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

Shao-Yi Wu[a,b], Wang-He Wei[a], and Hui-Ning Dong[b,c]

[a] Department of Applied Physics, University of Electronic Science and Technology of China, Chengdu 610054, P. R. China
[b] International Centre for Materials Physics, Chinese Academy of Sciences, Shenyang 110016, P. R. China
[c] College of Electronic Engineering, Chongqing University of Posts and Telecommunications, Chongqing 400065, P. R. China

Reprint requests to S.-Y. Wu; E-mail: wushaoyi@netease.com

Z. Naturforsch. **58a,** 672 – 676 (2003); received September 10, 2003

The local structure and the EPR parameters (zero-field splitting D, g factors $g_{\|}$ and $g_{\perp}$ and hyperfine structure constants $A_{\|}$ and $A_{\perp}$) 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 $[MnF_3O_3F'_3]^{8-}$ cluster. The central Mn^{4+} impurity is found to shift towards the oxygen triangle along the C_3 (or [111]) axis by an amount ΔZ (≈ 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 ΔZ 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 thermoluminiscence (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 (~ 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^- ligands may be replaced by O^{2-} ions for charge compensation [7]. As a result, $[UO_6]^{6-}$ complexes in LiF may have enough

0932–0784 / 03 / 1200–0672 $ 06.00

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 ΔZ 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 ΔZ 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 $[MnF_3O_3\,F'_3]^{8-}$ cluster and its axial displacement ΔZ.

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]:

$$D=\frac{2}{9}\zeta^2V\left(\frac{1}{E_1^2}-\frac{1}{E_3^2}\right)-\sqrt{2}\zeta^2V'\Big[\frac{2}{3E_1E_4}+\frac{1}{E_2E_3}+\frac{1}{3E_3E_4}+\frac{1}{E_2E_4}+\frac{4\sqrt{2}B}{E_1E_4E_5}+\frac{4B}{E_3E_4E_5}+\frac{9B}{2E_2^2E_3}\Big],$$

$$g_{\parallel}=g_s-\frac{8\zeta k}{3E_1}-\frac{2\zeta^2(k+g_s)}{3E_2^2}+\frac{4\zeta^2(k-2g_s)}{9E_3^2}+\frac{8\zeta^2(k-2g_s)}{9E_1^2}-\frac{4\zeta^2k}{3E_1E_2}+\frac{4\zeta^2k}{9E_1E_3}+\frac{4\zeta^2k}{3E_2E_3}+\frac{8\zeta kV}{9E_1^2}-\frac{8\sqrt{2}kV'}{3E_1E_4},$$

$$g_{\perp}=g_{\parallel}-\frac{4\zeta kV}{3E_1^2}+\frac{4\sqrt{2}\zeta kV'}{E_1E_4},$$

$$A_{\parallel}=P\Big[-\frac{8\zeta k}{3E_1^2}-\frac{2\zeta^2(k+g_s)}{3E_2^2}+\frac{4\zeta^2(k-2g_s)}{9E_3^2}+\frac{8\zeta^2(k-2g_s)}{9E_1^2}-\frac{4\zeta^2k}{3E_1E_2}+\frac{4\zeta^2k}{9E_1E_3}+\frac{4\zeta^2k}{3E_2E_3}+\frac{8\zeta kV}{9E_1^2}-\frac{8\sqrt{2}\zeta kV'}{3E_1E_4}-\kappa\Big],$$

$$A_{\perp}=P\Big[-\frac{8\zeta k}{3E_1^2}-\frac{2\zeta^2(k+g_s)}{3E_2^2}+\frac{4\zeta^2(k-2g_s)}{9E_3^2}+\frac{8\zeta^2(k-2g_s)}{9E_1^2}-\frac{4\zeta^2k}{3E_1E_2}+\frac{4\zeta^2k}{9E_1E_3}+\frac{4\zeta^2k}{3E_2E_3}-\frac{4\zeta kV}{9E_1^2}+\frac{4\sqrt{2}\zeta kV'}{3E_1E_4}-\kappa\Big], \qquad (1)$$

where E_i are the zero-order energy denominators defined in [8, 9], with the cubic field parameter D_q and the Racah parameters B and C for the $3d^3$ ion in the crystal. ζ 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. κ is the core polarization constant.

From the superposition model [10] and the local geometrical relation for the $[MnF_3O_3F'_3]^{8-}$ cluster in LiF, the trigonal field parameters V and V' in (1) can be written as

$$V=\sum_L\Big[\frac{9}{7}\bar{A}_2(L)\left(\frac{R}{R_L}\right)^{t2}(3\cos^2\beta_L-1)+\frac{20}{21}\bar{A}_4(L)\left(\frac{R}{R_L}\right)^{t4}(35\cos^4\beta_L-30\cos^2\beta_L+3)+\frac{20\sqrt{2}}{3}\bar{A}_4(L)\left(\frac{R}{R_L}\right)^{t4}\sin^3\beta_L\cos\beta_L\Big],$$

$$V'=\sum_L\Big[-\frac{3\sqrt{2}}{7}\bar{A}_2(L)\left(\frac{R}{R_L}\right)^{t2}(3\cos^2\beta_L-1)+\frac{5\sqrt{2}}{21}\cdot\bar{A}_4(L)\left(\frac{R}{R_L}\right)^{t4}(35\cos^4\beta_L-30\cos^2\beta_L+3)+\frac{10}{3}\bar{A}_4(R)\left(\frac{R}{R_L}\right)^{t4}\sin^3\beta_L\cos\beta_L\Big], \qquad (2)$$

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]. $\bar{A}_2(L)$ and $\bar{A}_4(L)$ are the intrinsic parameters for the ligand L.

R_L and β_L are, respectively, the impurity-ligand distance and the corresponding angle related to the C_3 axis for the ligand L. R 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^{4+} is different from the radius r_h of the host Li$^+$, the distance R may be unlike the host Li$^+$-F$^-$ bonding length $R_\mathrm{H}(\approx 2.0086$ Å [11]) in the pure crystal. However, we can reasonably estimate R from the following empirical formula [12, 13]

$$R \approx R_\mathrm{H} + (r_i - r_h)/2. \tag{3}$$

For the studied Mn^{4+} center in LiF, $r_i \approx 0.60$ Å and $r_h \approx 0.68$ Å [14], thus the distance $R \approx 1.9686$ Å can be obtained. When considering the displacement of the impurity Mn^{4+} along the C_3 axis, the above local bonding length R_L and the angle β_L for the ligand L can be calculated from R and ΔZ. For 3d^n ions in octahedra, $\bar{A}_4$(L) can be expressed in terms of the cubic field parameter for the Mn^{4+}-L cluster as $\bar{A}_4(\mathrm{L}) \approx (3/4)D_\mathrm{q}$(Mn^{4+}-L) [10]. $\bar{A}_2(\mathrm{L}) \approx (9 \sim 12)\bar{A}_4(\mathrm{L})$ for 3d^n ions in many crystals [15, 16], and we take $\bar{A}_2(\mathrm{L}) \approx 12\bar{A}_4(\mathrm{L})$ 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 cm^{-1}, B (Mn^{4+}-O^{2-}) $\approx$ 900 cm^{-1} and C (Mn^{4+}-O^{2-}) $\approx$ 2800 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 [CrO$_6$]$^{9-}$ cluster in Al$_2$O$_3$:Cr^{3+} by the approximation relationship

$$\frac{Q(\mathrm{Mn}^{4+}\text{-}\mathrm{F}^-)}{Q(\mathrm{Mn}^{4+}\text{-}\mathrm{O}^{2-})} \approx \frac{Q(\mathrm{Cr}^{3+}\text{-}\mathrm{F}^-)}{Q(\mathrm{Cr}^{3+}\text{-}\mathrm{O}^{2-})}, \tag{4}$$

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

$$D_\mathrm{q} \approx 2075\ \mathrm{cm}^{-1},\ B \approx 975\ \mathrm{cm}^{-1},\ C \approx 2875\ \mathrm{cm}^{-1}. \tag{5}$$

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

	D (cm^{-1})	$g_\parallel$	$g_\perp$	$A_\parallel$ (10^4 cm^{-1})	$A_\perp$ (10^4 cm^{-1})
Cal.[a]	0.36	1.963	1.961	−60.9	−61.3
Cal.[b]	−2.21	1.960	1.971	−64.5	−62.8
Expt. [6]	−2.39 (20)[c]	1.986 (5)	1.990 (5)	−52.8 (5)[d]	−68.4 (5)[d]

[a] Calculated by neglecting the displacement ΔZ, i. e., $\Delta Z = 0$. [b] Calculated by considering the displacement $\Delta Z \approx 0.29$ 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 $B_0 \approx 1160$ cm^{-1} and $C_0 \approx 4303$ cm^{-1} for Mn^{4+} [20], we obtain the covalency factor $f \approx (B/B_0 + C/C_0)/2 \approx 0.754$ for the [MnF$_3$O$_3$F'$_3$]$^{8-}$ cluster. Then the orbital reduction factor k, the spin-orbit coupling coefficient ζ and the dipole hyperfine structure parameter P can be expressed as

$$k \approx f^{1/2}, \quad \zeta \approx k_\mathrm{d}^0, \quad P \approx kP_0, \tag{6}$$

where $\zeta_\mathrm{d}^0 \approx 405$ cm^{-1} [20] and $P_0 \approx 235 \times 10^{-4}$ 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]

$$\kappa \approx -\frac{2\chi}{3\langle r^{-3}\rangle}, \tag{7}$$

where χ is characteristic of the density of unpaired spins at the nucleus of the central metal ion and $\langle r^{-3}\rangle$ the expectation value of the inverse cube of the radial wavefunction of the 3d orbital [22]. By using the value $\langle r^{-3}\rangle \approx 5.361$ 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^{4+} 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 ΔZ are comparable with the observed values. Several points may be discussed here.

1. The positive sign of the estimated displacement ΔZ 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 ΔZ. 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 ΔZ (≈ 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 $\Delta Z \approx 0.21$ Å, 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 ΔZ 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 $3d^n$ 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 $3d^n$ 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 ΔZ is still valid because the zero-field splitting D is much more sensitive to the trigonal distortion and hence to ΔZ 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.

[1] S. Ramos-Bernal, A. Negron-Mendoza, and E. Cruz-Zaragoza, Radiat. Phys. Chem. **57**, 735 (2000).

[2] Y. S. Horowitz, Thermoluminiscence and Thermoluminesscent Dosimetry, CRC Press, Boca Raton 1984.

[3] N. Suntharalingam, J. R. Cameron, E. Shuttleworth, M. West, and J. R. Fowler, Phys. Med. Biol. **13**, 97 (1967).

[4] W. Gellermann, J. Phys. Chem. Solids **52**, 249 (1991).

[5] V. V. Ter-Mikirtychev, J. Phys. Chem. Solids **58**, 893 (1997).

[6] T. Tsuboi, Nucl. Instr. and Meth. in Phys. B **166 – 167**, 804 (2000).

[7] V. Lupei and I. Voicu, J. Phys. Chem. Solids **37**, 1093 (1976).

[8] R. M. Macfarlane, Phys. Rev. B **1**, 989 (1970).

[9] R. M. Macfarlane, J. Chem Phys. **47**, 2066 (1970).

[10] D. J. Newman and B. Ng, Rep. Prog. Phys. **52**, 699 (1989).

[11] R. W. Wyckoff, Crystal Structure, Vol. 1, Interscience, New York 1951.

[12] Z. M. Li and W. L. Shuen, J. Phys. Chem. Solids **57**, 1073 (1996).

[13] S. Y. Wu and H. N. Dong, Z. Naturforsch. **58a**, 285 (2003).

[14] R. C. Weast, CRC Handbook of Chemistry and Physics, CRC Press, Boca Raton, 1989, F187.

[15] W. L. Yu, X. M. Zhang, L. X. Yang, and B. Q. Zen, Phys. Rev. B **50**, 6756 (1994).

[16] D. J. Newman, D. C. Pryce, and W. A. Runciman, Amer. Mineral. **63**, 1278 (1978).

[17] S. Geschwind, P. Kisliuk, M. P. Klein, J. P. Remeika, and D. L. Wood, Phys. Rev. **126**, 1684 (1962).

[18] N. S. Altshuler and A. L. Larinov, Opt. Spectrosc. **66**, 61 (1989).

[19] T. Kushida, J. Phys. Soc. Japan **21**, 1331 (1966).

[20] C. A. Morrison, Crystal Field for Transition Metal Ions in Laser Host Materials, Springer, Berlin 1992.

[21] B. R. McGarvey, J. Chem. Phys. **71**, 51 (1967).

[22] A. Abragam and B. Bleaney, Electron Paramagnetic Resonance of Transition Ions, Oxford University Press, London 1970.

[23] J. J. Davies, J. Phys. **C7**, 599 (1974).

[24] N. B. Manson and T. J. C. Hosea, Phys. Stat. Sol. **B146**, K153 (1988).

[25] M. J. L. Sangster and A. M. Stoneham, Phil. Mag. B **43**, 597 (1981).

[26] N. B. Manson and A. Edgar, Semicond. Insul. **3**, 209 (1978).

[27] A. Edgar, I. H. Brunskill, N. B. Manson, and Y. Haider, J. Phys. (Paris) **41**, C6 (1980).

[28] V. A. Krylov and L. S. Sochava, Sov. Phys. Solid State **21**, 1586 (1980).

[29] A. B. P. Lever, Inorganic Electronic Spectroscopy, Elsevier Science Publishers, Amsterdam 1984.