Theoretical Investigations of the Local Structure and the EPR Parameters of Mn$^{4+}$ in LiF:U:Mn Crystal

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The local structure and the EPR parameters (zero-field splitting $D$, $g$ factors $g_∥$ and $g_⊥$, and hyperfine structure constants $A_∥$ and $A_⊥$) of Mn$^{4+}$ in LiF:U:Mn crystal have theoretically been investigated by using the perturbation formulas of the EPR parameters for a 3d$^3$ ion in trigonally distorted octahedra. In this trigonal Mn$^{4+}$ center, three U$^{6+}$ ions locate on (1,1,0), (1,0,1) and (0,1,1) sites, each surrounded by six O$^{2-}$ ions. Thus, the studied system is characterized as the Mn$^{4+}$ associated with one host F$^-$ triangle, one O$^2$- triangle and an additional equivalent F' triangle containing the three U$^{6+}$ ions, i.e. an [MnF$_3$O$_3$F'O$_3$]$^{8-}$ cluster. The central Mn$^{4+}$ impurity is found to shift towards the oxygen triangle along the $C_3$ (or [111]) axis by an amount $\Delta Z \approx 0.29$ Å due to the strong electrostatic attraction between the Mn$^{4+}$ and the oxygen triangle (and also the additional equivalent F' triangle), which increases the trigonal distortion of the Mn$^{4+}$ center considerably. The calculated EPR parameters based on the above displacement $\Delta Z$ agree reasonably with the observed values.

Key words: Defect Structure; Electron Paramagnetic Resonance (EPR); Crystal-field Theory; Mn$^{4+}$; LiF.

1. Introduction

LiF containing transition-metal ions (e.g., Mn$^{4+}$, Cu$^{2+}$ and Ti$^{3+}$) and color centers has attracted interest due to their useful optical properties, such as thermoluminescence (TL) [1 – 3] and tunable solid state lasers [4 – 7]. For instance, uranium-doped LiF may induce six O$^{2-}$ ions replacing the six original F$^-$ ions around the substitutional U$^{6+}$ impurity on the host Li$^+$ site because of charge compensation. As a result, a bright green luminescence arising from the U$^{6+}$ was achieved, and an unusual Mn$^{4+}$ center, which had not been introduced in the common way, was observed in uranium-doped LiF with an excess of oxygen [7]. Further, an electron paramagnetic resonance (EPR) experiment on this Mn$^{4+}$ center was made, and the large zero-field splitting $D \sim 2.39$ in magnitude revealed considerable trigonal distortion of the studied system [7]. The authors [7] argued that U$^{6+}$ locates on the host Li$^+$ site with six nearest neighbouring F$^-$ ligands replaced with O$^{2-}$ ions, and so a trigonal Mn$^{4+}$ center is formed due to the three [UO$_6$]$^{6-}$ complexes on the plane perpendicular to the $C_3$ (or [111]) axis. Up to now, however, neither the above EPR experimental results nor the local structure of the Mn$^{4+}$ center has theoretically been studied. Since information about the EPR parameters (e.g., zero-field splitting, $g$ factors and hyperfine structure constants) and the local structure of the trigonal Mn$^{4+}$ center will be useful to understand the optical properties of uranium-doped LiF, theoretical investigations are significant. In this paper, a defect model for the trigonal Mn$^{4+}$ center is proposed, and its EPR parameters are studied by using the perturbation formulas of the EPR parameters for a 3d$^3$ ion in trigonally distorted octahedra. The results are discussed.

2. Calculations

In LiF:U:Mn crystal, U$^{6+}$ substitutes the host Li$^+$ ion and the six neighbouring F$^-$ ions may be replaced by O$^{2-}$ ions for charge compensation [7]. As a result, [UO$_6$]$^{6-}$ complexes in LiF may have enough
net effective negative charge to compensate other impurity ions of high valency, such as Mn$^{4+}$. Obviously, the very large positive charge of the impurity Mn$^{4+}$ locating on the host Li$^+$ site can be cancelled by the extra negative charge arising from the three [UO$_6$]$^{6-}$ complexes at (1,1,0), (1,0,1) and (0,1,1) sites. Based on this defect model, the trigonal Mn$^{4+}$ center may be characterized as Mn$^{4+}$ associated with one host F$^-$ triangle, one O$^{2-}$ triangle, and an additional equivalent F$^{-}$ triangle containing the three U$^{6+}$ ions. In addition, the impurity Mn$^{4+}$ is expected to shift towards the O$^{2-}$ triangle by an amount $\Delta Z$ along the C$_3$ axis due to the stronger electrostatic attraction between the Mn$^{4+}$ and the O$^{2-}$ triangle (and also the additional equivalent F$^{-}$ triangle) compared with that between the Mn$^{4+}$ and the host F$^-$ triangle. This displacement $\Delta Z$ may lead to even larger trigonal distortion, corresponding to the considerable magnitude of the observed zero-field splitting $D$. Thus, the studied trigonal center can be described by an [MnF$_3$O$_3$F$'$_3]$^{8-}$ cluster and its axial displacement $\Delta Z$.

For a 3d$^3$ ion in trigonally distorted octahedra, the zero-field splitting $D$ and the anisotropic $g$ factors $g_\parallel$ and $g_\perp$ can be calculated from the high-order perturbation formulas based on the strong-field scheme [8, 9]. Similarly, the perturbation formulas for the hyperfine structure constants $A_\parallel$ and $A_\perp$ can be derived. These formulas are [note: since the studied system has weak covalency and a much smaller spin-orbit coupling coefficient of the ligand (i.e., F$^-$ or O$^{2-}$) than that of the central Mn$^{4+}$ ion, the conventional one-spin-orbit-coupling-coefficient formulas are adopted here]:

$$D = \frac{2}{9} \xi^2 V \left( \frac{1}{E_1^2} - \frac{1}{E_3^2} \right) - \sqrt{2} \xi^2 V' \left[ \frac{2}{3E_1 E_4} + \frac{1}{E_2 E_3} \right] + \frac{1}{3E_3 E_4} + \frac{1}{E_2 E_4} + \frac{4\sqrt{2}B}{E_1 E_2 E_3 E_4} + \frac{4B}{E_2 E_3} + \frac{9B}{2E_2 E_3},$$

$$g_\parallel = g_\perp = \frac{8\xi k}{3E_1} - \frac{2\xi^2(k + g_s)}{3E_2} + \frac{4\xi^2(k - 2g_s)}{9E_3} + \frac{8\xi^2(k - 2g_s)}{9E_3^2} + \frac{4\xi^2 k}{3E_1 E_2} + \frac{4\xi^2 k}{9E_1 E_3} + \frac{4\xi^2 k}{3E_2 E_3} + \frac{8\xi k V}{9E_3^2} + \frac{8\sqrt{2}k V'}{3E_1 E_4},$$

$$A_\parallel = P \left[ -\frac{8\xi k}{3E_1} - \frac{2\xi^2(k + g_s)}{3E_2} + \frac{4\xi^2(k - 2g_s)}{9E_3^2} + \frac{8\xi^2(k - 2g_s)}{9E_3^2} + \frac{4\xi^2 k}{3E_1 E_2} + \frac{4\xi^2 k}{9E_1 E_3} + \frac{4\xi^2 k}{3E_2 E_3} + \frac{8\xi k V}{9E_3^2} + \frac{8\sqrt{2}k V'}{3E_1 E_4} - \kappa \right],$$

$$A_\perp = P \left[ -\frac{8\xi k}{3E_1} - \frac{2\xi^2(k + g_s)}{3E_2} + \frac{4\xi^2(k - 2g_s)}{9E_3^2} + \frac{8\xi^2(k - 2g_s)}{9E_3^2} + \frac{4\xi^2 k}{3E_1 E_2} + \frac{4\xi^2 k}{9E_1 E_3} + \frac{4\xi^2 k}{3E_2 E_3} + \frac{8\xi k V}{9E_3^2} + \frac{8\sqrt{2}k V'}{3E_1 E_4} - \kappa \right].$$

where $E_i$ are the zero-order energy denominators defined in [8, 9], with the cubic field parameter $D_{03}$ and the Racah parameters $B$ and $C$ for the 3d$^3$ ion in the crystal. $\xi$ is the spin-orbit coupling coefficient of the 3d$^3$ ion in the crystal. $k$ is the orbital reduction factor. $P$ is the dipole hyperfine structure parameter of the 3d$^3$ ion in the crystal. $\kappa$ is the core polarization constant.

From the superposition model [10] and the local geometrical relation for the [MnF$_3$O$_3$F$'$_3]$^{8-}$ cluster in LiF, the trigonal field parameters $V$ and $V'$ in (1) can be written as

$$V = \sum_L \left[ \frac{9}{7} A_2(L) \left( \frac{R}{R_L} \right)^{12} (3\cos^2 \beta_L - 1) + \frac{20}{21} A_4(L) \left( \frac{R}{R_L} \right)^{14} (35\cos^4 \beta_L - 30\cos^2 \beta_L) + 3 \right]$$

$$+ \frac{20\sqrt{2}}{3} A_4(L) \left( \frac{R}{R_L} \right)^{14} \sin^3 \beta_L \cos \beta_L],$$

$$V' = \sum_L \left[ -\frac{3}{7} A_2(L) \left( \frac{R}{R_L} \right)^{12} (3\cos^2 \beta_L - 1) + \frac{5\sqrt{2}}{21} \cdot A_4(L) \left( \frac{R}{R_L} \right)^{14} (35\cos^4 \beta_L - 30\cos^2 \beta_L) + 3 \right]$$

$$+ \frac{10}{3} A_4(R) \left( \frac{R}{R_L} \right)^{14} \sin^3 \beta_L \cos \beta_L],$$

where the sum is taken over three kinds of ligands $L$ (i.e., F$^-$, O$^{2-}$ and equivalent F$^-$). $t_2$ and $t_4$ are the power-law exponents, and we take $t_2 \approx 3$ and $t_4 \approx 5$ due to the ionic nature of the bonds [10]. $A_2(L)$ and $A_4(L)$ are the intrinsic parameters for the ligand $L$. 

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RL and $\beta_L$ are, respectively, the impurity-ligand distance and the corresponding angle related to the $C_3$ axis for the ligand $L$. $R_L$ is the reference bonding length or the effective impurity-ligand distance for all the ligands. Since the ionic radius $r_i$ of the impurity Mn$^{3+}$ is different from the radius $r_h$ of the host Li$^+$, the distance $R_L$ may be unlike the host Li$^+$-F$^-$ bonding length $R_H(\approx 2.0086\ \text{Å}[11])$ in the pure crystal. However, we can reasonably estimate $R$ from the following empirical formula $[12, 13]$

$$R \approx R_H + (r_i - r_h)/2. \quad (3)$$

For the studied Mn$^{4+}$ center in LiF, $r_i \approx 0.60\ \text{Å}$ and $r_h \approx 0.68\ \text{Å}[14]$, thus the distance $R \approx 1.9686\ \text{Å}$ can be obtained. When considering the displacement of the impurity Mn$^{3+}$ along the $C_3$ axis, the above local bonding length $R_L$ and the angle $\beta_L$ for the ligand $L$ can be calculated from $R$ and $\Delta Z$. For $3d^a$ ions in octahedra, $\Delta d(L)$ can be expressed in terms of the cubic field parameter for the Mn$^{4+}$-L cluster as $\Delta d(L) \approx (3/4)D_q(Mn^{4+}-L) [10]$. $\Delta d(L) \approx (9 \sim 12)\Delta d(L)$ for $3d^a$ ions in many crystals $[15, 16]$, and we take $\Delta d(L) \approx 12\Delta d(L)$ here.

For Mn$^{4+}$ in LiF crystal, to our knowledge no optical spectral data were reported. However, the optical spectra of the similar [MnO$_6$]$^{8-}$ cluster in Al$_2$O$_3$:Mn$^{4+}$ crystal yield the spectral parameters $D_q$(Mn$^{4+}$-O$^2-$) $\approx 2170\ \text{cm}^{-1}$, $B$ (Mn$^{4+}$-O$^2-$) $\approx 900\ \text{cm}^{-1}$ and $C$ (Mn$^{4+}$-O$^2-$) $\approx 2800\ \text{cm}^{-1}$ $[17]$. The spectral parameters for the [MnF$_6$]$^{2-}$ cluster can be obtained from those of the isoelectronic [CrF$_6$]$^{3-}$ cluster in KMgF$_3$:Cr$^{3+}$ and the [Cr$_3$O$_6$]$^{9-}$ cluster in Al$_2$O$_3$:Cr$^{3+}$ by the approximation relationship

$$\frac{Q(Mn^{4+}-F^-)}{Q(Mn^{4+}-O^2-)} \approx \frac{Q(Cr^{3+}-F^-)}{Q(Cr^{3+}-O^2-)} \quad (4)$$

where $Q$ denote $D_q$, $B$ and $C$. From $D_q$(Cr$^{3+}$-F$^-$) $\approx 1550\ \text{cm}^{-1}$, $B$ (Cr$^{3+}$-F$^-$) $\approx 815\ \text{cm}^{-1}$, $C$ (Cr$^{3+}$-F$^-$) $\approx 2950\ \text{cm}^{-1}$ for KMgF$_3$:Cr$^{3+}$ $[18]$, and $D_q$(Cr$^{3+}$-O$^2-$) $\approx 1700\ \text{cm}^{-1}$, $B$ (Cr$^{3+}$-O$^2-$) $\approx 700\ \text{cm}^{-1}$ and $C$ (Cr$^{3+}$-O$^2-$) $\approx 2800\ \text{cm}^{-1}$ for Al$_2$O$_3$:Cr$^{3+}$ $[19]$, we have $D_q$(Mn$^{4+}$-F$^-$) $\approx 1980\ \text{cm}^{-1}$, $B$ (Mn$^{4+}$-F$^-$) $\approx 1050\ \text{cm}^{-1}$ and $C$ (Mn$^{4+}$-F$^-$) $\approx 2950\ \text{cm}^{-1}$ for the [MnF$_6$]$^{2-}$ cluster. Thus, the total or effective spectral parameters for the studied [MnF$_6$O$_3$F]$^{8-}$ cluster in (1) can be taken as the averages of those for O$^{2-}$ and F$^-$ ligands, i.e.,

$$D_q \approx 2075\ \text{cm}^{-1}, \ B \approx 975\ \text{cm}^{-1}, \ C \approx 2875\ \text{cm}^{-1}. \quad (5)$$

### Table 1. The EPR parameters of the trigonal Mn$^{4+}$ center in LiF:U:Mn crystal.

<table>
<thead>
<tr>
<th>$D$ ($\text{cm}^{-1}$)</th>
<th>$g_\parallel$</th>
<th>$g_\perp$</th>
<th>$A_0$ ($10^4\ \text{cm}^{-1}$)</th>
<th>$A_\perp$ ($10^4\ \text{cm}^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cal.$^a$ 0.36</td>
<td>1.963</td>
<td>1.961</td>
<td>$-60.9 \sim -61.3$</td>
<td></td>
</tr>
<tr>
<td>Cal.$^b$ -2.21</td>
<td>1.960</td>
<td>1.971</td>
<td>$-64.5 \sim -62.8$</td>
<td></td>
</tr>
<tr>
<td>Expt. [6] -2.39 (20)$^c$</td>
<td>1.986 (5)</td>
<td>1.990 (5)</td>
<td>$-52.8 (5)^d \sim -68.4 (5)^d$</td>
<td></td>
</tr>
</tbody>
</table>

$^a$Calculated by neglecting the displacement $\Delta Z$, i.e., $\Delta Z = 0$. $^b$Calculated by considering the displacement $\Delta Z \approx 0.29\ \text{Å}$ towards the O$^2-$ triangle along the [111] axis. $^c$The negative sign of the experimental $D$ value is determined from the empirical relationship between $D$ and the anisotropy $\Delta g(=g_\parallel - g_\perp)$ $[22]$. $^d$The signs of the experimental values for $A$ factors were not given in [7]. The signs are determined from those of the observed $A$ values for Mn$^{4+}$ in various crystals $[21]$. From the free-ion parameters $B_0 \approx 1160\ \text{cm}^{-1}$ and $C_0 \approx 4303\ \text{cm}^{-1}$ for Mn$^{4+}$ $[20]$, we obtain the covalency factor $f \approx (B_0 + C_0)/2 \approx 0.754$ for the [MnF$_3$O$_3$F$'$]$^{8-}$ cluster. Then the orbital reduction factor $k$, the spin-orbit coupling coefficient $\zeta$ and the dipole hyperfine structure parameter $P$ can be expressed as

$$k \approx f/10, \ \zeta \approx k_0^0 P \approx kP_0, \quad (6)$$

where $\zeta_0^0 \approx 405\ \text{cm}^{-1}$ $[20]$ and $P_0 \approx 235 \times 10^{-4}\ \text{cm}^{-1}$ $[21]$ are the corresponding free-ion values.

The core polarization constant in the formulas of $A_\parallel$ and $A_\perp$ can be written as $[22]$

$$\kappa \approx -\frac{2\chi}{3(r^{-3})}, \quad (7)$$

where $\chi$ is characteristic of the density of unpaired spins at the nucleus of the central metal ion and $<r^{-3}>$ the expectation value of the inverse cube of the radial wavefunction of the 3d orbital $[22]$. By using the value $<r^{-3}> \approx 5.361$ a.u. $[22]$ for Mn$^{4+}$ and $\chi \approx -2.16$ a.u. $[21]$ for the similar Mn$^{4+}$-O$^2-$ pair in Al$_2$O$_3$:Mn$^{4+}$, we have $\kappa \approx 0.269$.

Substituting the above parameters into (1) and assuming that Mn$^{4+}$ locates on the ideal Li$^+$ site, we can calculate the EPR parameters for the trigonal Mn$^{4+}$ center in LiF. They are shown in Table 1. One can find that the above theoretical $D$ value is much smaller than the experimental one, suggesting that the estimated trigonal distortion is too small. This means that the impurity Mn$^{3+}$ may not occupy exactly the Li$^+$ position but shift towards the O$^2-$ triangle along the $C_3$ axis because of their strong electrostatic attraction.
increases the trigonal distortion and hence the calculated $D$ value. By fitting the calculated $D$ to the observed value, we obtain the displacement of the impurity Mn$^{4+}$ towards the O$^{2-}$ triangle along the $C_3$ axis, i.e.,

\[ \Delta Z \approx 0.29 \text{ Å} \quad (8) \]

The corresponding theoretical EPR parameters are also collected in Table 1.

3. Discussions

From Table 1, one can find that the calculated EPR parameters based on the displacement $\Delta Z$ are comparable with the observed values. Several points may be discussed here.

1. The positive sign of the estimated displacement $\Delta Z$ of the Mn$^{4+}$ agrees with the expectation based on the electrostatic interaction, suggesting that the direction of the displacement towards the O$^{2-}$ triangle is suitable. In fact, shifting towards the O$^{2-}$ triangle leads to a considerable increase in the theoretical $D$, which would be much smaller than the observed value in absence of the displacement $\Delta Z$. Meanwhile, the sign of the calculated $D$ is also reversed from positive to negative. Therefore, the sign of the experimental $D$ value is also determined.

2. The magnitude of $\Delta Z$ ($\approx 0.29$ Å) for the Mn$^{4+}$ in LiF obtained in this work is consistent with that of other impurities in LiF or similar AB-type crystal obtained in previous works [23–28]. For example, ENDOR measurements also found a similar off-center displacement $\Delta Z \approx 0.3$ Å along the [111] axis for Ti$^{3+}$ in LiF crystal [23]. In addition, Sangster et al. [24] obtained the displacements $\Delta Z \approx 0.21$, 0.21 Å, and 0.26 Å, respectively, along the [111] axis for the substitutional impurities Fe$^{2+}$, Co$^{2+}$, and Ni$^{2+}$ in SrO. Therefore, the large displacement $\Delta Z$ of the Mn$^{4+}$ along the [111] direction for the Mn$^{4+}$ center in this paper can be regarded as reasonable.

3. It can be seen from Table 1 that there is some discrepancy between theory and experiment, e.g., the calculated $g$ factors are smaller than the observed ones. This may be due to 1. the contribution to the $g$ factors from the spin-orbit coupling coefficient of the ligands and the admixture between the $d$ orbitals of the central ion and the $p$ orbitals of the ligands are not considered; 2. the contribution to the $g$ factors due to the charge-transfer (CT) effect is also ignored for the studied Mn$^{4+}$ center; 3. the displacements of the F$^-$ or O$^{2-}$ ligands are not included in the calculations. Among them, the contribution arising from the CT effect can be the most important one. For isoelectronic 3d$^x$ ions in crystals, since the energies of CT levels lower with increasing valence state [29], the contribution to the EPR parameters (especially $g$ factors) from the CT mechanism for the 3d$^x$ ion having a high valency (e.g., Mn$^{4+}$) may be important and cannot be ignored. This point remains to be further studied. Even so the above calculated displacement $\Delta Z$ is still valid because the zero-field splitting $D$ is much more sensitive to the trigonal distortion and hence to $\Delta Z$ than the $g$ or $A$ factor is.

In conclusion, the EPR parameters and the local structure for the Mn$^{4+}$ center in LiF:U:Mn crystal are theoretically investigated for the first time. The above studies may be useful for the understanding of the relationship between the defect structure and optical properties of uranium-doped LiF or other alkali fluorides.