investigations have been made on  $VCl_2$  and  $VBr_2$  from the perturbation formulas of the  $g$  factors for a  $3d^3$  ion in trigonal symmetry based on the cluster approach (Du and Li, 1994). In these formulas, not only the Spin-orbit (SO) coupling coefficient of the  $V^{2+}$  ion, but also that (as well as the  $p$  orbitals) of the ligands is taken into account (Du and Li, 1994). The theoretical results indeed show improvement compared with those based on only the SO coupling coefficient of the central ion. However, the trigonal crystal-field parameters in their calculations were taken as the adjustable parameters, without correlating with structural data of the studied systems. In addition, the experimental  $g$  factors of  $VI_2$  have not been explained uniformly. Since the S.O. coupling coefficient of the ligand  $I^-$  is much larger than that of the  $V^{2+}$ , the  $s$ -orbitals of the ligand may be important and lead to some contributions to the  $g$  factors. To investigate the  $g$  factors of  $VX_2$  to a better extent, in this study, the  $s$ -orbitals of the ligand are introduced to the single-electron wave functions of the  $3d^3$  octahedral clusters. Then the previous theoretical formulas are also modified and applied to the studied systems.

---

**Corresponding Author:** Shao-Yi Wu, Department of Applied Physics, University of Electronic Science and Technology of China, Chengdu 610054, Peoples's Republic of China

Theory and Calculations

In  $VX_2$ ,  $V^{2+}$  locates on the octahedral site with slight trigonal ( $D_{3d}$ ) distortion (Wyckoff, 1951). For a  $V^{2+}(3d^3)$  ion in trigonal symmetry, its ground  ${}^4A_2$  state would be split into two Kramers doublets due to the combination effect of the SO coupling and the trigonal crystal-field interactions. Thus, the perturbation formulas of the g-shifts  $\Delta g_i$  ( $=g_i - g_s$ , where  $g_s = 2.0023$  is the spin only value and  $I = //$  and  $\perp$ ) based on the cluster approach can be expressed as (Du and Li, 1994):

$$\begin{aligned} \Delta g_{//} = & -8 \zeta' k' / (3 E_1) - 2\zeta(2 k' \zeta - k \zeta' + 2g_s \zeta') / (9E_1^2) + 4\zeta'^2(k-2g_s) / 9E_3^2 \\ & - \zeta^2(k+g_s) / (3E_2^2) - 4\zeta\zeta' k' [1 / (3E_1 E_2) + 1 / (9E_1 E_3) + 1 / (3E_2 E_3)] \\ & + 8\zeta' k' V / (9E_1^2) - 4\sqrt{2}(k' \zeta + k \zeta') V' / (3E_1 E_4) \\ \Delta g_{\perp} = & \Delta g_{//} - \zeta' k' V / (3E_1^2) + \sqrt{2}(2k\zeta' + k' \zeta) V' / (3E_1 E_4). \end{aligned} \tag{1}$$

Here the energy denominators  $E_i$  ( $i = 1 \sim 5$ ) stand for the separations between the excited states  ${}^4T_2$ ,  ${}^2T_{2a}$ ,  ${}^2T_{2b}$ ,  ${}^4T_{1a}$  and  ${}^4T_{1b}$  and the ground state  ${}^4A_2$  in terms of the cubic field parameter  $Dq$  and the Racah parameters  $B$  and  $C$  for the studied  $3d^3$  clusters (Du and Li, 1994).  $V$  and  $V'$  are the trigonal field parameters.  $\zeta$  and  $\zeta'$  are the SO coupling coefficients, while  $k$  and  $k'$  are the orbital reduction factors. In the cluster approach of the previous treatments (Du and Li, 1994; Du and Rudowicz, 1992), the contributions of the s-orbitals of ligands were usually neglected for simplicity. Unlikely, the above contributions are considered here. Thus, the total single electron wave function including the ligand s-orbital contributions may be written as

$$\begin{aligned} \Psi_t = & N_t^{1/2} (\varphi_t - \lambda_t \chi_{pt}) \\ \Psi_e = & N_e^{1/2} (\varphi_e - \lambda_e \chi_{pe} - \lambda_s \chi_s) \end{aligned} \tag{2}$$

where  $\varphi_\gamma$  ( $\gamma = e$  and  $t$  denote the irreducible representations of the  $O_h$  group) are the d orbitals of the central metal ion.  $\chi_{p\gamma}$  and  $\chi_s$  stand for the p- and s- orbitals of the ligands.  $N_\gamma$  and  $\lambda_\gamma$  (or  $\lambda_s$ ) are, respectively, the normalization factors and the orbital mixing coefficients. From the semiempirical method similar to those in the previous treatments (Du and Li, 1994; Du and Rudowicz, 1992), we have the approximate relationships

$$\begin{aligned} f_t = & N_t^2 [1 + \lambda_t^2 S_{dpt}^2 - 2 \lambda_t S_{dpt}] \\ f_e = & N_e^2 [1 + \lambda_e^2 S_{dpe}^2 + \lambda_s^2 S_{ds}^2 - 2 \lambda_e S_{dpe} - 2 \lambda_s S_{ds}] \end{aligned} \tag{3}$$

and the normalization conditions

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

Here  $S_{d\gamma}$  (and  $S_{ds}$ ) are the group overlap integrals. Usually, 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  $e_g$ . In general, the covalency factors  $f_t$  and  $f_e$  can be determined from the ratio of the Racah parameters for the  $3d^3$  ion in a crystal to those in free state, i.e.,  $f_t \approx f_e \approx C/C_0$ .

According to the cluster approach containing the ligand s-orbital contributions, the SO coupling coefficients  $\zeta$ ,  $\zeta'$  and the orbital reduction factors  $k$ ,  $k'$  for the  $3d^3$  octahedral clusters may be expressed as

$$\begin{aligned} \zeta = & N_t (\zeta_d^0 + \lambda_t^2 \zeta_p^0 / 2), \zeta' = (N_t N_e)^{1/2} (\zeta_d^0 - \lambda_t \lambda_e \zeta_p^0 / 2) \\ k = & N_t (1 + \lambda_t^2 / 2), k' = (N_t N_e)^{1/2} [1 - \lambda_t (\lambda_e + \lambda_s A) / 2] \end{aligned} \tag{5}$$

where  $\zeta_d^0$  and  $\zeta_p^0$  are the SO coupling coefficients of the free  $3d^3$  and the ligand ions, respectively. A denotes the integral,  $R \langle ns | \frac{\partial}{\partial y} | np_y \rangle$  where R is the metal-ligand distance of the studied systems. Obviously, when taking  $S_{ds} = \lambda_s = 0$  and  $A = 0$ , the above formulas are reduced to those in the absence of the ligand s-orbital contributions (Du and Li, 1994; Du and Rudowicz, 1992).

From the superposition model (Newman and Ng, 1989), the trigonal field parameters V and V' for the studied systems are written as follows:

$$\begin{aligned} V &= (18/7)\bar{A}_2(R)(3\cos^2\beta - 1) + (40/21)\bar{A}_4(R)(35\cos^4\beta - 30\cos^2\beta + 3) \\ &\quad + (40\sqrt{2}/3)\bar{A}_4(R)\sin^3\beta\cos\beta, \\ V' &= (-6\sqrt{2}/7)\bar{A}_2(R)(3\cos^2\beta - 1) + (10\sqrt{2}/21)\bar{A}_4(R)(35\cos^4\beta - 30\cos^2\beta + 3) \\ &\quad + (20/3)\bar{A}_4(R)\sin^3\beta\cos\beta \end{aligned} \quad (6)$$

where  $\beta$  is the angle between the metal-ligand bond and the  $C_3$  axis. The magnitude and nature (elongation or compression along the  $C_3$  axis) of trigonal distortion can be characterized by the value and sign of the angular difference  $\delta\beta$  ( $= \beta - \beta_0$ , where  $\beta_0 \approx 54.74^\circ$  is the bonding angle in cubic symmetry).  $\bar{A}(R)$  and  $\bar{A}_4(R)$  are the intrinsic parameters with the reference bonding length R. For  $3d^n$  ions in octahedra, the relationships  $\bar{A}_4(R) \approx (3/4)Dq$  and  $\bar{A}_2(R)/\bar{A}_4(R) \approx 9 \sim 12$  have been proved to be valid in many crystals (Newman and Ng, 1989; Yu *et al.*, 1994; Edgar, 1976). Here we take  $\bar{A}_2(R) \approx 9\bar{A}_4(R)$ . Therefore, the trigonal distortion (or local structure) is related to the low symmetrical parameters V and V' and hence to the g factors (particularly the anisotropy  $g_{//} - g_{\perp}$ ) of the studied systems.

For  $VX_2$  (Wyckoff, 1951), the metal-ligand bonding lengths R and the angles  $\beta$  between R and the  $C_3$  axis are collected in Table 1. From the distances R and the Slater-type SCF functions (Clementi and Raimondi, 1963), the group overlap integrals  $S_{dpy}$  (as well as the integrals  $S_{ds}$  and A) are obtained and shown in Table 1.

Table 1: The metal-ligand distances and angles, group overlap integrals, the spectral parameters Dq, B and C ( $\text{cm}^{-1}$ ),  $N_y$  and  $\lambda_y$  (and  $\lambda_z$ ), SO coupling coefficients ( $\text{cm}^{-1}$ ), orbital reduction factors and the trigonal field parameters V and V' (in  $\text{cm}^{-1}$ ) for  $VX_2$  (X = Cl, Br, I)

	R (Å)	$\beta$ (°)	$S_{dpt}$	$S_{dpe}$	$S_{ds}$	A	Dq
VCl <sub>2</sub>	2.539	54.96	0.0232	0.0703	0.0408	1.2827	925
VBr <sub>2</sub>	2.668	54.62	0.0220	0.0697	0.0379	1.2028	890
VI <sub>2</sub>	2.848	54.17	0.0215	0.0682	0.0387	1.0861	850
	B	C	$f_y$	$N_y$	$N_z$	$\lambda_y$	$\lambda_z$
VCl <sub>2</sub>	610	2375	0.832	0.919	0.939	0.321	0.302
VBr <sub>2</sub>	565	2365	0.828	0.917	0.936	0.324	0.309
VI <sub>2</sub>	530	2350	0.823	0.914	0.933	0.329	0.310
	$\lambda_z$	$\zeta$	$\zeta'$	k	k'	V	V'
VCl <sub>2</sub>	0.175	181	129	0.966	0.850	-133	99
VBr <sub>2</sub>	0.168	272	41	0.965	0.849	68	-50
VI <sub>2</sub>	0.176	403	-85	0.963	0.847	314	-230

Table 2: The gyromagnetic factors for  $VX_2$  at 300 K

		$\Delta g_{//}$	$\Delta g_{\perp}$	$g_{//} - g_{\perp}$
VCl <sub>2</sub>	Cal. <sup>a</sup>	-0.0323	-0.0313	-0.001
	Cal. <sup>b</sup>	-0.0323	-0.0313	-0.001
	Expt. <sup>c</sup>	-0.0323 (20)	-0.0283 (20)	-0.004 (4)
VBr <sub>2</sub>	Cal. <sup>a</sup>	-0.0073	-0.0073	~ 0
	Cal. <sup>b</sup>	-0.0103	-0.0103	~ 0
	Expt. <sup>c</sup>	-0.010 (2)	-0.007 (2)	-0.003 (4)
VI <sub>2</sub>	Cal. <sup>a</sup>	0.0317	0.0317	~ 0
	Cal. <sup>b</sup>	0.0227	0.0227	~ 0
	Expt. <sup>c</sup>	-0.0023 (200)	-0.0023 (200)	~ 0

<sup>a</sup> Calculations based on neglecting of the contributions from the s-orbitals of the ligands, i.e., similar to the treatments in Du and Li (1994); Du and Rudowicz (1992). <sup>b</sup> Calculations based on inclusion of the contributions from the s-orbitals of the ligands in this work. <sup>c</sup> Yamada *et al.* (1984)

The spectral parameters  $Dq$ ,  $B$  and  $C$  are acquired from the optical spectra for these systems (Erk and Hass, 1975) and collected in Table 1. By using Eq. 3 and 4 and the free-ion parameters  $B_0 \approx 766 \text{ cm}^{-1}$  and  $C_0 \approx 2855 \text{ cm}^{-1}$  (Griffith, 1964) for  $V^{2+}$ , the covalency factor  $f_v$  and hence the molecular orbital coefficients  $N_v$  and  $\lambda_v$  can be calculated. From the free-ion values  $\zeta_d^0 \approx 167 \text{ cm}^{-1}$  (Griffith, 1964) for  $V^{2+}$  and  $\zeta_p^0 \approx 587, 2460$  and  $5060 \text{ cm}^{-1}$  for  $X = \text{Cl}, \text{Br}$  and  $\text{I}$  (McPerson *et al.*, 1974), the parameters  $\zeta, \zeta', k$  and  $k'$  are obtained from Eq. 5 and also shown in Table 1.

Substituting the related parameters into Eq. 1, the theoretical  $g$  factors are obtained and compared with the observed values in Table 2. For comparisons, the calculated results by neglecting the contributions from the  $s$ -orbitals of the ligands (i.e.,  $S_{ds} = \lambda_s = 0$  and  $A = 0$ , corresponding to the previous treatments (Du and Li, 1994; Du and Rudowicz, 1992) ) are also given in Table 2.

## Discussion

From Table 2, one can find that the theoretical  $g$  factors including the ligand  $s$ -orbital contributions are in good agreement with the observed values. This means that the ligand  $s$ -orbital contributions seem not negligible in the analyses of the EPR  $g$  factors for  $VX_2$  systems, especially for the larger ligands  $\text{Br}$  and  $\text{I}$ .

For  $X = \text{Cl}$ , the magnitudes of the theoretical  $\Delta g_i$  by including the ligand  $s$ -orbital contributions differ little (no more than 1%) from the results on neglecting the above contributions. So the previous treatments (Du and Li, 1994; Du and Rudowicz, 1992) can be regarded as good approximations for this ligand. Nevertheless, for  $V\text{Br}_2$  and  $V\text{I}_2$  the calculated  $\Delta g_i$  in the absence of the ligand  $s$ -orbital contributions are about 39% smaller and 28% larger than the experimental values, respectively. This means that the contributions from the SO coupling (which are much larger than that of  $V^{2+}$ ) of the ligands  $\text{Br}^-$  and  $\text{I}^-$  are somewhat overestimated, if only the contributions from the  $p$ -orbitals of the ligands are considered. In fact, inclusion of the  $s$ -orbitals of the ligands can modify the parameters  $N_s$  and  $\lambda_s$ , then change the magnitudes of  $k'$  and  $\zeta'$  and finally lead to more reasonable  $\Delta g_i$ . For  $X = \text{Br}$ , the significantly larger  $\Delta g_i$  in magnitude by considering the ligand  $s$ -orbital contributions compared with those by neglecting the above contributions can be attributed to the noticeable (twice) increase in the positive  $\zeta'$  related to the very small value (about  $13 \text{ cm}^{-1}$ ) in the absence of the contributions. Therefore, the useful assumption that the contributions of the  $s$  orbitals of the ligands may be negligible for  $3d^n$  ions in octahedra (e.g.,  $\text{KNiF}_3$ ) (Du and Li, 1994) seems not always valid for ligands having much larger SO coupling coefficient (e.g.,  $\text{I}^-$ ) and so the ligand  $s$ -orbital contributions should be considered in the studies of the  $g$  factors for  $VX_2$  here.

In the above calculations, the trigonal field parameters  $V$  and  $V'$  are determined from the structural data of the systems under study and the superposition model, instead of taking as adjustable parameters. The calculated anisotropies of the  $g$  factors are also comparable with experiment. The negative  $g_{\parallel} - g_{\perp}$  for  $V\text{Cl}_2$  is in consistence with the fact that the ligand octahedron is slightly compressed (i.e.,  $\delta\beta \approx 0.22^\circ > 0$ ). For  $V\text{Br}_2$  and  $V\text{I}_2$ , the small calculated anisotropies agree largely with the nearly isotropic  $g$  factors (the observed anisotropies are almost zero within the experimental errors (Yamada *et al.*, 1984). This point may be interpreted as the small magnitudes of  $\zeta'$  (Table 1) due to the larger  $\zeta_p^0$  for both ligands (Eq. 1 and 5) and the very slightly elongated ligand octahedra (i.e.,  $\delta\beta \approx -0.12^\circ$  and  $-0.57^\circ < 0$  for  $X = \text{Br}$  and  $\text{I}$ , respectively). Thus, the trigonal field parameters obtained from the superposition model in this work can also be regarded as reasonable.

## Conclusions

The gyromagnetic factors for the layered antiferromagnets  $VX_2$  are theoretically studied by using the perturbation formulas of the  $g$  factors including the contributions from the  $s$ -orbitals of the ligands in this study. The above investigations seem to be useful to the experimentalists working on magnetic properties of these materials by mean of EPR technique.

## **Acknowledgement**

This research was supported by the Youth Fundation of Science and Technology of UESTC under grant No. JX04022.

## **References**

- Bauhofer, W., G. Guntherodt, E. Anastassakis, A. Frey and G. Benede, 1980. Raman scattering and far-infrared studies of the vanadium dihalides with layered structure. *Phys. Rev.*, B 22: 5873.
- Bondarenko, I.N., R.S. Gekht and V.I. Ponomarev, 1996. Magnetic transitions in layered triangular antiferromagnets. *Phys. Lett.*, A 22: 269.
- Clementi, E. and D.L. Raimondi, 1963. Atomic screen constants from SCF functions. *J. Chem. Phys.*, 38: 2686.
- Du, M.L. and Z.M. Li, 1994. The contribution from spin-orbit coupling of ligand ions to g-factors in  $VCl_2$  and  $VBr_2$ . *J. Phys. Condens. Matter*, 6: 6279.
- Du, M.L. and C. Rudowicz, 1992. Gyromagnetic factors and zero-field splitting of  $t_2^3$  term of  $Cr^{3+}$  clusters with trigonal symmetry:  $Al_2O_3$ ,  $CsMgCl_3$  and  $CsMgBr_3$ . *Phys. Rev.*, B 46: 8974.
- Edgar, A., 1976. Electron paramagnetic resonance studies of divalent cobalt ions in some chloride salts. *J. Phys. C: Solid State Phys.*, 9: 4303.
- Erk, W. van and C. Hass, 1975. Optical absorption of  $VI_2$ . *Phys. Stat. Sol.*, B 71: 537.
- Griffith, J.S., 1964. *The Theory of Transition-Metal Ions*, Cambridge University Press, London.
- Guntherodt, G., W. Bauhofer and G. Benedek, 1979. Zone-boundary-phonon Raman scattering in  $VI_2$  due to modulation of exchange interaction. *Phys. Rev. Lett.*, 43: 1427.
- Kawamura, H., 1988. Critical properties of helical magnets and triangular antiferromagnets. *J. Applied Phys.*, 63: 3086.
- McPerson, G.L., R.C. Kach and G.D. Stucky, 1974. Electron spin resonance spectra of  $V^{2+}$ ,  $Mn^{2+}$  and  $Ni^{2+}$  in single crystals of  $CsMgBr_3$  and  $CsMgI_3$ . *J. Chem. Phys.*, 60: 1424.
- Newman, D.J. and B. Ng, 1989. The superposition model of crystal field. *Rep. Prog. Phys.*, 52: 699.
- Rastelli, E. and A. Tassi, 1996. Quantum fluctuations in antiferromagnets of the  $BX_2$  family. *J. Applied Phys.*, 79: 5745.
- Watabe, Y., T. Suzuki and Y. Natsume, 1995. Theoretical study on quantum effects in triangular antiferromagnets with axial anisotropy using the numerically constructed Bogoliubov transformation for magnons. *Phys. Rev.*, B 52: 3400.
- Wyckoff, R.W., 1951. *Crystal Structures*. Interscience Press, New York. Vol. 1.
- Yamada, I., K. Ubukoshi and K. Hirakawa, 1984. ESR study of the triangular lattice Heisenberg antiferromagnets  $VX_2$  ( $X = Cl, Br$  and  $I$ ). *J. Phys. Soc. Japan*, 53: 381.
- Yu, W.L., X.M. Zhang, L.X. Yang and B.Q. Zen, 1994. Spectroscopic properties of  $Cr^{3+}$  ions at the defect sites in cubic fluoroperovskite crystals. *Phys. Rev.*, B 50: 6756.