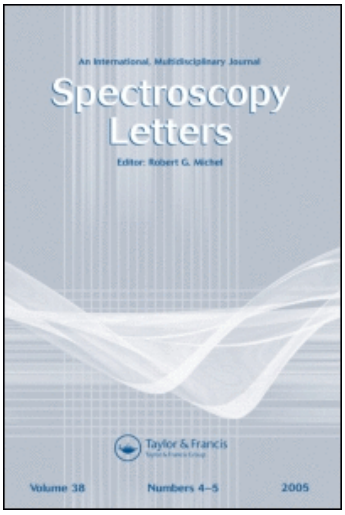

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Theoretical Explanations of the *g* Factors for Ni^{3+} Ions in $KMgF_3$ and $CsCaF_3$ Crystals

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ABSTRACT By using the optical spectral parameters of $(NiF_6)^{3-}$ clusters in $KMgF_3$:Ni^{3+} and $CsCaF_3$:Ni^{3+} crystals estimated from the observed values in pure K_3NiF_6 crystal, the electron paramagnetic resonance (EPR) *g* factors for $KMgF_3$:Ni^{3+} and $CsCaF_3$:Ni^{3+} are calculated from the second-order perturbation formula (with the high-spin ground orbital state) based on the cluster approach. The results are in reasonable agreement with the observed values. The spin transition from the low-spin state in pure K_3NiF_6 crystal to the high-spin state in $KMgF_3$:Ni^{3+} and $CsCaF_3$:Ni^{3+} crystals owing to the slight increase of $Ni^{3+} - F^-$ distance is discussed.

KEYWORDS crystal- and ligand-field theory, $CsCaF_3$, electron paramagnetic resonance, $KMgF_3$, Ni^{3+}, spin transition

INTRODUCTION

In crystal theory, according to the Tanabe-Sugano diagram,[1] the ground orbital state (which is related to optical spectra) for some $3d^n$ ions in crystals depends upon the ratio $|Dq/B|$ (where Dq is the cubic field parameter and B is the Racah parameter).[1–3] For example, for $3d^7$ ions in octahedral clusters, when $|Dq/B| > 2.2$, the ground orbital state is the low-spin ($S = 1/2$) state ^2E.[1,2] In this strong field case, the average EPR $\bar{g}$ factor is close to 2.[3,4] Whereas if $|Dq/B| < 2.2$, the ground orbital state should be the high-spin ($S = 3/2$) state $^4T_1(F)$;[1,2] the $\bar{g}$ factor in this weak field case is close to 13/3 ($\approx$4.33).[3,4] For an $(NiF_6)^{3-}$ cluster in pure K_3NiF_6 crystal, the optical spectra studies suggested that $Dq \approx -1620\,cm^{-1}$, $B \approx 703\,cm^{-1}$, and so $|Dq/B| \approx 2.3$.[5] Thus, its ground orbital state is the low-spin ^2E.[5] This point was supported by the EPR experiments for $(NiF_6)^{3-}$ clusters in the pure crystals K_3NiF_6, Na_3NiF_6, Cs_2NaNiF_6, Cs_2KNiF_6, and Rb_2KNiF_6.[6] Considering that the cubic field parameter Dq decreases by the relation $Dq \propto R^{-n}$ (where $n \approx 3.5 \sim 6.5$[7,8]), and the Racah parameter B increases slightly with the increasing metal-ligand (e.g., $Ni^{3+} - F^-$ here) distance R because of the decreasing covalence reduction effect,[9,10] the value of $|Dq/B|$ for the $(NiF_6)^{3-}$ clusters should decrease with the increase of distance R and may be smaller than 2.2 in some systems. Thus, the ground orbital state changes from the low-spin to high-spin state. For Ni^{3+} in cubic perovskites $KMgF_3$ and $CsCaF_3$, since the ionic radii r_b of the replaced host ions Mg^{2+} ($r_b \approx 0.86$ Å[11]) and Ca^{2+} ($r_b \approx 1.14$ Å[11]) are larger than the radius

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r_i (≈0.74 Å in the high-spin state[11]) of the impurity Ni^{3+}, the $Ni^{3+} - F^-$ distance R in the two crystals should be larger than that in the pure crystal. Thus, the values of $|Dq/B|$ may be smaller than 2.2, and the ground state may be of high spin. The observed EPR g factors for Ni^{3+} in both crystals[12,13] support this point. No theoretical calculations for these g factors of Ni^{3+} in $KMgF_3$ and $CsCaF_3$ crystals were made. In this article, these g factors are calculated from the second-order perturbation formulas based on the cluster approach. In the calculations, the optical spectra parameters (Dq and B) are estimated reasonably from those observed in pure K_3NiF_6 crystals and the above rules related to optical spectral parameters Dq, B, and metal-ligand distance R. The results are discussed.

CALCULATION

For $3d^7$ ions in a weak octahedral crystal field, the ground orbital state $^4T_1(F)$ splits into three Kramers doublets ($J' = 5/2$, $3/2$, and $1/2$). The lowest Kramers doublet is $|\pm 1/2>$.[4] Thus, considering the covalency effect in $3d^n$ clusters, the second-order perturbation formula of a g factor based on the cluster approach for $3d^7$ ions in cubic crystals can be expressed as[14]

$$g = \frac{10}{3} + \frac{2}{3}k\alpha + \frac{5k'\zeta'\varepsilon^2}{2\Delta_F}, \tag{1}$$

where k and k' are the orbital reduction factors. ζ' (and ζ) are the spin-orbit (SO) coupling parameters. Δ_F is the energy separation between the excited state $^4T_2(F)$ and the ground state $^4T_1(F)$, which can be calculated from the optical spectra parameters. α is the effective Lande factor and reads

$$\alpha = \frac{3}{2}\varepsilon^2 - \tau^2, \tag{2}$$

in which the parameters ε and τ are related to the interaction (or admixture) between $^4T_1(P)$ and $^4T_1(F)$ and can be obtained from the optical spectra parameters by using the relationships[14]

$$\varepsilon^2 + \tau^2 = 1, \quad \frac{\tau}{\varepsilon} = \frac{-4Dq}{15B - 6Dq}. \tag{3}$$

According to the cluster approach, the parameters ζ, ζ', k, and k' can be written as[14,15]

$$\begin{aligned}
\zeta &= N_t(\zeta_d^0 + \lambda_t^2\zeta_p^0/2),\\
\zeta' &= \sqrt{N_tN_e}(\zeta_d^0 + \lambda_t^2\zeta_p^0/2),\\
k &= N_t[1 - 2\lambda_t S_{dp}(t_{2g}) + \lambda_t^2/2],\\
k' &= \sqrt{N_tN_e}[1 - \lambda_t S_{dp}(t_{2g}) - \lambda_e S_{dp}(e_g) - \lambda_t\lambda_e/2],
\end{aligned} \tag{4}$$

where ζ_d^0 and ζ_p^0 are, respectively, the SO coupling parameter of free $3d^n$ ion and that of free ligand ion. For the $(NiF_6)^{3-}$ clusters under study, ζ_d^0 (Ni^{3+}) ≈ 749 cm^{-1},[16] ζ_p^0 (F^-) ≈ 220 cm^{-1}.[17] $S_{dp}(\gamma)$ ($\gamma = t_{2g}$ or e_g) is the group overlap integral. N_γ and λ_γ are the normalization coefficient and orbital mixing coefficient in the linear combination of atomic orbitals (LCAO) molecular orbital (MO). They can be obtained from the normalization relation[14,18]

$$N_\gamma = [1 - 2\lambda_\gamma S_{dp}(\gamma) + \lambda_\gamma^2]^{-1} \tag{5}$$

and the approximate condition[14,18]

$$f_\gamma \approx B/B_0 \text{ (or } C/C_0) \approx N_\gamma^2[1 + \lambda_\gamma^2 S_{dp}^2(\gamma) - 2\lambda_\gamma S_{dp}(\gamma)], \tag{6}$$

where B_0 and C_0 are the Racah parameters of a free $3d^n$ ion. For the free Ni^{3+} ion, we have $B_0 \approx$ 1195 cm^{-1} and $C_0 \approx 4808$ cm^{-1}.[16]

The integral $S_{dp}(\gamma)$ of a $3d^n$ cluster can be calculated from the Slater-type self–consistent field (SCF) functions[19,20] and the average metal-ligand distance R. Generally speaking, for $3d^n$ impurities in crystals, the impurity-ligand distance R is different from the corresponding distance R_H in the host crystal because of the size and/or charge mismatch. The impurity-ligand distance R in crystals can be obtained by analyzing the experimental (e.g., extended x–ray absorption fine structure (EXAFS) and superhyperfine constant experiments[21]) data or by using the theoretical calculations (e.g., using the embedded-quantum-cluster approach[22] or a lattice relaxation model[23,24]). For the studied $KMgF_3$:Ni^{3+} and $CsCaF_3$:Ni^{3+} crystals, no such experimental and theoretical studies were done. According to the impurity-ligand distances R for Mn^{2+} in fluoroperovskites derived from the experimental superhyperfine constant A_s, EXAFS measurements and crystal-field spectrum analysis,[21] an approximate formula

$$R \approx R_H + (r_i - r_h)/2 \tag{7}$$

TABLE 1 Mixing Parameters ε and τ, MO Coefficients, Orbital Reduction Factors, and SO Coupling Parameters for Ni^{3+} in $KMgF_3$ and $CsCaF_3$ Crystals

	ε	τ	N_t	N_e	λ_t	λ_e	k	k'	ζ'
$KMgF_3:Ni^{3+}$	0.9590	0.2835	0.7728	0.7814	0.5495	0.5564	0.8833	0.6436	604.5
$CsCaF_3:Ni^{3+}$	0.9634	0.2680	0.7758	0.7825	0.5430	0.5486	0.8856	0.6518	558.1

is suggested in the estimation of the impurity-ligand distance R in crystals.[25] So, it is applied here. From the r_i, r_b given in the Introduction and $R_H \approx 1.994$ and 2.262 Å[21] for $KMgF_3$ and $CsCaF_3$, respectively, $R \approx 1.934$ and 2.062 Å are obtained for $(NiF_6)^{3-}$ clusters in $KMgF_3:Ni^{3+}$ and $CsCaF_3:Ni^{3+}$ crystals. Thus, the integrals $S_{dp}(\gamma)$ can be calculated. They are $S_{dp}(t_{2g}) \approx 0.00728$, $S_{dp}(e_g) \approx 0.02682$ for $KMgF_3:Ni^{3+}$ and $S_{dp}(t_{2g}) \approx 0.00547$, $S_{dp}(e_g) \approx 0.02102$ for $CsCaF_3:Ni^{3+}$.

No optical spectra of $(NiF_6)^{3-}$ clusters in $KMgF_3:Ni^{3+}$ and $CsCaF_3:Ni^{3+}$ crystals were reported. We estimate reasonably the optical spectra parameters B, C, and Dq for both crystals from the optical spectra parameters of K_3NiF_6 crystal[5] and the rules mentioned in the Introduction. Thus, from the $Ni^{3+} - F^-$ distances R in K_3NiF_6, $KMgF_3:Ni^{3+}$, and $CsCaF_3:Ni^{3+}$ (note: for the pure K_3NiF_6, considering that the metal-ligand distance in pure crystal is very close to the sum of ionic radii, it is taken that $R \approx 1.89$ Å, where $r(Ni^{3+}) \approx 0.70$ Å in the low-spin state and $r(F^-) \approx 1.19$ Å[11]), we have $Dq \approx -1410\ cm^{-1}$, $B \approx 708\ cm^{-1}$, and hence, $f_\gamma \approx 0.5925$ for $KMgF_3:Ni^{3+}$ and $Dq \approx -1280\ cm^{-1}$, $B \approx 715\ cm^{-1}$, and hence, $f_\gamma \approx 0.5980$ for $CsCaF_3:Ni^{3+}$.

By using these optical spectra parameters for Ni^{3+} in both crystals, the parameters ε and τ are calculated from Eq. (3), and the MO coefficients N_γ and λ_γ are obtained from Eqs. (5) and (6). Thus, the parameters k, k', and ζ' can be calculated from Eq. (4). These calculated results are shown in Table 1.

Applying the parameters in Table 1 to Eq. (1), the g factors for Ni^{3+} ions in $KMgF_3$ and $CsCaF_3$ are calculated. They are compared with the observed values in Table 2.

TABLE 2 EPR g Factors for Ni^{3+} in $KMgF_3$ and $CsCaF_3$ Crystals

	$KMgF_3:Ni^{3+}$	$CsCaF_3:Ni^{3+}$
Calculation	4.163	4.186
Experiment	4.163 (1)[a]	4.183[b]

[a]Reference 12.
[b]Reference 13.

DISCUSSION

In the above calculations, one can find that the values $|Dq/B| \approx 1.99$ and 1.79 for Ni^{3+} ions in $KMgF_3$ and $CsCaF_3$ crystals, respectively. Both values are smaller than 2.2, and so the ground orbital state of $(NiF_6)^{3-}$ clusters in the two crystals is, as suggested in the Introduction, the high-spin state rather than the low-spin state in K_3NiF_6 crystal. So, although there may be small errors in the estimated impurity-ligand distances in $KMgF_3:Ni^{3+}$ and $CsCaF_3:Ni^{3+}$ crystals because of the application of the approximate formula (i.e., Eq. (7)), the optical spectra parameters in the two crystals estimated from those in pure K_3NiF_6 crystal, and these distances are suitable. By using these parameters, the g factors of $KMgF_3:Ni^{3+}$ and $CsCaF_3:Ni^{3+}$ crystals are reasonably explained from the second-order perturbation formula based on the cluster approach for the high-spin $3d^7$ ions in cubic symmetry (see Table 2).

It should be pointed out that in the crystal-field theory, there are two theoretical methods—the complete diagonalization (of energy matrix) method (CDM)[26–29] and the perturbation theory method (PTM),[26–29]—in the calculations of spin-Hamiltonian parameters (including g factors) for $3d^n$ ions in crystals. Generally speaking, the PTM is simpler, and the CDM can provide more exact calculated results of spin-Hamiltonian parameters because it takes into account the contributions from all $3d^n$ excited states.[26,27] However, for the g factors of $3d^n$ ions in crystals, the calculated results from both the CDM and PTM are close to each other.[26–29] Recently, a fuller CDM[27,30] was developed, in which in addition to the SO interaction in the conversional CDM, the spin-spin (SS) and spin-other-orbit (SOO) interactions are considered in the CDM calculations of spin-Hamiltonian parameters. Even so, the calculations for $3d^8$ and $3d^2$ ions in some crystals show that the contributions to g factors from the SS, SOO, and combined SO-SS-SOO interactions are

small.[27,30] So, the calculated g factors of $KMgF_3:Ni^{3+}$ and $CsCaF_3:Ni^{3+}$ crystals using the simple PTM can be regarded as reasonable.

CONCLUSION

The theoretical calculations from the second-order perturbation formula (with the high-spin ground orbital state) based on the cluster approach confirmed that the ground state of the $(NiF_6)^{3-}$ clusters in $KMgF_3:Ni^{3+}$ and $CsCaF_3:Ni^{3+}$ crystals is the high-spin $^4T_1(F)$ rather than the low-spin ^2E in K_3NiF_6 crystal. This spin transition from the low-spin to the high-spin for $(NiF_6)^{3-}$ cluster is due to the slight increase of $Ni^{3+} - F^-$ distance R.

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