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Studies of the local lattice distortions for the various rhombic Ru^{3+} centres in AgX (X = Cl and Br)

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ABSTRACT

The local lattice distortions of the various rhombic Ru^{3+} centres (*A*, *A*′, *B*, *B*′, *X* and *X*′) in AgX (X = Cl and Br) are quantitatively investigated from the perturbation calculations of the anisotropic *g* factors and hyperfine structure constants for a $4d^5$ ion in rhombically distorted octahedra. Centre *A* or *A*′ is assigned to the substitutional Ru^{3+} on Ag^+ site associated with one nearest neighbor silver vacancy V_{Ag} in the [1 1 0] axis and one next nearest neighbor V_{Ag} in the [$\bar{1}$ 0 0] axis due to charge compensation. Ru^{3+} is found to undergo the off-centre displacement 0.022 or 0.017 Å along the [1 1 0] axis, while the halide ligands closest to the V_{Ag} move away from the vacancies by 0.030 or 0.005 Å in AgBr or AgCl, respectively, due to the electrostatic interactions of the V_{Ag}. Centre *B* or *B*′ is ascribed to Ru^{3+} associated with each nearest neighbor V_{Ag} in the [1 1 0] and [$\bar{1}$ $\bar{1}$ 0] axes. The two axial ligands experience the displacement 0.036 or 0.015 Å along the *Z* (or [0 0 1]) axis, and the four planar ligands shift away from the vacancies by about 0.006 or 0.001 Å, respectively. Centre *X* or *X*′ can be described as Ru^{3+} associated with one nearest neighbor V_{Ag} and one next nearest neighbor V_{Ag} in the [1 1 0] and [0 0 1] axes, respectively. Ru^{3+} may undergo the off-centre displacement 0.019 or 0.015 Å along the [1 1 0] axis, while the ligands closest to the V_{Ag} move away from the V_{Ag} by 0.022 or 0.006 Å. The present studies would be helpful to the investigations on the structures and properties for Ru^{3+} in AgX and similar halides.

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1. Introduction

Silver halides (e.g., AgCl and AgBr) doped with transition-metal ruthenium exhibit novel electrochemical, catalytic [1–4], photoinduced DNA interactive [5], bioelectrochemical [6,7] and transient photoconductive [8] properties as well as promising applications in amperometric glucose biosensors [9,10] and solar cells [11]. The above properties and applications may be closely relevant to the local environments (e.g., occupation, charge compensation and local lattice distortions) and electronic states of the Ru dopants. As a typical $4d^5$ ion with one 4d hole, Ru^{3+} in AgX (X = Cl, Br) can be regarded as a model system for the studies of impurity behaviours and local structures in the well known NaCl – type halides. In order to research the local structures and electronic properties for Ru^{3+} in the halides, the electron paramagnetic resonance (EPR) measurements were conducted for AgX:Ru^{3+}, and the spin Hamiltonian parameters (SHPs), g factors and hyperfine structure constants, were acquired for the various tetragonal and rhombic impurity Ru^{3+} centres [12]. The EPR spectra of the tetragonal Ru^{3+} centres C and C' in AgX have been theoretically interpreted, and the information of the local structures around Ru^{3+} has been obtained [13]. For the more complicated rhombic centres *A*, *A*′, *B*, *B*′, *X* and *X*′, however, the defect structural information has not been quantitative determined so far. In Ref. [12], these rhombic centres were analysed from the simple *g* formulae including the adjusted normalization coefficients (relevant to the same fitted axial splittings Δ for AgCl and AgBr) and orbital reduction factors, without involving the local lattice distortions around Ru^{3+}. In order to make further studies on the SHPs and local structures of the rhombic Ru^{3+} centres, a more complete scheme should be established by correlating the EPR analysis with the local distortions around the impurities.

In general, the microscopic mechanisms and impurity behaviours can be helpful to clarify the relationships between local structures and performance of the materials with ruthenium dopants. And further theoretical analysis on g factors and hyperfine structure constants of these rhombic Ru^{3+} centres would enhance the knowledge of magnetic resonance area. So, the present studies

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on the EPR spectra and defect structures for the rhombic Ru^{3+} centres in AgX are of fundamental and practical significance. In this article, the perturbation formulae of the SHPs for a rhombically distorted octahedral $4d^5$ cluster are utilized, and the influences of the local lattice distortions due to charge compensation are quantitatively involved from the superposition model.

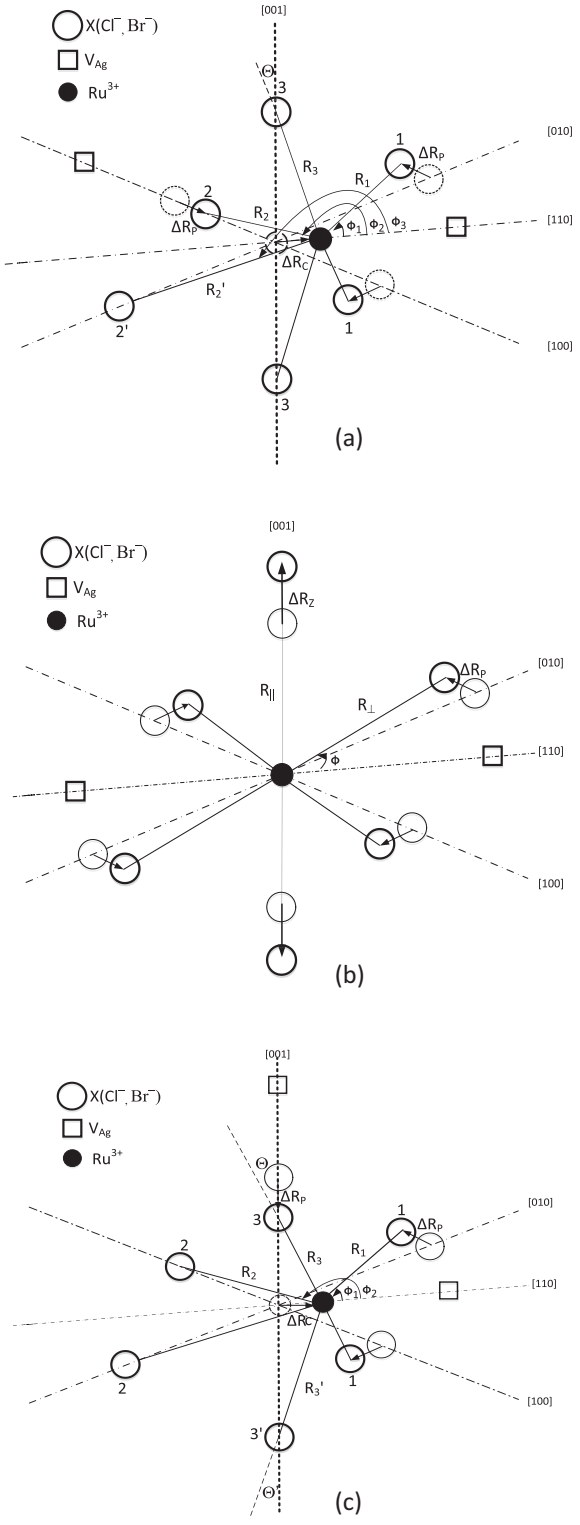

Fig. 1. Defect structures of centres *A*, *A*′ (a), *B*, *B*′ (b) and *X*, *X*′ (c) in AgX:Ru^{3+} (X = Cl and Br).

2. Theoretical formulae and calculations

Ru^{3+} doped into AgX may occupy substitutionally host Ag^+ site, with several means of charge compensation due to extra charge of Ru^{3+}. The simple tetragonal Ru^{3+} centres C and C' can be ascribed to one and two next nearest neighbor cation vacancies V_{Ag} in the [001] axis, respectively [13]. The more complicated rhombic Ru^{3+} centres are attributed to the substitutional Ru^{3+} containing one or two nearest neighbor V_{Ag} in the [110] or [$\bar{1}\,\bar{1}$0] axis or/and one next nearest neighbor V_{Ag} in the [$\bar{1}$00] or [001] axis [12]. For example, centre *A* or *A*′ is assigned to Ru^{3+} associated with one nearest neighbor V_{Ag} in the [110] axis and one next nearest neighbor V_{Ag} in the [$\bar{1}$00] axis due to charge compensation in AgBr or AgCl, respectively. Centre *B* or *B*′ is ascribed to Ru^{3+} with each nearest neighbor V_{Ag} in the [110] and [$\bar{1}\,\bar{1}$0] axes, while centre *X* or *X*′ is described as Ru^{3+} with one nearest neighbor V_{Ag} in the [110] axis and one next nearest neighbor V_{Ag} in the [001] axis, respectively. The central ion Ru^{3+} and the related halide ligands closest to V_{Ag} may undergo the respective displacements under the electrostatic interactions of the V_{Ag} with one effective negative charge, which reduces the local symmetry from original cubic of host Ag^+ site to rhombic (C_{2v}) in the $[RuX_6]^{3-}$ clusters (see Fig. 1).

2.1. Perturbation formulae of the SHPs for a rhombically distorted $4d^5$ cluster

Dissimilar to the weak or intermediate crystal-field (CF) case of high spin ($S = 5/2$) for conventional $3d^5$ ions such as Fe^{3+} and Mn^{2+}, Ru^{3+} ($4d^5$) belongs to the strong CF case of low spin ($S = 1/2$). The five 4d electrons occupy the t_{2g} orbitals (equivalent to one t_{2g} hole), corresponding to the ground orbital triplet $^2T_{2g}$ with low spin ($S = 1/2$) [13–15]. As the ligand octahedron is rhombically elongated or compressed, the $^2T_{2g}$ state is separated into three orbital singlets $^2B_{1g}$ (ζ), $^2B_{2g}$ (η) and $^2B_{3g}$ (ξ), with $^2B_{1g}$ (ζ) or $^2B_{3g}$ (ξ) lying lowest. The axial and perpendicular rhombic splittings Δ and δ are introduced to describe the separation between $^2B_{1g}$ (ζ) and $^2B_{3g}$ (ξ) and that between $^2B_{2g}$ (η) and $^2B_{3g}$ (ξ), respectively. For rhombically elongation or compression distortion, the axial splitting Δ is positive or negative, corresponding to the positive or negative g anisotropy Δg [$=(g_x + g_y)/2 - g_z$]. In the light of the experimental SHPs [12] for the various rhombic centres, *A*, *A*′, *B* and *B*′ have elongation distortions, whereas *X* and *X*′ exhibit compression ones.

The perturbation formulae of the SHPs for a rhombically distorted octahedral $4d^5$ cluster can be expressed as follows [14]:

$$
\begin{aligned}
g_x &= 2\sin(2\beta)(\cos\alpha + k'\sin a/\sqrt{2}) - 2\cos^2\beta[\sin^2\alpha + k\sin(2\alpha)/\sqrt{2}],\\
g_x &= -2\sin(2\beta)(\cos\alpha + k'\sin a/\sqrt{2}) - 2\cos^2\beta[\sin^2\alpha + k\sin(2\alpha)/\sqrt{2}],\\
g_z &= 2\cos^2\beta[\sin^2\alpha - (1+k)\cos^2 a] + 2\sin^2\beta(k'-1),
\end{aligned}
$$

$$
\begin{aligned}
A_x &= 2P'\{-\cos^2\beta[\sin^2\alpha/7 + 11\sin(2\alpha)/(14\sqrt{2}) - \kappa\sin^2\alpha/2]\\
&\quad - 3\sin^2\alpha/7 - \sin(2\beta)[\cos\alpha/7 - 17\sin\alpha/(7\sqrt{2}) + \kappa\cos\alpha]/2\},\\
A_y &= 2P'\{-\cos^2\beta[\sin^2\alpha/7 + 11\sin(2\alpha)/(14\sqrt{2}) - \kappa\sin^2\alpha/2]\\
&\quad - 3\sin^2\alpha/7 + \sin(2\beta)[\cos\alpha/7 - 17\sin\alpha/(7\sqrt{2}) + \kappa\cos\alpha]/2\},\\
A_x &= 2P\cos^2\beta[-2/7 - 6\cos^2\alpha/7 + 3\sin(2\alpha)/(7\sqrt{2})\\
&\quad + \kappa\cos(2\alpha)/2 + \sin^2\beta(7/6 + \kappa/2)]
\end{aligned}
\qquad (1)
$$

with the angular quantities

$$
\alpha = \frac{1}{2}\tan^{-1}\frac{\sqrt{2}\zeta'}{\frac{1}{2}\zeta - \Delta}, \qquad \beta = \tan^{-1}\frac{\delta\cos\alpha}{2\zeta} \qquad (2)
$$

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