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# Investigations of the electron paramagnetic resonance parameters and the tetragonal local structure for $(VCl_6)^{4-}$ coordination complex in MCl:$V^{2+}$ (M=Na, K, Rb) systems*

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By simulating the electron paramagnetic resonance (EPR) and optical spectra on the basis of the 120×120 complete energy matrix, this paper determines the local lattice structure parameters $R_1$ and $R_2$ for MCl:$V^{2+}$ (M=Na, K, Rb) systems at 77 K, 195 K and RT (room temperature 295 K or 302 K), respectively. The theoretical results indicate that there exists a compressed distortion in MCl:$V^{2+}$ systems. Meanwhile, it finds that the structure parameters $R_1$, $R_2$ and $|\Delta R|$ $(= R_1 - R_2)$ increase with the rising temperature. Subsequently, from the analysis it concludes that the relation of EPR parameter $D$ vs. $\Delta R$ is approximately linear. Finally, the effects of orbital reduction factor $k$ on the $g$ factors for the three systems have been discussed.

**Keywords:** complete energy matrix, EPR parameters, $(VCl_6)^{4-}$ coordination complex, local structure

**PACC:** 7170C, 7630, 7630F

## 1. Introduction

With the rapid development of experiment techniques, impurity ions in host crystals have been a subject of widespread interest in recent years, as doped crystals can display new properties which are absent in pure crystals.[1−4] In order to understand the influence of impurity ion on the host crystal, it is necessary to investigate the local lattice structure around the impurity ion. As we know, the electron paramagnetic resonance (EPR) spectrum is very sensitive to the immediate environment of an impurity ion in crystals, and the EPR parameters ($D$, $g_\parallel$, $g_\perp$) may reflect unambiguously the local distortion structure of the impurity ion centres. Therefore, EPR method has been widely used to obtain valuable information about the structure of the doped crystal.[5−9]

In recent decades, much attention has been paid to the investigations of transition-metal $V^{2+}$ ions doped into cubic type MCl (M denotes an alkali metal) single crystals with respect to their electronic properties and suitability as laser material for vibronic-laser operation.[10−17] The EPR and optical spectra of $V^{2+}$ ions in the cubic crystals MCl (M=K, Na, Rb) have been experimentally observed at different temperatures by Vanhaelst *et al.*[14] These experimental results give important information about the ground state of transition metal $V^{2+}$ ion and form a useful starting point for understanding the interrelationships between electronic and molecular structure of $V^{2+}$ ion in the $(VCl_6)^{4-}$ coordination complex. However, so far, there has been no satisfactory and quantitative unified explanation for the EPR and optical spectra, and the local structure of $V^{2+}$ ions in MCl (M=K, Na, Rb) crystals. For instance, Du[10] has carried out a theoretical calculation of the $g$ factor in MCl:$V^{2+}$ systems based on the cluster approximation. According to the two spin-orbit coupling parameter model and high-order perturbation formulas. Wu *et al*[12] have discussed the zero-field splitting (ZFS) and gyromagnetic factors for the tetragonal $V^{2+}$ ions in MCl

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(M=K, Na, Rb) crystals. Wu *et al*[13] have estimated the local structure of MCl:$V^{2+}$ systems on the basis of the high-order perturbation formulas and the empirical formula $R \approx R_0 + (r_i - r_h)/2$. Unfortunately, the empirical formula is not suitable for all doped systems according to previous researches.[18,19] Therefore, the results are uncertain and it is necessary to confirm the local structure using other dependable methods.

In this paper, we perform a systematical investigation of the EPR and optical spectra for $V^{2+}$ ion doped into MCl (M=K, Na, Rb) crystals by diagonalizing the 120×120 complete energy matrix. The goal of the present study is twofold: to elucidate a microscopic origin of various ligand field parameters which are usually used empirically for the interpretation of EPR and optical absorption experiments; to provide powerful guidelines for future experimental studies aimed at pinpointing how actually $V^{2+}$ enters the simple MCl (M=K, Na, Rb) ionic crystals.

The paper is organized as follows. In Section 2, the spin Hamiltonian and 120×120 complete energy matrix for a $3d^3$ configuration ion in tetragonal ligand field are described and the microscopic formulas of EPR parameters for the ground state are given. In Section 3, the local structure of $(VCl_6)^{4-}$ coordination complex in MCl:$V^{2+}$ (M=Na, K, Rb) systems have been determined. Furthermore, the interrelationships between zero-field splitting parameter $D$ and local structure parameters of tetragonal $V^{2+}$ centres in $(VCl_6)^{4-}$ coordination complex are discussed and the dependence of anisotropic $g$ factors on orbital reduction factor $k$ are presented. Conclusions are summarized in the final section.

## 2. Theoretical method

### 2.1. Complete energy matrix for $3d^3$ configuration ions

In order to construct the complete matrix, the $|J, M_J\rangle$ basic functions need to be expanded into the form of the $|L,\ S,\ M_L,\ M_S\rangle_i$ basic functions. This expansion may be realized in terms of the Clebsch–Gordon coefficients which are associated with the coupling of two angular moments. In general, the expansion can be written as[20]

$$\begin{aligned} |J, M_J\rangle &= \sum_i C_i \, |L, S, M_L, M_S\rangle_i \\ &= \sum_i \sum_j C_i C_j \, \Phi_j, \end{aligned} \tag{1}$$

where $C_i$ and $C_j$ are the Clebsch–Gordon coefficients, $\Phi_j$ is one of the 120 basic Slater determinants. According to the $|L,\ S,\ M_L,\ M_S\rangle_i$ functions of the $3d^3$ configuration ion in a tetragonal ligand field, we have constructed the complete energy matrix of the Hamiltonian[21]

$$\begin{aligned} \hat{H} &= \hat{H}_{\rm ee} + \hat{H}_{\rm LF} + \hat{H}_{\rm SO} + \hat{H}_{\rm Zeeman} \\ &= \sum_{i<j} \frac{e^2}{r_{i,j}} + \sum_i V_i + \zeta \sum_i \boldsymbol{l}_i \cdot \boldsymbol{s}_i \\ &\quad + \sum_i \mu_{\rm B} (k\boldsymbol{l}_i + g_e \boldsymbol{s}_i) \cdot \boldsymbol{H}, \end{aligned} \tag{2}$$

where $\hat{H}_{\rm ee}$, $\hat{H}_{\rm LF}$, $\hat{H}_{\rm SO}$ and $\hat{H}_{\rm Zeeman}$ are the electron-electron repulsion interaction, the ligand field interaction, the spin-orbit coupling interaction and the Zeeman interaction, respectively. $\zeta$ is the spin-orbit coupling coefficient and $k$ is the orbital reduction factor. $V_i$ is the ligand field potential. The matrix elements are functions of the Racah parameters $B$ and $C$, the spin-orbit coupling coefficient $\zeta$, and the ligand field parameters $B_{20}$, $B_{40}$, $B_{44}^c$, $B_{44}^s$ which can be derived in terms of the point-dipole model as[22]

$$\begin{aligned} B_{20} &= \frac{1}{2} \sum_\tau G_2(\tau)(3\cos^2\theta_\tau - 1)\left(1 + \frac{3\mu}{eR_\tau}\right), \\ B_{40} &= \frac{1}{8} \sum_\tau G_4(\tau)(35\cos^4\theta_\tau - 30\cos^2\theta_\tau + 3) \\ &\quad \times \left(1 + \frac{5\mu}{eR_\tau}\right), \\ B_{44}^c &= \frac{\sqrt{70}}{16} \sum_\tau G_4(\tau)\sin^4\theta_\tau \cos 4\phi_\tau \left(1 + \frac{5\mu}{eR_\tau}\right), \\ B_{44}^s &= {\rm i}\frac{\sqrt{70}}{16} \sum_\tau G_4(\tau)\sin^4\theta_\tau \cos 4\phi_\tau \left(1 + \frac{5\mu}{eR_\tau}\right), \end{aligned} \tag{3}$$

where $\mu$ is the electric dipole moment of a ligand ion. For the parameter $\mu$ in $(VCl_6)^{4-}$ coordination complex, we take the typical value $0.82eR_\tau$ approved by Li *et al.*[23] For MCl: $V^{2+}$ (M=K, Na, Rb) systems, we choose the $Z$-axis along the $C_4$ axis. Then, the ligand field parameter $B_{44}^s$ will vanish and the parameters $G_2(\tau)$ and $G_4(\tau)$ can be derived as

$$\begin{aligned} G_2(\tau) &= -eq_\tau G^2(\tau), \\ G_4(\tau) &= -eq_\tau G^4(\tau), \\ G^k(\tau) &= \int_0^{R_\tau} R_{\rm 3d}^2(r) r^2 \frac{r^k}{R_\tau^{k+1}} {\rm d}r \\ &\quad + \int_{R_\tau}^{\infty} R_{\rm 3d}^2(r) r^2 \frac{R_\tau^k}{r^{k+1}} {\rm d}r, \end{aligned} \tag{4}$$

where $q_\tau$ represents the effective charge of the $\tau$-th ligand. According to the Van Vleck approximation for

$G^k(\tau)$ integral[24]

$$G_2(\tau) = \frac{A_2}{R_\tau^3},\ G_4(\tau) = \frac{A_4}{R_\tau^5}, \tag{5}$$

where

$$\begin{aligned} A_4 &= -eq_\tau\langle r^4\rangle\left(1+\frac{5\mu}{eR_\tau}\right),\\ A_2 &= -eq_\tau\langle r^2\rangle\left(1+\frac{3\mu}{eR_\tau}\right),\\ A_2/A_4 &= \langle r^2\rangle\left(1+\frac{3\mu}{eR_\tau}\right)/\langle r^4\rangle\left(1+\frac{5\mu}{eR_\tau}\right), \end{aligned} \tag{6}$$

$B_{20}$, $B_{40}$, $B_{44}^c$ can be expressed as

$$\begin{aligned} B_{20} &= A_2\left(\frac{1}{R_1^3}-\frac{1}{R_2^3}\right),\\ B_{40} &= A_4\left(\frac{1}{R_1^5}-\frac{1}{2R_2^5}\right),\\ B_{44}^c &= \left(\frac{35}{8}\right)^{1/2}\frac{A_4}{R_2^5}. \end{aligned} \tag{7}$$

where $R_1$ and $R_2$ are the V–Cl bond length in MCl:$V^{2+}$ systems, as plotted in Fig.1.

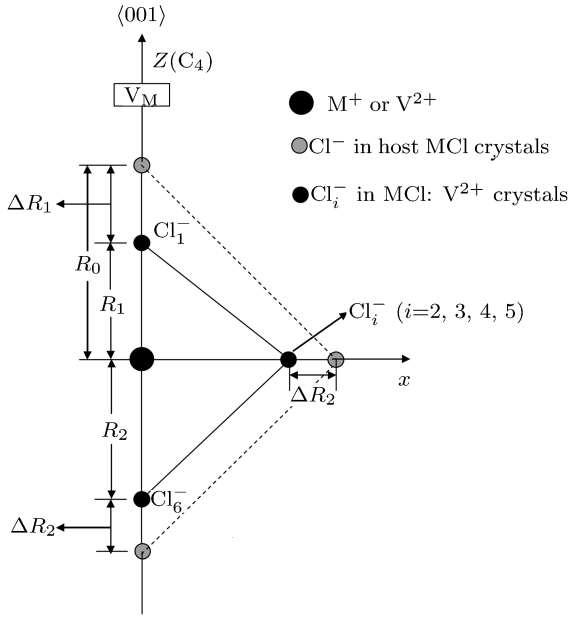



**Fig.1.** Local structure of $(VCl_6)^{4-}$ coordination complex for MCl:$V^{2+}$ (M=Na, K, Rb) systems. $R_0$ is original octahedral cubic $(MCl_6)^{4-}$ structure parameter. $\Delta R_1$ and $\Delta R_2$ denote, respectively, the shift of $Cl_1^-$ and $Cl_i^-$ ($i$=2, 3, 4, 5, 6) along the crystallographic axes to $V^{2+}$ when $V^{2+}$ replaces the $M^+$. $R_1$ is $V^{2+}$–$Cl_1^-$ distance and $R_2$ is $V^{2+}$–$Cl_i^-$ distance ($i$=2, 3, 4, 5, 6).

The ratio $\langle r^2\rangle/\langle r^4\rangle = 0.1956$ for $V^{2+}$ ion can be obtained from the radial wave function.[23] The value of $A_4$ can be determined from optical spectrum[25] and the V–Cl bond length of $VCl_2$.[26] In this way, we derive $A_4 = 64.31$ a.u. for the octahedral $(VCl_6)^{4-}$ coordination complex. The value of $A_4$ will be employed in the following calculation.

## 2.2. EPR parameters for $3d^3$ configuration ions

EPR spectrum of $V^{2+}$ ion in a tetragonal ligand field can be described by the spin Hamiltonian[27]

$$\begin{aligned} \hat{H}_S = {}& \mu_B g_\parallel H_z S_z + \mu_B g_\perp (H_x S_x + H_y S_y)\\ & + D\left[S_z^2 - \frac{1}{3}S(S+1)\right], \end{aligned} \tag{8}$$

where $D$ is ZFS parameter, $g_\parallel$ and $g_\perp$ are anisotropic $g$ factors. In the absence of the external magnetic field, the corresponding ground-state zero field splitting $\Delta E$ can be expressed as a function of the parameter $D$,

$$\Delta E = E\left(\pm\frac{3}{2}\right) - E\left(\pm\frac{1}{2}\right) = 2D. \tag{9}$$

The ZFS energy $\Delta E$ can be obtained by diagonalizing the complete energy matrix corresponding to Hamiltonian Eq.(2) without the Zeeman term. Considering the external magnetic field, the Kramer's degeneracy of the ground state $^4A_2$ will be completely removed. For $H_\parallel \neq 0$, $H_\perp = 0$ ($H_\parallel = H_Z$), the splitting energy levels of the ground state can be expressed as

$$\begin{aligned} E_1 &= D + \frac{3}{2}g_\parallel\mu_B H_z,\\ E_2 &= -D + \frac{1}{2}g_\parallel\mu_B H_z,\\ E_3 &= -D - \frac{1}{2}g_\parallel\mu_B H_z,\\ E_4 &= D - \frac{3}{2}g_\parallel\mu_B H_z. \end{aligned} \tag{10}$$

For $H_\perp \neq 0$, $H_\parallel = 0$ ($H_\perp = H_x = H_y$), the splitting energy levels of the ground state can be expressed as:

$$\begin{aligned} E_1 &= -\frac{1}{2}g_\perp\mu_B H_x + \sqrt{g_\perp^2\mu_B^2 H_x^2 + D^2 + Dg_\perp\mu_B H_x},\\ E_2 &= -\frac{1}{2}g_\perp\mu_B H_x - \sqrt{g_\perp^2\mu_B^2 H_x^2 + D^2 + Dg_\perp\mu_B H_x},\\ E_3 &= \frac{1}{2}g_\perp\mu_B H_x + \sqrt{g_\perp^2\mu_B^2 H_x^2 + D^2 - Dg_\perp\mu_B H_x},\\ E_4 &= \frac{1}{2}g_\perp\mu_B H_x - \sqrt{g_\perp^2\mu_B^2 H_x^2 + D^2 - Dg_\perp\mu_B H_x}. \end{aligned} \tag{11}$$

As for the case of $H_\parallel = H_z$, by diagonalizing the complete energy matrix corresponding to Hamiltonian Eq.(2) including the Zeeman term, we may obtain

the four ground-state splitting energy levels. Subsequently, taking the calculated splitting energy levels into Eq.(10), we may deduce the value of $g_{\parallel}$. Similarly, we may evaluate the $g_{\perp}$ by diagonalizing the complete energy matrix for $H_{\perp} = H_x$ with the aid of Eq.(11).

# 3. Calculation and analysis

## 3.1. Calculation of local structure for tetragonal $V^{2+}$ centres in $(VCl_6)^{4-}$ coordination complex

In MCl (M=K, Na, Rb) crystals, $M^+$ ions are surrounded by six chlorine ions, respectively, the local symmetry belongs to the space group $O_h$. When the transition-metal $V^{2+}$ ions are doped into KCl, NaCl and RbCl crystals, the $V^{2+}$ ions will substitute for $Na^+$, $K^+$ and $Rb^+$ ions respectively. As we know, the transition-metal ion $V^{2+}$ has an obviously smaller ionic radius ($r_i$=0.93 Å, 1 Å=0.1 nm) and more effective charge than that of $M^+$ ions ($r_h$=1.16 Å, 1.52 Å and 1.66 Å, corresponding to $Na^+$, $K^+$ and $Rb^+$, respectively),[28] so it is reasonable to predict that the $V^{2+}$ ion will pull the six chlorine ions to move toward the $V^{2+}$ centre along crystallographic axes. In addition, the next nearest cation site around $V^{2+}$ ion along $\langle 001 \rangle$ direction will be occupied by a vacancy $V_M$ due to the local charge compensation.[14–16] Considering the vacancy, which has a negative effective charge, we find that it dominantly affects the $Cl^-$ ion intervening the $V^{2+}$ and $V_M$. So we may consider that the shift of the intervening $Cl^-$ ion towards the central ion is obviously larger than that of the other five $Cl^-$ (similar to $Cr^{3+}$-$V_M$ centre in MgO:$Cr^{3+}$ system.[29]) Therefore, in our study, we have approximately regarded the shift of the lower five $Cl_i^-$ ($i$=2, 3, 4, 5, 6) to be equivalent (see Fig.1). According to above analysis, the local structure parameters $R_1$ and $R_2$ can be expressed as

$$R_1 = R_0 + \Delta R_1, \; R_2 = R_0 + \Delta R_2, \qquad (12)$$

where $R_0$ is the M–Cl bond length of host cubic crystals and the values are $R_0$ = 2.81 Å, 3.14 Å and 3.27 Å for NaCl, KCl and RbCl, respectively.[30] In order to decrease the number of adjustable parameters and reflect the effect of covalency, we take an average covalency factor $N$ and use the following relation:[31]

$$B = N^4 B_0, \; C = N^4 C_0, \; \zeta = J^2 \zeta_0. \qquad (13)$$

The values of the free-ion parameters for $V^{2+}$ ion have been reported as[32]

$$B_0 = 766\,\mathrm{cm}^{-1}, \;\; C_0 = 2855\,\mathrm{cm}^{-1}, \;\; \zeta_0 = 167\,\mathrm{cm}^{-1}. \qquad (14)$$

The $N = 0.923$ can be obtained by fitting optical spectrum of NaCl:$V^{2+}$ system. Up to now, the optical spectra of $V^{2+}$ ions doped in KCl and RbCl have not been reported. However, because the MCl:$V^{2+}$ systems have the similar configuration and the same type of ligand, we can take the average covalency factor of NaCl:$V^{2+}$ system into the calculation of MCl:$V^{2+}$ systems. The slightly adjusted value from the formula $k \approx N^2$ can also be evaluated in order to obtain the precise calculations of $g$ factors ($g_{\parallel}$, $g_{\perp}$).

By employing the above parameters, the EPR and optical spectra of NaCl:$V^{2+}$ system as functions of $R_1$ and $R_2$ can be calculated by diagonalizing the complete energy matrix for $3d^3$ configuration $V^{2+}$ ion in a tetragonal ligand field, and the results are listed in Tables 1 and 2. As for KCl:$V^{2+}$ and RbCl:$V^{2+}$ systems, we can determine the local structure parameters $R_1$ and $R_2$ by simulating cubic crystal field parameter $Dq$ and the EPR parameters simultaneously. The theoretical results $Dq = 660.3\,\mathrm{cm}^{-1}$ and $Dq = 621.2\,\mathrm{cm}^{-1}$ are consistent with the experimental findings $Dq = 660\,\mathrm{cm}^{-1}$ and $Dq = 622\,\mathrm{cm}^{-1}$[14] which are corresponding to KCl:$V^{2+}$ and RbCl:$V^{2+}$ systems, respectively. The EPR parameters ($D$, $g_{\parallel}$, $g_{\perp}$) and local structure parameters are listed in Table 1.

From Tables 1 and 2, we can clearly see that the optical spectra and EPR parameters ($D$, $g_{\parallel}$, $g_{\perp}$) can be satisfactorily simulated by the structure parameters $R_1$ and $R_2$. We note that $R_1 < R_2 < R_0$ for the three systems at different temperatures, which indicates that the local lattice structure around the $V^{2+}$-$V_M$ centres in MCl:$V^{2+}$ (M=Na, K, Rb) systems has a compression distortion from the cubic configuration. It may mainly arise from the more effective charge and smaller ionic radius of $V^{2+}$ (0.93 Å) in comparison with those of host ions $Na^+$ (1.16 Å), $K^+$ (1.52 Å) and $Rb^+$ (1.66 Å). The relation $R_1 < R_2$ implies that the compression distortion magnitude along $\langle 001 \rangle$ axis is larger than that of along other axes and this may be attributed to that the influence of the vacancy $V_M$ on $Cl_1^-$ ion intervening in the $V^{2+}$ and $V_M$ is much larger than that of other five $Cl_i^-$ ($i$=2, 3, 4, 5, 6) ions. Comparison of our results with Wu's[13] is shown in Table 3, we find that the local structure

parameters $R_1$ and $R_2$ estimated by them are larger than ours. This difference may be ascribed to that the compression distortion induced by the different effective charge between $V^{2+}$ ion and host $M^+$ ions cannot be considered in the impurity-ligand distance formula $R \approx R_0 + (r_i - r_h)/2$ in Wu's calculations. Of course, in order to detailedly clarify the local distortion of $V^{2+}$-$V_M$ centres in MCl:$V^{2+}$ systems, more careful experiments especially ENDOR should be required.

**Table 1.** EPR parameters ($D$, $g_\parallel$, $g_\perp$) for $V^{2+}$–$V_M$ centres in MCl crystals as a function of the structure parameters $R_1$ and $R_2$. ($\Delta R = R_1 - R_2$).

| compounds | $T$/K | $R_1$/Å | $R_2$/Å | $\Delta R$/Å | $D$/cm$^{-1}$ | $g_\parallel$ | $g_\perp$ |
|---|---|---|---|---|---|---|---|
| RbCl | 295 | 2.6430 | 2.7713 | –0. 1283 | –0.08331 | 1.9536 | 1.9566 |
| expt. [14] | | | | | –0.08333 | 1.9537 | 1.9579 |
| KCl | 295 | 2.6073 | 2.7385 | –0. 1312 | –0.08011 | 1.9565 | 1.9593 |
| expt. [14] | | | | | –0.08013 | 1.9564 | 1.9603 |
| NaCl | 302 | 2.5306 | 2.6445 | –0. 1139 | –0.05744 | 1.9628 | 1.9651 |
| expt. [14] | | | | | –0.05741 | 1.9629 | 1.9660 |
| NaCl | 195 | 2.5173 | 2.6304 | –0.1131 | –0.05537 | 1.9637 | 1.9660 |
| expt. [14] | | | | | –0.05536[a] | 1.9638[b] | 1.9668[b] |
| NaCl | 77 | 2.5138 | 2.6243 | –0.1105 | –0.05337 | 1.9647 | 1.9667 |
| expt. [14] | | | | | –0.05335 | 1.9647 | 1.9676 |

[a]For NaCl:$V^{2+}$ system, the data of ZFS parameter $D$ at $T = 195$ K are estimated according to the relation given by Vanhaelst:[14]

$$D = m_1 T + c_1$$

[b]Estimated according to the relation between $g$ factors and temperature.

**Table 2.** Comparison of optical spectra between theoretical and experimental values for $V^{2+}$–$V_{Na}$ centres in NaCl crystal at different temperatures, all values in units of cm$^{-1}$.

| | $T = 302$/K | | $T = 195$/K | | $T = 77$/K | |
|---|---|---|---|---|---|---|
| transition $^4A_2 \rightarrow$ | Cal. | Expt.[14] | Cal. | Expt.[14] | Cal. | Expt.[14] |
| $^4T_2$ | 7547 | 7547 | 7752 | 7752 | 7843 | 7843 |
| | 7968 | | 8182 | | 8269 | |
| $^4T_1$(F) | 12124 | 12121 | 12391 | 12270 | 12503 | 12346 |
| | 12767 | | 13061 | | 13172 | |
| $^4T_1$(P) | 19560 | 19608 | 19926 | 19763 | 20076 | 20000 |
| | 19688 | | 20039 | | 20180 | |
| $^2E$ | 41819 | 41841 | 42254 | 42017 | 42434 | 43103 |
| | 41949 | | 42341 | | 42501 | |

**Table 3.** Comparing the two results calculated at room temperature by different methods..

| compounds | NaCl:$V^{2+}$ | | KCl:$V^{2+}$ | | RbCl:$V^{2+}$ | |
|---|---|---|---|---|---|---|
| $R_1$/ Å | 2.5306[a] | 2.555[b] | 2.6073[a] | 2.680[b] | 2.6430[a] | 2.742[b] |
| $R_2$/ Å | 2.6445[a] | 2.695[b] | 2.7385[a] | 2.845[b] | 2.7713[a] | 2.905[b] |

[a]The results from our calculations.

[b]The results of Wu *et al.*[13]

From our calculation, we find that the structure parameters $R_1$, $R_2$ and the absolute values of $\Delta R(= R_1 - R_2)$ for $V^{2+}$ ion doped in NaCl have different values at different temperatures, namely, $R_1 = 2.5138$ Å, $R_2 = 2.6243$ Å, $|\Delta R| = 0.1105$ Å at 77 K; $R_1 = 2.5173$ Å, $R_2 = 2.6304$ Å, $|\Delta R| = 0.1131$ Å at 195 K; $R_1 = 2.5306$ Å, $R_2 = 2.6445$ Å, $|\Delta R| = 0.1139$ Å at 302 K. We can see that the structure parameters $R_1$, $R_2$ and the $|\Delta R|$ increase with the rising temperature. From the above analysis, we note that the difference

between $R_1$ and $R_2$ mainly arises from the influence of the vacancy $V_M$. So we will reach a conclusion that the effects of the vacancy $V_M$ on the tetragonal distortion are enhanced with rising temperature.

## 3.2. The influences of the local structure parameters $R_1$ and $R_2$ on the ZFS parameter $D$

The relationships between ZFS parameter $D$ and $\Delta R(= R_1 - R_2)$ for the MCl:$V^{2+}$ systems at different temperatures are plotted in Fig.2. It can be seen that the relation of ZFS parameter $D$ vs. $\Delta R$ is approximately linear and proportional in the distortion region. Meanwhile, all the relative curves pass the same point (0, 0), because $\Delta R = 0$, i.e. $R_1 = R_2$, is related to the cubic structure whose ZFS parameter $D$ equals zero. Furthermore, we note that the sign of $\Delta R$ is same to that of the ZFS parameter $D$, namely, when $\Delta R > 0$, then $D > 0$, conversely, when $\Delta R < 0$, then $D < 0$. The magnitude of ZFS parameter $|D|$ will increase with the increase of $|\Delta R|$. From the relative curves in Fig.2, we also find that the slopes $\partial D/\partial(\Delta R)$ are slight different, which indicates that the change rate of ZFS parameter $D$ varying with $\Delta R$ is different for the different systems.

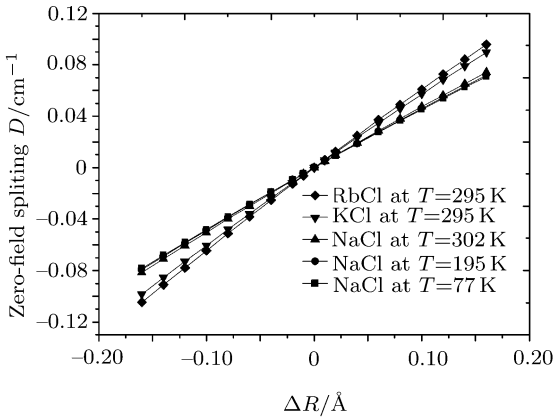
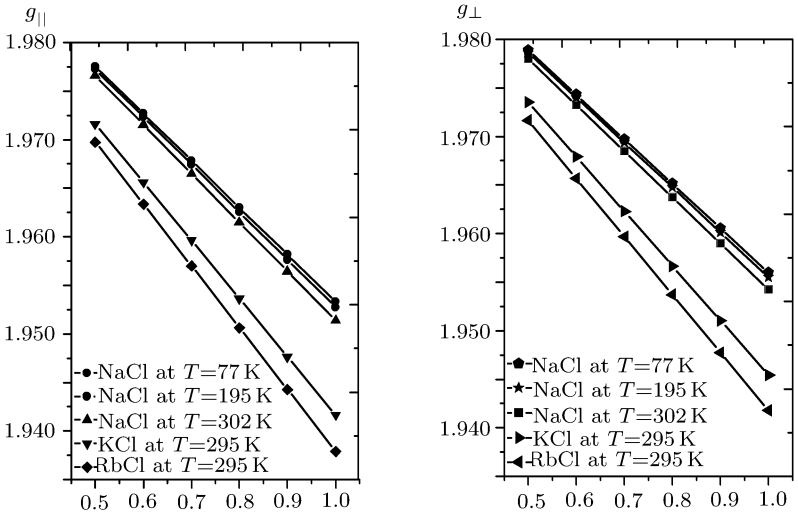



**Fig.2.** The dependence of ZFS parameter $D$ on $\Delta R$ of $(VCl_6)^{4-}$ coordination complex for MCl:$V^{2+}$ (M=Na, K, Rb) systems at different temperatures. $B_0 = 766\,\mathrm{cm}^{-1}$, $C_0 = 2855\,\mathrm{cm}^{-1}$, $\zeta_0 = 167\,\mathrm{cm}^{-1}$, $N = 0.923$. $R_2 = 2.6445$ Å at $T = 302$ K, $R_2 = 2.6304$ Å at $T = 195$ K, $R_2 = 2.6243$ Å at $T = 77$ K for NaCl, $R_2 = 2.7385$ Å at $T = 295$ K for KCl, $R_2 = 2.7713$ Å at $T = 295$ K for RbCl.

## 3.3. The influences of the orbital reduction factor $k$ on the $g$ factors ($g_\parallel, g_\perp$ and $\Delta g$)

It is well known that the orbital reduction factor $k$ has an important influence on anisotropic $g$ factors ($g_\parallel, g_\perp$). In this paper, we calculate the $g$ factors ($g_\parallel, g_\perp$) by adjusting the orbital reduction factor $k$ ($0.5 < k < 1$) and fixing the remaining parameters. According to the calculated results, we draw the relative curves of $g_\parallel$ vs. $k$, $g_\perp$ vs. $k$, and $\Delta g(= g_\parallel - g_\perp)$ vs. $k$ for MCl:$V^{2+}$ systems as plotted in Fig.3. We can see that the relations between $g$ factors ($g_\parallel$, $g_\perp$ and $\Delta g$) and $k$ are linear for the three systems at different temperatures. Meanwhile, the values of $g$ factors ($g_\parallel$, $g_\perp$ and $\Delta g$) have a slowly falling trend with the increase of orbital reduction factor $k$. This means that the delocalization effect which reduces the role of the




(a) Orbital reduction factor $k$

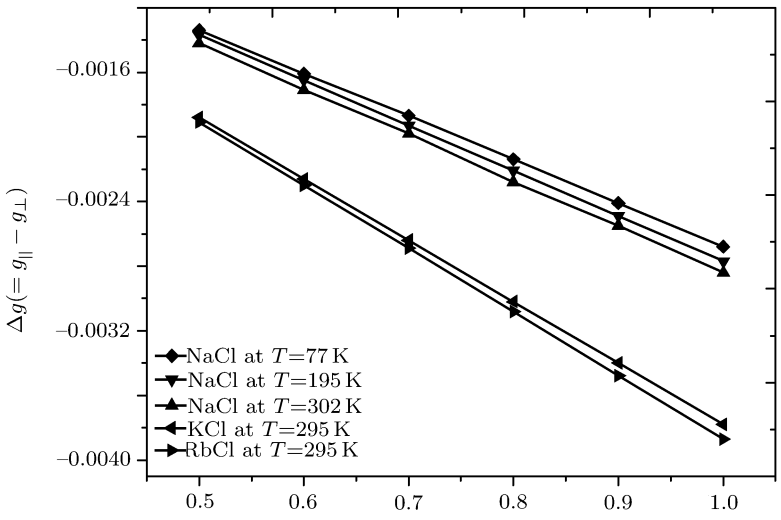



**Fig.3.** The relationships between $g_{\|}$, $g_{\perp}$, $\Delta g(=g_{\|}-g_{\perp})$ and orbital reduction factor $k$, respectively.

orbital momentum cannot be neglected for $3d^3$ configuration ions in tetragonal ligand field. As for the NaCl:$V^{2+}$ system at different temperatures, the slopes $\partial g_{\|}/\partial k$, $\partial g_{\perp}/\partial k$ and $\partial(\Delta g)/\partial k$ are adjacent, as shown in Fig.3. This can be attributed to the fact that local environment in NaCl:$V^{2+}$ system has the similar $(VCl_6)^{4-}$ coordination complex at three different temperatures, which have been determined in our work.

## 4. Conclusions

From the above studies, we have the following conclusions.

(i) The local structure parameters $R_1 = 2.5138-2.5306$ Å, $R_2 = 2.6243-2.6445$ Å for NaCl:$V^{2+}$ system in the temperature range 77 K–302 K; $R_1 = 2.6073$ Å, $R_2 = 2.7385$ Å for KCl:$V^{2+}$ system at 295 K; $R_1 = 2.6430$ Å, $R_2 = 2.7713$ Å for RbCl:$V^{2+}$ system at 295 K are determined, respectively. It is worth noting that the local structure around the octahedral $V^{2+}$ ion centre has a compression tetragonal distortion. Moreover, the theoretical results also show that the empirical formula $R \approx R_0 + (r_i - r_h)/2$ is unsuitable for the MCl:$V^{2+}$ (M=Na, K, Rb) systems.

(ii) The values of local structure parameters $R_1$, $R_2$ and the absolute values of $\Delta R(=R_1-R_2)$ will increase with the increase of temperature. It is found that the relation of ZFS parameter $D$ vs. $\Delta R$ is approximately linear and proportional in the distortion region which is of significance in broadening our understanding of the physical and chemical properties and clarifying the detailed relationship between $D$ and $\Delta R$.

(iii) The relations of anisotropic $g$ factors ($g_{\|}$, $g_{\perp}$ and $\Delta g$) vs. $k$ are linear, and the values of $g_{\|}$, $g_{\perp}$ and $\Delta g$ will decrease with the increase of orbital reduction factor $k$. This implies that the orbital reduction effect cannot be ignored in MCl:$V^{2+}$ systems.

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