Investigations on the Gyromagnetic Factors for the Layered Triangular Antiferromagnets VX$_2$ (X = Cl, Br, I)

1,2 Shao-Yi Wu, 1 Xiu-Ying Gao, 1 Qiang Fu and 1 Ji-Zi Lin
1 Department of Applied Physics, University of Electronic Science and Technology of China, Chengdu 610054, People’s Republic of China
2 International Center for Materials Physics, Chinese Academy of Sciences, Shenyang 110016, People’s Republic of China

Abstract: The gyromagnetic factors $g_s$ and $g_l$ 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 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 VX$_2$ show some improvement compared with those in the absence of the ligand s-orbital contributions.

Keywords: 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 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 $g_s$ and $g_l$ 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 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$^{3+}$ 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 VX$_2$ have not been explained uniformly. Since the S.O. coupling coefficient of the ligand I$^-$ is much larger than that of the V$^{3+}$, 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$^5$ 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, People’s Republic of China
Theory and Calculations

In VXₙ, V²⁺ locates on the octahedral site with slight trigonal (D₃ₐ) distortion (Wyckoff, 1951). For a V²⁺(3d⁶) ion in trigonal symmetry, its ground ¹A₁ 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 Δgₜₜ (=-gₚ - gₚ' where gₚ = 2.0023 is the spin only value and I = // and \perp) based on the cluster approach can be expressed as (Du and Li, 1994):

\[
\Delta g_{\perp} = -8 \zeta' k' V(3E_z) - 2\zeta (2k' \zeta' - k \zeta) (9E_z^2) + 4\zeta'^2 (k - 2k') (9E_z^2) - 2\zeta (k + g_\perp) (3E_z) + 4\zeta (k + g_\perp) (1/(3E_z) + 1/(9E_z) + 1/(3E_z^2)) \\
+ 8\zeta'^2 k V(9E_z^2) - 4\zeta' k V(9E_z^2) - 4\zeta k V(3E_z) + 4\zeta k^2 V(3E_z) + 2\zeta k V(9E_z) (1)
\]

Here the energy denominators ΔE (I = // - \perp) stand for the separations between the excited states \( ^2T_{2g}, ^2T_{2g'}, ^2T_{2g}, {^2}T_{2g}, \) and \( ^2T_{2g}, \) and the ground state \( ^1A_1 \) in terms of the cubic field parameter Dq and the Racah parameters B and C for the studied 3d³ 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. Unlike the above contributions are considered here. Thus, the total single electron wave function including the ligand s-orbital contributions may be written as

\[
\Psi = N_e^t \psi_e (\lambda_e, \chi_{sp}) + N_e^t \psi_e (\lambda_e, \chi_{sp})
\]

where \( \psi_e (\chi_e, \psi_e) \) denote the irreducible representations of the O₃₉ group) are the d orbitals of the central metal ion \( \chi_{sp} \) and \( \chi_e \) stand for the p- and s- orbitals of the ligands. \( N_e \) and \( \lambda_e \) (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

\[
f_\perp = N_e^t \left[1 + \lambda_e^2 S_{sp} - 2 \lambda_e S_{sp}\right]
\]

\[
f_e = N_e^t \left[1 + \lambda_e^2 S_{sp} - 2 \lambda_e S_{sp}\right]
\]

and the normalization conditions

\[
N_e \left(1 - 2\lambda_e S_{sp} + \lambda_e^2\right) = 1,
\]

\[
N_e \left(1 - 2\lambda_e S_{sp} - 2\lambda_e S_{sp} + \lambda_e^2\right) = 1.
\]

Here \( S_{sp} \) (and \( S_{sp'} \)) 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., \( \lambda_e S_{sp} = \lambda_s S_{sp} \) within the same irreducible representation \( \eta \). In general, the covalency factors \( f_e \) and \( f_\perp \) can be determined from the ratio of the Racah parameters for the 3d³ ion in a crystal to those in free state, i.e., \( f_e = \zeta = C/C_0 \).

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 3d³ octahedral clusters may be expressed as

\[
\zeta = N_e (\zeta_e + \lambda_e^2 \zeta_e^3/2), \quad \zeta' = (N_e N_s)^{\alpha} (\zeta_e - \lambda_e \zeta_e^3/2)
\]

\[
k = N_e (1 + \lambda_e^2/2), \quad k' = (N_e N_s)^{\alpha} (1 - \lambda_e \lambda_e + \lambda_e A)/2
\]

427
where $\zeta^e$ and $\zeta^o$ are the SO coupling coefficients of the free $3d^5$ and the ligand ions, respectively. $A$ denotes the integral, $R \left\{ \text{ns} \left( \frac{1}{2} | np \right) \right\}$, where $R$ is the metal-ligand distance of the studied systems. Obviously, when taking $S_{6h} = \lambda = 0$ 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:

$$
V = (18/7)A_3(R)(35\cos^2\theta - 1) + (40/21)A_4(R)(35\cos^2\theta - 30\cos^2\theta + 3)
$$
$$
+ (40/21)A_6(R)\sin^2\theta \cos^2 \theta
$$
$$
V' = (-6/21)A_3(R)(35\cos^2\theta - 1) + (10/21)A_4(R)(35\cos^2\theta - 30\cos^2\theta + 3)
$$
$$
+ (20/3)A_6(R)\sin^2\theta \cos \theta
$$

where $\theta$ 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 $\delta\theta = \theta - \theta_0$, where $\theta_0 = 54.74^\circ$ is the bonding angle in cubic symmetry. $A(R)$ and $A_3(R)$ are the intrinsic parameters with the reference bonding length $R$. For $3d^6$ ions in octahedra, the relationships $A_3(R) = (3/4)Dq$ and $A_4(R)/A_6(R) = 9 \sim 12$ have been proved to be valid in many crystals (Newman and Ng, 1989; Yu et al., 1994; Edgar, 1976). Here we take $A_4(R) = 9A_6(R)$. 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 $g_0 - g$) of the studied systems.

For VCl$_3$ (Wyckoff, 1951), the metal-ligand bonding lengths $R$ and the angles $\theta$ 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 $S_{6h}$ (as well as the integrals $S_{6h}$ and $A$) are obtained and shown in Table 1.

<table>
<thead>
<tr>
<th>X</th>
<th>$\beta$</th>
<th>$S_{6h}$</th>
<th>$S_{2h}$</th>
<th>$S_{0}$</th>
<th>$A$</th>
<th>$Dq$</th>
</tr>
</thead>
<tbody>
<tr>
<td>VCl$_3$</td>
<td>54.96</td>
<td>0.0232</td>
<td>0.0703</td>
<td>0.0408</td>
<td>1.2827</td>
<td>925</td>
</tr>
<tr>
<td>VBr$_3$</td>
<td>54.62</td>
<td>0.0220</td>
<td>0.0697</td>
<td>0.0379</td>
<td>1.2028</td>
<td>950</td>
</tr>
<tr>
<td>VI$_3$</td>
<td>54.17</td>
<td>0.0215</td>
<td>0.0682</td>
<td>0.0387</td>
<td>1.0861</td>
<td>850</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>X</th>
<th>$\lambda$</th>
<th>$\zeta'$</th>
<th>$\zeta$</th>
<th>$k$</th>
<th>$k'$</th>
<th>$V$</th>
<th>$V'$</th>
</tr>
</thead>
<tbody>
<tr>
<td>VCl$_3$</td>
<td>0.610</td>
<td>2375</td>
<td>0.832</td>
<td>0.919</td>
<td>0.930</td>
<td>0.321</td>
<td>0.302</td>
</tr>
<tr>
<td>VBr$_3$</td>
<td>0.565</td>
<td>2365</td>
<td>0.828</td>
<td>0.917</td>
<td>0.936</td>
<td>0.324</td>
<td>0.307</td>
</tr>
<tr>
<td>VI$_3$</td>
<td>0.530</td>
<td>2350</td>
<td>0.823</td>
<td>0.914</td>
<td>0.933</td>
<td>0.329</td>
<td>0.311</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>X</th>
<th>$g_0 - g$</th>
<th>$Ag_0$</th>
<th>$Ag$</th>
<th>$Ag_0$</th>
<th>$g_0 - g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>VCl$_3$</td>
<td>-0.0323</td>
<td>-0.0313</td>
<td>-0.001</td>
<td></td>
<td></td>
</tr>
<tr>
<td>VBr$_3$</td>
<td>-0.0323 (20)</td>
<td>-0.0283 (20)</td>
<td>-0.004 (4)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>VI$_3$</td>
<td>-0.0103</td>
<td>-0.0103</td>
<td>-0.003 (4)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

^a 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).^b Calculations based on inclusion of the contributions from the $s$-orbitals of the ligands in this work. ^c Yamada et al. (1984)
The spectral parameters Dq, B and C are acquired from the optical spectra for these systems (Ersk and Hass, 1975) and collected in Table 1. By using Eq. 3 and 4 and the free-ion parameters Bn = 756 cm⁻¹ and Cn = 2855 cm⁻¹ (Griffith, 1964) for V⁵⁺, the covalency factor ζ, and hence the molecular orbital coefficients Nk and λk, can be calculated. From the free-ion values ζν = 167 cm⁻¹ (Griffith, 1964) for V⁵⁺ and ζν = 587, 2460 and 5060 cm⁻¹ for X = Cl, Br and I (McPerson et al., 1974), the parameters ζ, ζν, 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., So = λo = 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 VX₅ systems, especially for the larger ligands Br and I.

For X = Cl, the magnitudes of the theoretical Δg, 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 VBr₅ and V₁₁, the calculated Δg 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 V⁵⁺) of the ligands Br⁻ and 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 Nk and λk, then change the magnitudes of k' and ζν, and finally lead to more reasonable Δg. For X = Br, the significantly larger Δg 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 ζν related to the very small value (about 13 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 ions in octahedra (e.g., KNbF₅) (Du and Li, 1994) seems not always valid for ligands having much larger SO coupling coefficient (e.g., I⁻) and so the ligand s-orbital contributions should be considered in the studies of the g factors for VX₅ 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 gᵥ-gᵥ for VCl₅ is in consistency with the fact that the ligand octahedron is slightly compressed (i.e., δβ = 0.22°<0. For VBr₅ and V₁₁, 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 ζν (Table 1) due to the larger ζν for both ligands (Eq. 1 and 5) and the very slightly elongated ligand octahedra (i.e., δβ = -0.12° and -0.57°<0 for X = Br and 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 VX₅ 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


