Theoretical studies of the local structures and the spin Hamiltonian parameters of the tetragonal Ru\textsuperscript{3+} centers in AgCl and AgBr

Shao-Yi Wu\textsuperscript{a,b,*}, Qiang Fu\textsuperscript{a}, Hua-Ming Zhang\textsuperscript{a}, Guang-Duo Lu\textsuperscript{a}

\textsuperscript{a} Department of Applied Physics, University of Electronic Science and Technology of China, Chengdu 610054, PR China
\textsuperscript{b} International Centre for Materials Physics, Chinese Academy of Sciences, Shenyang 110016, PR China

Received 18 December 2006; received in revised form 12 January 2007; accepted 12 January 2007
Available online 18 January 2007

Abstract

The local structures and the spin Hamiltonian parameters of the tetragonal Ru\textsuperscript{3+} centers in AgCl and AgBr are theoretically studied from the perturbation formulas of these parameters for a 4d\textsuperscript{5} ion in tetragonally distorted octahedra. In these formulas, the contributions from the spin–orbit coupling coefficient and the s- and p- orbitals of the ligands are taken into account from the cluster approach. Based on the studies, the impurity centers are attributed to the substitutional Ru\textsuperscript{3+} occupying the Ag\textsuperscript{+} site associated with one and two next nearest neighbouring cation vacancy V\textsubscript{Ag} along the [1 0 0] (or C\textsubscript{4}) axis for AgCl and AgBr, respectively. Due to the electrostatic repulsion of the V\textsubscript{Ag}, the halide ligand(s) intervening in the V\textsubscript{Ag} and the impurity Ru\textsuperscript{3+} are found to displace away from the vacancy by an amount $\Delta Z \approx 0.156$ Å (or 0.185 Å) along the C\textsubscript{4} axis for AgCl (or AgBr), respectively. The theoretical results based on the above defect models and the displacements $\Delta Z$ show good agreement with the experimental data. The contributions to the spin Hamiltonian parameters from the ligand orbitals and spin–orbit coupling coefficient are also discussed.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Inorganic materials; Crystal and ligand fields; Point defects; Electron paramagnetic resonance

1. Introduction

AgX (X = Cl and Br) containing Ru has interesting properties of electrocatalytic water oxidation and photoconductivity [1–4]. In addition, these materials doped with transition-metal impurities can exhibit unique laser light generation and color image formation as well as low-temperature radiative recombination [5–7]. Particularly, ionic conductivity studies due to the silver vacancies were also carried out for AgX crystals with transition-metal ions dopants (e.g., Co\textsuperscript{2+}, V\textsuperscript{2+}, Ni\textsuperscript{2+}) [8]. It is known that electron paramagnetic resonance (EPR) is a useful technique to study local structure properties and electronic states for transition-metal ions in crystals. EPR investigations have been made for some ions (e.g., V\textsuperscript{2+}, Cr\textsuperscript{3+}, Co\textsuperscript{2+}, Ni\textsuperscript{2+}) in these crystals [9–12]. However, the EPR studies on the second group of transition-metal (4d\textsuperscript{n}) ions in AgX are relatively fewer.

For example, various (tetragonal and rhombic) impurity Ru\textsuperscript{3+} (4d\textsuperscript{5}) centers in AgX with Ru dopants were extensively investigated by means of EPR technique, and the spin Hamiltonian parameters, g factors and the hyperfine structure constants were also estimated [13]. These impurity centers have been ascribed to different cases of charge compensation (i.e. dissimilar positions of the compensator silver vacancy, V\textsubscript{Ag}) [13]. To interpret the above experimental results, the tetragonal distortion parameters $\Delta$ were obtained by fitting the theoretical g factors to the observed values [13]. On the other hand, although the structure models for these centers were tentatively proposed, they have not been theoretically verified. For instance, the tetragonal centers C (AgCl) and C' (AgBr) may be attributed to one or two V\textsubscript{Ag} located on the next nearest neighbour of the impurity Ru\textsuperscript{3+} along the [1 0 0] (or C\textsubscript{4}) axis [13]. In their treatments, the contributions from the spin–orbit coupling coefficient and the orbitals of the ligands were not considered. In fact, the contributions due to the ligands (especially for Br\textsuperscript{−}) may be important because of the large ligand spin–orbit coupling coefficient. Meanwhile, the local lattice distortion due to the presence of V\textsubscript{Ag} was also ignored in the above analyses.
In order to explain the above EPR experimental data to a better extent and to verify the local structure models of the tetragonal Ru\(^{3+}\) centers (C and C') in AgX, in this work, the above spin Hamiltonian parameters and defect structures are theoretically studied from the perturbation formulas of these parameters for a 4d\(^5\) ion in tetragonally distorted octahedra. In these formulas, the contributions from the spin–orbit coupling coefficient and the s- and p- orbitals of the ligands are taken into account based on the cluster approach.

2. Calculations

For Ru\(^{3+}\) in AgX, it may replace the Ag\(^{+}\) ion. Since the impurity Ru\(^{3+}\) has extra charge, several means of charge compensation can occur. For the studied tetragonal Ru\(^{3+}\) centers in this work, they are attributed to the substitutional Ru\(^{3+}\) associated with one or two next nearest neighbouring Ag\(^{+}\) along the C\(_4\) axis, i.e. Ru\(^{3+}\)–Ag\(^{+}\) (case I) or V\(_{Ag}\) –Ru\(^{3+}\)–Ag\(^{+}\) (case II), as mentioned in Ref. [13]. Presence of the cation vacancies reduces the symmetry of the [RuX\(_6\)]\(^{3−}\) clusters from cubic to tetragonal (C\(_{4v}\) or D\(_{4h}\) for case I or II, respectively). Since the effective charge of Ag\(^{+}\) is negative, the halide ligand(s) intervening in the V\(_{Ag}\) and the Ru\(^{3+}\) are expected to shift away from the V\(_{Ag}\) due to the electrostatic repulsion. Therefore, the ligand octahedra in the [RuX\(_6\)]\(^{3−}\) clusters may be tetragonally compressed.

Unlike Fe\(^{3+}\) and Mn\(^{2+}\) (3d\(^5\)) ions, octahedrally coordinated Ru\(^{3+}\) ions are characterized by strong crystal field. The five 4d electrons occupy the t\(_{2g}\) orbitals (corresponding to one t\(_{2g}\)) and t\(^0\) (or 2A\(_{1g}\)) components. Obviously, the tetragonal distortion parameter is originated from the tetragonal field parameters D\(_s\) and D\(_t\), i.e. \(\Delta = 3D_s - 5D_t\). \(P(\pi \sigma \chi_0 \beta_\eta \beta_\eta (r^{-3}))\) is the dipolar hyperfine structure parameter of Ru\(^{3+}\). \(\kappa\) is the core polarization constant.

In view of the possible displacements of the intervening ligand(s) due to the single (or double) next nearest neighbouring vacancy, the local structures of the studied impurity centers can be determined from the host cation-anion distance \(R\) and the ligand displacement \(\Delta Z\). Here, the subscript \(j = I\) or II denotes the single or double cation vacancies along the [1 0 0] axis for case I or II. For convenience, the distance from the impurity and the intervening ligand is labeled as \(R_1 = (R - \Delta Z)\) due to the ligand displacement, while the other impurity–ligand distances are approximately the same as the original \(R\) in the host. Meanwhile, the contributions to the tetragonal distortion from the \(x = (1)\) or (2) vacancies in case I or II are also taken into account in view of the effective negative charge of V\(_{Ag}\), with the parameter \(x\) denoting the number of vacancies. Therefore, the tetragonal field parameters \(D_s\) and \(D_t\) can be calculated from the local structures of the impurity centers, by using the generalized crystal-field model [17–19]:

\[
D_s = eq(r^2)\left[1/R_1^3 - 1/R^3 - x/(2R)^3\right]/(7R^3),
\]

\[
D_t = eq(r^4)\left[1/R_1^5 - 1/R^5 - x/(2R)^5\right]/(21R^5),
\]

where \(q = 2\pi^2\) is the effective charge of the halide ligand in view of the possible r\(_i\) hole in the central Ru\(^{3+}\) ion. Therefore, the local structure (or tetragonal distortion characterized by the tetragonal distortion \(\Delta Z\)) of the impurity centers is connected with the tetragonal field parameters \(D_s\) and \(D_t\) and hence with the spin Hamiltonian parameters, particularly the anisotropy \(\Delta g\) (\(\tilde{g}_{||} < \tilde{g}_{\perp}\)). \((\rho^3)\) (\(n = 2, 4\)) are the expectation values of the radial coordinate calculated by using the 4d radial wave functions, which can be expressed in terms of the corresponding free-ion values [14] and the average covalency factor \(N\) in consideration of the covalency (or admixture) between the central metal and the ligand orbitals [19]:

\[
\langle r^2 \rangle \approx 2.31N^2 \text{a.u.}, \quad \langle r^4 \rangle \approx 9.17N^2 \text{a.u.}
\]

Now the related parameters \((k_\pi, k_\sigma, \xi_\pi\) and \(\xi_\sigma\)) in the above formulas can be determined from the cluster approach similar to the treatments in Ref. [16]. Thus, the total single electron wave functions including the contributions from the s- and p-orbitals of the ligands may be expressed as:

\[
\psi_i^\pm = N_i^{1/2}(\psi_\pi - \lambda_\rho \pi \chi_p \eta^0),
\]

\[
\psi_i^0 = N_i^{1/2}(\psi_\sigma - \lambda_\rho \sigma \chi_p^0 - \lambda_{\sigma \sigma} \chi_s),
\]

where \(\phi_\gamma\) (\(\gamma = \pi\) and \(\sigma\)) denote the pure d orbitals of the central metal ion. \(\chi_p\) and \(\chi_s\) stand for the p- and s-orbitals of the
ligands. \( N_y \) and \( \lambda_{\pi y} \) (or \( \lambda_{\sigma y} \)) are, respectively, the normalization factors and the orbital admixture coefficients. They can be obtained from the empirical relationship:

\[
N^2 = N_y^2 [1 + \lambda_{\pi \alpha}^2 S_{\pi \alpha}^2 - 2 \lambda_{\pi \alpha} S_{\pi \alpha}], \quad N^2 = N_y^2 [1 + \lambda_{\pi \alpha}^2 S_{\pi \alpha}^2 + \lambda_{\sigma \alpha}^2 S_{\sigma \alpha}^2 - 2 \lambda_{\pi \alpha} S_{\pi \alpha} - 2 \lambda_{\sigma \alpha} S_{\sigma \alpha}],
\]

and the normalization conditions

\[
N_{\pi}^2(1 - 2 \lambda_{\pi \alpha} S_{\pi \alpha} + \lambda_{\pi \alpha}^2) = 1, \quad N_{\sigma}^2(1 - 2 \lambda_{\pi \alpha} S_{\pi \alpha} - 2 \lambda_{\sigma \alpha} S_{\sigma \alpha} + \lambda_{\pi \alpha}^2 + \lambda_{\sigma \alpha}^2) = 1.
\]

Here, \( S_y \) (\( \gamma = \pi, \sigma \) and \( s \)) are the group overlap integrals between central ion and the ligand orbitals. In general, the admixture coefficients increase with increasing the group overlap integrals, and one can approximately apply the proportional relationship between the admixture coefficients and the related group overlap integrals, i.e. \( \lambda_{\pi \alpha}/\lambda_{\sigma \alpha} \approx \lambda_{\sigma \alpha}/\lambda_{\pi \alpha} \) within the same \( \sigma \) component. Therefore, the orbital reduction factors \( k_{\pi}, k_{\sigma} \) and the spin–orbit coupling coefficients \( \xi_{\pi}, \xi_{\sigma} \) in Eqs. (1) and (2) can be determined, by considering the ligand orbital and spin–orbit coupling contributions:

\[
k_{\pi} = N_{\pi} \left( \frac{1 + \lambda_{\pi \alpha}^2 S_{\pi \alpha}^2}{2} \right), \quad k_{\sigma} = (N_{\pi} N_{\sigma})^{1/2} \left[ 1 - \frac{\lambda_{\pi \alpha}(\lambda_{\pi \alpha} + \lambda_{\sigma \alpha} A)}{2} \right], \quad \xi_{\pi} = N_{\pi} \left( \frac{\zeta_{\pi}^0 + \lambda_{\pi \alpha} \zeta_{\pi}^0}{2} \right), \quad \xi_{\sigma} = (N_{\pi} N_{\sigma})^{1/2} \left[ \frac{\zeta_{\sigma}^0 - \lambda_{\pi \alpha} \zeta_{\sigma}^0}{2} \right],
\]

where \( A \) denotes the integral \( \langle \alpha | \partial^2 / \partial \gamma^2 | \beta \rangle \). \( \zeta_{\pi}^0 \) and \( \zeta_{\sigma}^0 \) are the spin–orbit coupling coefficients of the free \( 4d^5 \) and the ligand ions, respectively. Obviously, when taking \( S_y = \lambda_{\gamma} = 0 \) and \( A = 0 \), the above formulas return to those in the absence of the ligand contributions [13–15].

For the studied Ru\(^{3+} \) centers, the related free-ion values are \( \zeta_{\pi}^0 \approx 1180 \text{ cm}^{-1} \) [14] and \( P \approx 139 \times 10^{-6} \text{ cm}^{-1} \) [16] for Ru\(^{3+} \), \( \zeta_{\sigma}^0 \approx 587 \) and \( 2460 \) cm\(^{-1} \) [20] for Cl\(^- \) and Br\(^- \). The host cation–anion distances are \( R \approx 2.7746 \) and 2.8873 Å for AgCl and AgBr, respectively [21]. From the distance \( R \) and the Slater-type SCF functions [22,23], the group overlap integrals \( S_y \) (as well as the integral \( A \)) are obtained. These values are shown in Table 1.

As mentioned before, the halide ligand intervening in the vacancy (i.e. single \( V_{\text{Ag}} \) or double \( V_{\text{Ag}} \)) and the Ru\(^{3+} \) may be displaced away from the \( V_{\text{Ag}} \) by an amount (i.e. \( \Delta Z_1 \) or \( \Delta Z_2 \)) along the [1 0 0] axis due to the electrostatic repulsion for case I or II, respectively. Thus, only the average covalency factor \( N \) and the ligand displacement \( \Delta Z_1 \) or \( \Delta Z_2 \) are unknown in the formulation of the \( g \) factors. Substituting these values into Eqs. (1)–(3) and (8) and fitting the calculated \( g \) factors to the observed values, one can obtain

\[
N \approx 0.925 \text{ and } 0.893, \quad \Delta Z_1 \approx 0.156 \text{ and } 0.075 \text{ Å}, \quad \Delta Z_2 \approx 0.254 \text{ and } 0.185 \text{ Å},
\]

for AgCl and AgBr, respectively. Here, the displacement direction away from the \( V_{\text{Ag}} \) is defined as positive. The relative ratios of the ligand displacement to the original distance \( R \) are 0.056 and 0.092 for cases I and II in AgCl, and 0.026 and 0.064 for cases I and II in AgBr, respectively. The related molecular orbital coefficients and parameters are given in Table 1.

In order to make comparisons between the covalency properties for \( 4d^5 \) and \( 3d^5 \) clusters, the relevant parameters (e.g., the group overlap integrals and the molecular orbital coefficients, etc.) for CsMgCl\(_3\):Mn\(^{2+}\) (3d\(^5\)) crystal (with the covalency factor \( N \approx 0.960 \) and the metal–ligand distance \( R \approx 2.545 \text{ Å} \) [24]) are also collected in Table 1. The corresponding spin Hamiltonian parameters are shown in Table 2. Substituting the above parameters into the formulas of the hyperfine structure constants and fitting the calculated results to the experimental data for AgCl, we determine the optimized core polarization constant \( \kappa \approx 1.84 \) (11) for both crystals. The corresponding theoretical results (Cal.\(^4\)) are shown in Table 2. For comparison, the calculation results

### Table 1

<table>
<thead>
<tr>
<th>Centers</th>
<th>( S_y )</th>
<th>( S_{\alpha} )</th>
<th>( S_{\sigma} )</th>
<th>( A )</th>
<th>( N_y )</th>
<th>( N_{\alpha} )</th>
<th>( \lambda_{\pi \alpha} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgCl:Ru(^{3+})</td>
<td>0.0089</td>
<td>0.0324</td>
<td>0.0164</td>
<td>1.4017</td>
<td>0.928</td>
<td>0.935</td>
<td>0.288</td>
</tr>
<tr>
<td>AgBr:Ru(^{3+})</td>
<td>0.0089</td>
<td>0.0336</td>
<td>0.0157</td>
<td>1.3016</td>
<td>0.896</td>
<td>0.905</td>
<td>0.350</td>
</tr>
<tr>
<td>CsMgCl(_3):Mn(^{2+})</td>
<td>0.0124</td>
<td>0.0402</td>
<td>0.0217</td>
<td>1.2857</td>
<td>0.963</td>
<td>0.970</td>
<td>0.210</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Centers</th>
<th>( \lambda_{\pi \alpha} )</th>
<th>( \lambda_{\sigma \alpha} )</th>
<th>( \xi_{\pi} )</th>
<th>( \xi_{\sigma} )</th>
<th>( k_{\pi} )</th>
<th>( k_{\sigma} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgCl:Ru(^{3+})</td>
<td>0.269</td>
<td>0.136</td>
<td>1117</td>
<td>1078</td>
<td>0.966</td>
<td>0.870</td>
</tr>
<tr>
<td>AgBr:Ru(^{3+})</td>
<td>0.328</td>
<td>0.153</td>
<td>1192</td>
<td>936</td>
<td>0.951</td>
<td>0.818</td>
</tr>
<tr>
<td>CsMgCl(_3):Mn(^{2+})</td>
<td>0.200</td>
<td>0.108</td>
<td>346</td>
<td>324</td>
<td>0.984</td>
<td>0.932</td>
</tr>
</tbody>
</table>

\* Ref. [24].
(Cal.\textsuperscript{a}) of the g factors by directly fitting the tetragonal distortion parameters \( \Delta \) to the experimental data in the previous work \cite{13} are also collected in Table \ref{table2}. In addition, the calculated spin Hamiltonian parameters (Cal.\textsuperscript{b}) in the absence of the ligand displacements (i.e. \( \Delta Z = 0 \)) and the theoretical values (Cal.\textsuperscript{c}) based on the ligand displacements in Eq. (10) and neglecting of the ligand orbital and spin–orbit coupling contributions (i.e. \( k_r = k_o = N \) and \( \xi_r = \xi_o = N\zeta_{\parallel} \)) in this work are shown in Table \ref{table2}, too.

### 3. Discussion

From Table \ref{table2}, we find that the theoretical spin Hamiltonian parameters (Cal. \textsuperscript{d}) based on the above defect models and the corresponding ligand displacements (especially \( \Delta Z_I \approx 0.156 \text{ Å} \) for AgCl and \( \Delta Z_{II} \approx 0.185 \text{ Å} \) for AgBr) in Eq. (10) of this work are in better agreement with the observed values than the results of the previous studies (Cal.\textsuperscript{a}) and those in the absence of the ligand displacements (Cal.\textsuperscript{b}) or ligand orbital and spin–orbit coupling contributions (Cal.\textsuperscript{c}).

(1) Seen from Eq. (10), the positive signs of the ligand displacements \( \Delta Z \) are in consistence with the expectation based on the electrostatic interactions between the intervening halide ligand(s) and the \( V_{Ag} \). Interestingly, for the similar tetragonal \( \text{Cr}^{3+} \text{–V}_{\text{Mg}} \) center in \( \text{MgO} \text{–Cr}^{3+} \), the ligand displacement \( \Delta Z \approx 0.054R \) and \( (0.077 \pm 0.032)R \) were obtained from embedded-quantum-cluster calculation \cite{25} and the extended X-ray absorption fine structure (EXAFS) and X-ray absorption near edge structure (XANES) experiments \cite{26}, respectively. So the fitted displacements \( \Delta Z/I/R \approx 0.056 \) for AgCl and \( \Delta Z_{II}/R \approx 0.064 \) for AgBr are in good agreement with the above findings, while the results of the other cases (i.e. \( \Delta Z/I \approx 0.092 \) for AgCl and \( \Delta Z_{II}/R \approx 0.026 \) for AgBr) seem somewhat larger and smaller for X=Cl and Br, respectively. On the other hand, the cation–anion interaction (or combination energy) in AgCl may be stronger than that in AgBr due to the shorter distance \( R \) in the former. Thus, the probability of generation of cation vacancies can be greater in AgBr because of its relatively weaker Ag\textsuperscript{+}–Br\textsuperscript{−} bonding. Thus, the monovacancy (case I) for AgCl and the divacancy (case II) for AgBr can be understood. Additionally, in view of the better agreement between theory and experiment based on \( \Delta Z_{II} \approx 0.156 \text{ Å} \) for AgCl and \( \Delta Z_{II} \approx 0.185 \text{ Å} \) for AgBr than that based on the other cases (i.e. \( \Delta Z_{II} \approx 0.254 \text{ Å} \) for AgCl and \( \Delta Z_{II} \approx 0.075 \text{ Å} \) for AgBr), the above assignment of one (or two) \( V_{Ag} \) for X=Cl (or Br) seems more suitable.

(2) The calculated g anisotropies for AgCl and AgBr based on the previous studies (Cal.\textsuperscript{a}) are, respectively, smaller and larger than the observed values. This may be due to the direct fitting of the tetragonal distortion parameters \( \Delta \) to the experimental g factors, without involving the local structure (i.e. the lattice distortion arising from the ligand displacements \( \Delta Z \) due to the \( V_{Ag} \)) in the previous work \cite{13}. In the present studies, the results (Cal.\textsuperscript{b}) based on neglecting of the displacements (\( \Delta Z_I \) for AgCl and \( \Delta Z_{II} \) for AgBr) of the intervening ligand are also in poor agreement with the experimental data, especially the anisotropies \( \Delta g \) are opposite in signs and about 16–20\% smaller in magnitude than the observed values. According to the calculations, the tetragonal distortion parameters in the absence of the ligand

<table>
<thead>
<tr>
<th>Hosts</th>
<th>Cases</th>
<th>( g_{\parallel} )</th>
<th>( g_{\perp} )</th>
<th>( \Delta g = (g_{\parallel} - g_{\perp}) )</th>
<th>( A_{II} ) (10(^{4}) cm(^{-1}))</th>
<th>( A_{\perp} ) (10(^{4}) cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgCl</td>
<td>Cal.\textsuperscript{a}</td>
<td>2.0763</td>
<td>1.7811</td>
<td>0.2952</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>Cal.\textsuperscript{b}</td>
<td>1.6976</td>
<td>1.9454</td>
<td>–2.478</td>
<td>63</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td>Cal.\textsuperscript{c}</td>
<td>1.9869</td>
<td>1.8563</td>
<td>0.1306</td>
<td>48</td>
<td>53</td>
</tr>
<tr>
<td></td>
<td>Cal.\textsuperscript{d}</td>
<td>2.0745</td>
<td>1.7672</td>
<td>0.3073</td>
<td>47</td>
<td>53</td>
</tr>
<tr>
<td></td>
<td>Expt. \cite{13}</td>
<td>2.0743 (5)</td>
<td>1.7671 (5)</td>
<td>0.3072 (5)</td>
<td>47 (2)</td>
<td>51 (2)</td>
</tr>
<tr>
<td>AgBr</td>
<td>Cal.\textsuperscript{a}</td>
<td>2.0416</td>
<td>1.6866</td>
<td>0.3550</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>Cal.\textsuperscript{b}</td>
<td>1.9000</td>
<td>1.7733</td>
<td>0.1267</td>
<td>43</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>Cal.\textsuperscript{c}</td>
<td>1.7569</td>
<td>1.9073</td>
<td>–1.504</td>
<td>46</td>
<td>38</td>
</tr>
<tr>
<td></td>
<td>Cal.\textsuperscript{d}</td>
<td>2.0571</td>
<td>1.6971</td>
<td>0.3600</td>
<td>35</td>
<td>44</td>
</tr>
<tr>
<td></td>
<td>Expt. \cite{13}</td>
<td>2.0502 (5)</td>
<td>1.7006 (5)</td>
<td>0.3496 (5)</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

\( ^{a} \) Calculations based on the direct fitting of the tetragonal distortion parameters \( \Delta \) to the experimental data in the previous work \cite{13}.

\( ^{b} \) Calculations based on inclusion of the ligand orbital and spin–orbit coupling contributions and neglecting of the displacements of the intervening ligand (i.e. \( \Delta Z_I = 0 \), with \( j = I \) and II for the two cases) in this work.

\( ^{c} \) Calculations based on the ligand displacements in Eq. (10) and neglecting of ligand orbital and spin–orbit coupling contributions in this work.

\( ^{d} \) Calculations based on inclusion of both the ligand displacements in Eq. (10) and the ligand orbital and spin–orbit coupling contributions in this work.

<table>
<thead>
<tr>
<th>Hosts</th>
<th>Cases</th>
<th>( g_{\parallel} )</th>
<th>( g_{\perp} )</th>
<th>( \Delta g = (g_{\parallel} - g_{\perp}) )</th>
<th>( A_{II} ) (10(^{4}) cm(^{-1}))</th>
<th>( A_{\perp} ) (10(^{4}) cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgCl</td>
<td>Cal.\textsuperscript{a}</td>
<td>2.0763</td>
<td>1.7811</td>
<td>0.2952</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>Cal.\textsuperscript{b}</td>
<td>1.6976</td>
<td>1.9454</td>
<td>–2.478</td>
<td>63</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td>Cal.\textsuperscript{c}</td>
<td>1.9869</td>
<td>1.8563</td>
<td>0.1306</td>
<td>48</td>
<td>53</td>
</tr>
<tr>
<td></td>
<td>Cal.\textsuperscript{d}</td>
<td>2.0745</td>
<td>1.7672</td>
<td>0.3073</td>
<td>47</td>
<td>53</td>
</tr>
<tr>
<td></td>
<td>Expt. \cite{13}</td>
<td>2.0743 (5)</td>
<td>1.7671 (5)</td>
<td>0.3072 (5)</td>
<td>47 (2)</td>
<td>51 (2)</td>
</tr>
<tr>
<td>AgBr</td>
<td>Cal.\textsuperscript{a}</td>
<td>2.0416</td>
<td>1.6866</td>
<td>0.3550</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>Cal.\textsuperscript{b}</td>
<td>1.9000</td>
<td>1.7733</td>
<td>0.1267</td>
<td>43</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>Cal.\textsuperscript{c}</td>
<td>1.7569</td>
<td>1.9073</td>
<td>–1.504</td>
<td>46</td>
<td>38</td>
</tr>
<tr>
<td></td>
<td>Cal.\textsuperscript{d}</td>
<td>2.0571</td>
<td>1.6971</td>
<td>0.3600</td>
<td>35</td>
<td>44</td>
</tr>
<tr>
<td></td>
<td>Expt. \cite{13}</td>
<td>2.0502 (5)</td>
<td>1.7006 (5)</td>
<td>0.3496 (5)</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>
displacements are about −30 and 22% those including these displacements for X=Cl and Br, respectively. It seems that the displacements of the intervening ligand(s) dominate contributions to the tetragonal compression of the ligand octahedra and cannot be neglected in the calculations.

(3) When the ligand orbital and spin–orbit coupling contributions were neglected, the theoretical results (Cal.c) are not as good as those including the above contributions, particularly, the calculated anisotropies Δg are only half of the exact result (the theoretical value even has the wrong sign for AgBr). For AgX:Ru3+, due to the trivalent state of Ru3+ belonging to the second group of transition-metal ions and the covalency of Cl− or Br−, the systems may exhibit some covalency in the halides [20]. This point can be illustrated by the covalency factors N (∼0.925 and 0.893 for Cl and Br, which are also comparable with the directly fitted values 0.90 and 0.86 for Cl and Br in the previous studies [13]) and the moderate orbital admixture coefficients (λπ ∼ λσ ∼ 0.3 and λg ∼ 0.1) obtained in this work. Furthermore, based on neglecting of the contributions from the ligand orbitals and spin–orbit coupling coefficient, good agreement between theory and experiment can hardly be achieved, by adjusting the values of N and ΔZ. Therefore, the anisotropic contributions to the g factors from different (π and σ) components of the spin–orbit coupling and the orbital angular momentum interactions should be taken into account based on the cluster approach, in consideration of the admixture (or covalency effect) of the metal and ligand orbitals. Unlike, for some 3d5 clusters, e.g., CsMgCl3:Mn2+, the covalency is relatively weaker (with the larger N ∼ 0.960 [24]) and the orbital admixture coefficients are also smaller (see Table 1). It is understandable that the contributions to the spin Hamiltonian parameters from the ligand orbital and spin–orbit coupling coefficient for this 3d5 cluster are less significant than those for the studied 4d5 systems.

(4) For the Ru3+ centers in AgX, the g factors deviate obviously from the spin-only value gS (=2.0023), and the anisotropies Δg are also significant due to the ground orbital triplet 2T2g with low spin ⟨S⟩ = 1/2 for a 4d5 ion under strong fields. This point is quite unlike the case of the ground orbital singlet 6A1g with high spin ⟨S⟩ = 5/2 for a 3d5 ion under weak fields, where the g factors are usually close to gS and the anisotropies may be negligible within experimental errors. From the different form of the perturbation formulas of the g factors for 3d5 ions in tetragonally distorted octahedra [27], the above discrepancy can be understood.

(5) In the above calculations, the displacements of the impurity Ru3+ and the other five nearest ligands are not considered. For example, the Ru3+ in AgCl may be attracted to shift towards the single VAg along the [1 0 0] axis. However, due to its large distance from the VAg the displacement of the impurity could be regarded as much smaller than that (ΔZI) of the intervening Cl−. Similarly, since the distances from the other ligands to the VAg are larger than that between the intervening halide ion to the VAg, the shifts of these ligands would also be neglected. Thus, the fitted displacements (ΔZI for AgCl and ΔZII for AgBr) obtained in this work can be conveniently and safely regarded as the effective (or tentative) values, and the errors due to the possible modifications of the positions for the impurity and the other ligands are approximately absorbed in the matched ΔZ. Therefore, for the sake of simplicity and reduction in the number of adjustable parameters, only the displacements of the intervening ligands are taken into account here.

Acknowledgement

This work was supported by the Support Program for Academic Excellence of UESTC.

References