The EPR Zero-Field Splitting *D* and its Pressure and Temperature Dependence for Trigonal Mn^{2+} Centers in $[Zn(H_2O)_6](BF_4)_2$:Mn^{2+} Crystal

Hong-Gang Liu[a], Xiao-Xuan Wu[a,b,c], Wen-Chen Zheng[a,c], and Lv He[a]

[a] Department of Material Science, Sichuan University, Chengdu 610064, People's Republic of China
[b] Department of Physics, Civil Aviation Flying Institute of China, Guanghan 618307, People's Republic of China
[c] International Centre for Materials Physics, Chinese Academy of Sciences, Shenyang 110016, People's Republic of China

Reprint requests to W.-C. Z.; Fax: +86-28-85416050; E-mail: zhengwc1@163.com

Z. Naturforsch. **61a,** 289 – 292 (2006); received February 21, 2006

The EPR zero-field splitting D $(= b_2^0)$ and its pressure and temperature dependence for trigonal Mn^{2+} centers in low and room temperature phases in $[Zn(H_2O)_6](BF_4)_2:Mn^{2+}$ crystal are studied by a high-order perturbation formula based on the dominant spin-orbit coupling mechanism. From the studies, the local trigonal distortion angles, the local angular compressibilities and the local angular thermal expansion coefficients for Mn^{2+} centers in both phases of the $[Zn(H_2O)_6](BF_4)_2$ crystal are estimated. The results are discussed.

Key words: Electron Paramagnetic Resonance; Crystal- and Ligand-Field Theory; Defect Structure and Properties; Mn^{2+}; $[Zn(H_2O)_6](BF_4)_2$.

1. Introduction

Crystals of $[Zn(H_2O)_6](BF_4)_2$ and its isomorphous compounds doped with bivalent $3d^n$ ions have attracted great interest because: (i) there are several phase transitions induced by weak orientation interaction forces in these crystals [1, 2]; (ii) these crystals have unusual properties caused by bivalent impurity ions arranged in the form of chains weakly linked to each other [3]; (iii) they are very compressible and can serve as model objects in studies at high pressure [4, 5]. So, many EPR spectra for bivalent $3d^n$ ions (e. g., Mn^{2+}, Ni^{2+} and Co^{2+}) in these crystals have been measured [4 – 8]. Among them, Neilo et al. [5] studied experimentally the zero-field splitting $D(= b_2^0$ in the spin Hamiltonian in [5]) and the effect of hydrostatic pressure and temperature on D for Mn^{2+} at the trigonally octahedral Zn^{2+} site of $[Zn(H_2O)_6](BF_4)_2$ crystal. In these studies it is found that $[Zn(H_2O)_6](BF_4)_2:Mn^{2+}$ undergoes a second-order phase transition at $T \approx 196$ K, and the splitting D and its pressure and temperature dependences at the room and low temperature phases are different. Since the zero-field splitting D of a $3d^5$ ion in crystals is sensitive to its immediate environment [here it is the $(H_2O)_6$ octahedron surrounding the Mn^{2+} ion], these differences are related to the structure changes of the host crystal. Detailed structural data of $[Zn(H_2O)_6](BF_4)_2$ (in particular, the atomic position parameters and hence the trigonal distortion angle in the $[Zn(H_2O)_6]^{2+}$ octahedron) were not reported. In fact, even if detailed structural data of the host $[Zn(H_2O)_6](BF_4)_2$ crystal are known, the local structural data of the impurity centers in doped crystals may be unlike the corresponding data in the host crystal because of the impurity-induced local lattice relaxation. No theoretical studies for the splitting D and its pressure and temperature dependence related to the local structure of the trigonal Mn^{2+} center in $[Zn(H_2O)_6](BF_4)_2:Mn^{2+}$ were made. In this paper, we calculate the zero-field splitting D and its pressure and temperature dependence for Mn^{2+} in $[Zn(H_2O)_6](BF_4)_2:Mn^{2+}$ crystal by a high-order perturbation formula based on the dominant spin-orbit coupling mechanism. From the calculations, the local trigonal distortion angles, the local angular compressibilities and the local angular thermal expansion coefficients of $[Mn(H_2O)_6]^{2+}$ centers in $[Zn(H_2O)_6](BF_4)_2:Mn^{2+}$ crystal are estimated. The results are discussed.

0932–0784 / 06 / 0500–0289 \$ 06.00

2. Calculations

The $[Mn(H_2O)_6]^{2+}$ impurity center in $[Zn(H_2O)_6](BF_4)_2:Mn^{2+}$ crystal is a trigonally distorted (the point symmetry is approximately D_{3d}) octahedron [5]. The $Mn^{2+}(3d^5)$ ion is a ^6S state ion. Because of the lack of the orbital angular momentum in the ^6S ground state, the microscopic origin of the zero-field splitting D of the ^6S state ion in crystals is complex. Several mechanisms can contribute to the zero-field splitting [9–11]. Among them, the spin-orbit coupling mechanism is believed to be dominant [9, 11]. According to this mechanism, the high- (fourth- and sixth-) order perturbation formula of the zero-field splitting D for $3d^5$ ions in trigonal symmetry can be written as [12]:

$$
\begin{aligned}
D &= D^{(4)} + D^{(6)},\\
D^{(4)} &= 3\zeta^2(-B_{20}^2 - 21\zeta B_{20})/(70P'^2D') + \zeta^2(-10B_{40}^2 + 7B_{43}^2)/(126P'^2G),\\
D^{(6)} &= -B_{20}^2\zeta^2[175B_{43}^2 + 2(24B_{20} - 25B_{40})^2]/(360150P'^2D'^2F) - 9\zeta^2B_{20}^4/(2450P'^3D'^2)\\
&\quad - B_{20}^2\zeta^2(11B_{43}^2 + 10B_{40}^2)/(735P'^3D'G)\\
&\quad + \zeta^2\left[7B_{20}B_{43}^2(25B_{40} - 68B_{20}) + 10B_{20}B_{40}(B_{20} + B_{40})(24B_{20} - 25B_{40})\right]/36015P'^2D'FG\\
&\quad - 5\zeta^2(B_{40}^2 - 7B_{43}^2/10)(29B_{43}^2 + 10B_{40}^2)/(3969P'^3G^2)\\
&\quad + \zeta^2\left[-5(B_{40}^2 - 7B_{43}^2/10)(15B_{40}^2 - 14B_{43}^2) + 7B_{20}B_{43}^2(57B_{20} - 120B_{40})\right.\\
&\qquad \left. - 75B_{40}^2B_{20}(B_{20} + 2B_{40})\right]/(21609P'^2G^2F)
\end{aligned}
\tag{1}
$$

with

$$
\begin{aligned}
P' &= 7B + 7C, \quad D' = 17B + 5C,\\
G &= 10B + 5C, \quad F = 22B + 7C,
\end{aligned}
\tag{2}
$$

in which ζ denotes the spin-orbit coupling parameter. B and C stand for the Racah parameters. B_{kq} are the trigonal field parameters, which can be calculated from the superposition model [13]. These trigonal field parameters in the superposition model are given as:

$$
\begin{aligned}
B_{20} &= 6\bar{A}_2(R)(3\cos^2\theta - 1),\\
B_{40} &= 6\bar{A}_4(R)(35\cos^4\theta - 30\cos^2\theta + 3),\\
B_{43} &= -12\sqrt{35}\bar{A}_4(R)\sin^3\theta\cos\theta,
\end{aligned}
\tag{3}
$$

where the trigonal distortion angle θ stands for the angle between the metal-ligand bond and the C_3 axis in the impurity center. $\bar{A}_2(R)$ and $\bar{A}_4(R)$ are the intrinsic parameters. For $3d^n$ ions in an octahedral site we have $\bar{A}_4(R) = \frac{3}{4}Dq$ [9, 13], where Dq is the cubic field parameter. For the ratio $\bar{A}_2(R)/\bar{A}_4(R)$ between 9 and 12, obtained for the $3d^n$ ion in many crystals [14–16], we take the average value, i. e., $\bar{A}_2(R)/\bar{A}_4(R) \approx 10.5$.

Table 1. The optical spectral bands (in cm^{-1}) of some $Mn[(H_2O)_6]^{2+}$ octahedra in crystals.

		$^4T_{1a}$	$^4T_{2a}$	$^4A_1, {}^4E$	$^4T_{2b}$	^4E	$^4T_{1b}$
Calculation[a]		18976	22533	24300	28224	29970	32884
Experiment	I[b]	18690	22990	25000	27970	29850	32260
	II[c]	18870	22990	25000	28090	29850	31750

[a] Calculated by using the parameters B, C and Dq in (4).
[b] Obtained from $[Mn(H_2O)_6](ClO_4)_2$ crystal [17].
[c] Obtained from $Mn[SiF_6]\cdot 6H_2O$ crystal [17].

The parameters B, C and Dq can be obtained from the optical spectra of the studied system. Since the optical spectra of $[Zn(H_2O)_6](BF_4)_2:Mn^{2+}$ were not reported, we estimate these parameters from the optical spectra of similar $[Mn(H_2O)_6]^{2+}$ octahedra in other crystals. The optical spectra of $[Mn(H_2O)_6]^{2+}$ octahedra in crystals, e. g., in $[Mn(H_2O)_6](ClO_4)_2$ (the isomorphous compounds of $[Zn(H_2O)_6](BF_4)_2$ [17]) and $Mn[SiF_6]\cdot 6H_2O$ [17] are very close to each other (see Table 1). From these optical spectra, we obtain

$$
B \approx 810\ \mathrm{cm}^{-1},\ C \approx 3240\ \mathrm{cm}^{-1},\ Dq \approx 750\ \mathrm{cm}^{-1}. \tag{4}
$$

A comparison between the calculated and experimental optical spectra is shown in Table 1. Obviously, these parameters can be used to the case of $[Mn(H_2O)_6]^{2+}$ octahedra in $[Zn(H_2O)_6](BF_4)_2$ crystal. The spin-orbit coupling parameters ζ in the crystal can be estimated by the formula [12] $\zeta = N^2\zeta_0$, where $N^2[\approx(\sqrt{B/B_0} + \sqrt{C/C_0})/2]$ is the average covalence reduction factor, and ζ_0, B_0 and C_0 are the corresponding parameters of the free $3d^n$ ion. For the free Mn^{2+} ion [18], we have $B_0 \approx 960\ \mathrm{cm}^{-1}$, $C_0 \approx 3325\ \mathrm{cm}^{-1}$ and $\zeta_0 \approx 347\ \mathrm{cm}^{-1}$. Thus, for $[Zn(H_2O)_6](BF_4)_2:Mn^{2+}$, we have $\zeta \approx 330\ \mathrm{cm}^{-1}$.

Table 2. The zero-field splitting D and its pressure (P) and temperature (T) dependence for Mn^{2+} in $[Zn(H_2O)_6](BF_4)_2$ crystal.

T (K)	D (10^{-4} cm^{-1})		$\Delta D/P$ (10^{-4} cm^{-1}/kbar)		$\Delta D/T$ (10^{-4} cm^{-1}/K)	
	Cal.	Expt. [5]	Cal.	Expt. [5]	Cal.	Expt. [5]
77	−140.5	−140.0(1)	4.3	4.3	−0.189	−0.189
293	−170.1	−170.1(1)	7.9	7.9	−0.113	−0.113

As has been said before, the angle θ_h in the host $[Zn(H_2O)_6](BF_4)_2$ crystal is not known, and the local angle θ in the $[Mn(H_2O)_6]^{2+}$ impurity center in $[Zn(H_2O)_6](BF_4)_2:Mn^{2+}$ crystal may be different from the host one, so we take the angle θ as an adjustable parameter. By calculating the splittings D at liquid nitrogen and room temperatures we obtain at $T \approx 77$ K

$$\theta \approx 52.94° \tag{5}$$

and at $T \approx 293$ K

$$\theta \approx 52.61°. \tag{6}$$

The calculated splittings D are compared with the observed values in Table 2. We find that the relative magnitude of the ratio $D^{(6)}/D^{(4)}$ is smaller than 5%, suggesting that the convergence of the used perturbation formula is good.

For $3d^n$ ions in crystals with small trigonal distortion [characterized by $(\theta-\theta_0)$, where $\theta_0 \approx 54.74°$, the corresponding angle in cubic symmetry], the zero-field splitting D can be expanded to first-order $(\theta-\theta_0)$ and $(R-R_0)$, [19]:

$$\begin{aligned} D &\approx D(R_0,\theta_0)+(R-R_0)(\frac{\partial D}{\partial R})_0+(\theta-\theta_0)(\frac{\partial D}{\partial \theta})_0 \\ &= (\theta-\theta_0)(\frac{\partial D}{\partial \theta})_0, \end{aligned} \tag{7}$$

in which the subscript 0 denotes the value in cubic symmetry [thus, $D(R_0,\theta_0)=(\frac{\partial D}{\partial R})_0=0$ in cubic symmetry]. So, the splitting D depends mainly on the trigonal distortion angle θ. For simplicity, in the following studies of the effects of pressure and temperature on the splitting D of $[Zn(H_2O)_6](BF_4)_2:Mn^{2+}$, we consider only the changes of θ with the pressure and temperature, i. e.,

$$\begin{aligned} \theta(P) &= \theta\left[1+\left(\frac{\mathrm{d}\ln\theta}{\mathrm{d}P}\right)P\right], \\ \theta(T) &= \theta\left[1+\left(\frac{\mathrm{d}\ln\theta}{\mathrm{d}T}\right)T\right], \end{aligned} \tag{8}$$

where $\mathrm{d}\ln\theta/\mathrm{d}P$ and $\mathrm{d}\ln\theta/\mathrm{d}T$ are the local angular compressibility and thermal expansion coefficient. Thus, by fitting the calculated pressure and temperature dependence of the zero-field splitting D (characterized by $\Delta D/\Delta P$ and $\Delta D/\Delta T$) to the observed values, we obtain for $[Zn(H_2O)_6](BF_4)_2:Mn^{2+}$ at $T \approx 77$ K

$$\begin{aligned} \mathrm{d}\ln\theta/\mathrm{d}P &\approx 9.5\cdot 10^{-4}/\text{kbar}, \\ \mathrm{d}\ln\theta/\mathrm{d}T &\approx -4.16\cdot 10^{-5}/\text{K} \end{aligned} \tag{9}$$

and at $T \approx 293$ K

$$\begin{aligned} \mathrm{d}\ln\theta/\mathrm{d}P &\approx 17.2\cdot 10^{-4}/\text{kbar}, \\ \mathrm{d}\ln\theta/\mathrm{d}T &\approx -2.24\cdot 10^{-5}/\text{K}. \end{aligned} \tag{10}$$

The calculated and experimental pressure and temperature dependences of the zero-field splitting D are also compared in Table 2.

3. Discussion

From the above calculations we find that for the $[Mn(H_2O)_6]^{2+}$ octahedron in the two phases of the $[Zn(H_2O)_6](BF_4)_2$ crystal the trigonal distortion angle $\theta < \theta_0$. That is to say, this octahedron is trigonally elongated. This is consistent with the fact that $\theta \approx 51.82° < \theta_0$ in the $[Hg(H_2O)_6]^{2+}$ octahedron in the pure and isomorphous compound $[Hg(H_2O)_6](ClO_4)_2$ [20]. In addition, for $3d^n$ ions in the trigonal octahedron we have [21]

$$\begin{aligned} \Delta g = g_{\parallel}-g_{\perp} &\approx (\theta-\theta_0)\left(\frac{\partial \Delta g}{\partial \theta}\right)_0 \\ &\approx -3\sqrt{2}(\theta-\theta_0)F_{44}, \end{aligned} \tag{11}$$

where F_{44} is the spin-lattice coupling coefficient in cubic symmetry. Since for $3d^7$ ions in octahedra, $F_{44} > 0$, e. g., Co^{2+} in MgO, $F_{44} \approx 10$ [22], from the $\Delta g(\approx 2.249) > 0$ obtained for $[Zn(H_2O)_6](BF_4)_2:Co^{2+}$ [6], it can be found that $\theta < \theta_0$ for the $[Co(H_2O)_6]^{2+}$ octahedron, another $3d^n$ impurity center, in $[Zn(H_2O)_6](BF_4)_2$. So, we suggest that in the host $[Zn(H_2O)_6](BF_4)_2$ crystal the $[Zn(H_2O)_6]^{2+}$ octahedron may be trigonally elongated (i. e., $\theta < \theta_0$). This point remains to be checked by a more detailed X-ray diffraction experiment. (Note: for Mn^{2+} the lack of the orbital momentum in the ^6S ground state makes the g factors of Mn^{2+} in crystals a little different from the free-electron value $g_e \approx$

2.0023. So, the g factors and the anisotropy Δg are insensitive to the local structure in crystals doped with Mn^{2+}. In the $[Zn(H_2O)_6](BF_4)_2:Mn^{2+}$ crystal [5], $g_\parallel \approx g_\perp \approx 2.001(1)$, so (11) can not be used here.)

The compressibility and thermal expansion coefficient for the same compound are different from phase to phase. So, the local angular compressibility and local thermal expansion coefficient of the impurity center in different phases in a crystal should be unlike. The above calculations for Mn^{2+} centers in low and room temperature phases of $[Zn(H_2O)_6](BF_4)_2$ confirm this point.

The positive local angular compressibility and the negative local angular thermal expansion coefficient for Mn^{2+} in both phases of $[Zn(H_2O)_6](BF_4)_2$ suggest that, when the volume of the $[Mn(H_2O)_6]^{2+}$ octahedron decreases owing to an increase in pressure or a decrease in temperature, the trigonal distortion angle θ increases. So, these compressibilities and thermal expansion coefficients are physically reasonable. It should be pointed out that the temperature dependence of the zero-field splitting D results from both the implicit, or static, contribution due to the lattice thermal expansion and the explicit, or vibrational, contribution due to the electron-phonon interaction [23 – 26]. In the above calculation of the temperature dependence of splitting D, for simplicity the vibrational contribution is neglected. So, there may be small errors in the above local angular thermal expansion coefficients.

Acknowledgements

This project was supported by the CAAC Scientific Research Base of Civil Aviation Flight Technology and Safety.

[1] M. A. White and M. Palk, J. Chem. Phys. **84**, 3484 (1986).
[2] E. Mikuli, A. Migdal-Mikuli, and S. Wrobel, Z. Naturforsch. **54a**, 225 (1999).
[3] S. Ghosh, M. Makherjee, A. Seal, and S. Ray, Acta Crystallogr. B **53**, 639 (1997).
[4] I. M. Krygin, A. A. Prokhorov, G. N. Neilo, and A. D. Prokhorov, Phys. Solid State **45**, 2242 (2001).
[5] G. N. Neilo, A. A. Prokhorov, and A. D. Prokhorov, Phys. Solid State **42**, 1134 (2000).
[6] G. N. Neilo, A. A. Prokhorov, S. N. Lykin, A. S. Karhachev, and A. D. Prokhorov, Phys. Status Solidi B **236**, 640 (2003).
[7] W. Sano, J. B. Domiciano, and J. A. Ochi, Phys. Rev. B **50**, 2958 (1994).
[8] V. K. Jain, Z. Naturforsch. **35a**, 1304 (1980).
[9] W. L. Yu and M. G. Zhao, Phys. Rev. B **37**, 9254 (1988).
[10] V. K. Jain and G. Lehmann, Phys. Status Solidi B **159**, 459 (1990).
[11] R. R. Sharma, Phys. Rev. **176**, 476 (1968).
[12] W. L. Yu, M. G. Zhao, and Z. Q. Lin, J. Phys. C **18**, 1857 (1985).
[13] D. J. Newman and N. Betty, Rep. Prog. Phys. **52**, 699 (1989).
[14] A. Edgar, J. Phys. C **9**, 4304 (1976).
[15] C. Rudowicz and Y. Y. Zhou, J. Magn. Magn. Mater. **111**, 153 (1992).
[16] T. H. Yeom, S. H. Choh, M. L. Du, and M. S. Tang, Phys. Rev. B **53**, 3415 (1996).
[17] L. L. Lohr Jr. and D. S. McCluer, J. Chem. Phys. **49**, 3516 (1968).
[18] J. S. Griffith, The Theory of Transition-Metal Ions, Cambridge University Press, London 1964.
[19] W. C. Zheng, Solid State Commun. **94**, 317 (1995).
[20] G. Johansson and M. Sandstorm, Acta Chem. Scand. A **32**, 109 (1978).
[21] W. C. Zheng and S. Y. Wu, Physica B **307**, 28 (2001).
[22] E. B. Tucker, Phys. Rev. **143**, 264 (1966).
[23] W. M. Walsh Jr., Phys. Rev. **114**, 1473 (1959).
[24] K. N. Schrivastava, Phys. Rep. **20**, 137 (1975).
[25] W. C. Zheng and S. Y. Wu, Phys. Rev. B **54**, 1117 (1996).
[26] S. V. Bhat, V. Dhar, and R. Sirhivasan, Indian J. Pure Appl. Phys. **21**, 516 (1983).