Physica B 438 (2014) 127–130

Contents lists available at ScienceDirect

Physica B

journal homepage: www.elsevier.com/locate/physb

On the ground-state splitting, fine structure of multiplets and EPR spectrum of Ni^{2+} doped in MgF_2 crystal with orthorhombic site symmetry

Wang Fang [a,*], Xun Xiang [a], Heng-Jie Chen [a], Wen-Chen Zheng [b,c], Hai-Yan Tang [a]

[a] *Department of Mathematics and Physics, Chongqing University of Science and Technology, Chongqing 401331, People's Republic of China*
[b] *Department of Material Science, Sichuan University, Chengdu 610064, People's Republic of China*
[c] *International Centre for Materials Physics, Chinese Academy of Sciences, Shenyang 110016, People's Republic of China*

ARTICLE INFO

Article history:
Received 15 November 2013
Received in revised form
27 December 2013
Accepted 30 December 2013
Available online 9 January 2014

Keywords:
Ground-state splitting
Fine structure of multiplets
D_{2h} site symmetry
Defect structure

ABSTRACT

The 45 × 45 complete energy matrix for $3d^8$ ion at D_{2h} site symmetry is used to calculate and assign the ground-state splitting and the fine structure of the multiplets of $Ni^{2+}(3d^8)$ doped in MgF_2 crystal with rutile type structure by the complete diagonalizaton method (CDM) in the frame of semi-empirical molecular orbital (MO) scheme in the strong crystal field (CF) approximation. In the calculation, all the configuration interactions though the cubic CF part, low-symmetry component (tetragonal and orthorhombic parts), Coulomb interaction and the spin–orbit coupling (SOC) interaction (both of the central ion and the liangds) are taken into account completely. The calculated results are in good agreement with the experimental data. In addition, the ground-state splitting is also calculated by the high-order perturbation method (PTM), together with the electron paramagnetic resonance (EPR) parameters D, E and g-factors (g_x, g_y and g_z). The results of the spin–orbit splitting of the ground state calculated by CDM and PTM are not only close to each other, but also in good agreement with the observed data. The relationship between crystalline parameters and the fine structure of multiplets and EPR spectrum is established and the local defect structure is determined.

1. Introduction

Ni^{2+}-doped crystals have been attracting a great deal of attention [1–10] because of their potential applications in tunable solid-state lasers [1–6 and the references therein] and in upconversion luminescent materials [7–8 and the references therein]. Decades ago tunable laser generation was obtained for Ni^{2+}-doped MgF_2 crystal [1], since then, optical properties of Ni^{2+}-doped MgF_2 crystal have been investigated extensively by many authors [2–4,9,10]. In this paper, theoretical investigations of the ground-state splitting [9,10], the fine structure of multiplets [9] and EPR parameters of the Ni^{2+} doped in MgF_2 crystal are performed. When the divalent Ni^{2+} ion is doped into MgF_2 crystal, it will substitute for the divalent Mg^{2+} ion and be coordinated by six F^- ions to form D_{2h} site symmetry (Fig. 1) [9]. The ground state of the cubic term $^3A_{2g}$ will split further by the combined action of the SOC interaction and the orthorhombic component of crystal field, and the spin–orbit components of the split ground state $^3A_{2g}$ are A_g, B_{2g} and B_{2g} which can be judged from the group theory [10]. Obviously, to study the ground-state splitting and the fine structure of multiplets of the Ni^{2+}, it is necessary to take the combined action of the SOC interaction and the orthorhombic crystal field into account simultaneously, besides the conventional cubic and tetragonal crystal field part and the electrostatic Coulomb interaction [11], which have not been reported, yet. In this paper, 45 × 45 complete energy matrix for $3d^8$ configuration is constructed, in which the low-symmetry component (tetragonal and orthorhombic parts), the SOC interaction (of both the central ion and the ligands), the Coulomb interaction and the cubic crystal field part are taken into account completely. The 45 × 45 energy matrix is applied to calculate and assign the ground-state splitting and the fine structure of the multiplets of Ni^{2+} by the CDM. Furthermore, we also carry out a calculation of the ground-state splitting by the high-order PTM, together with the EPR parameters D, E and g-factors (g_x, g_y and g_z) at the same time. The results are discussed.

2. Calculation

To carry out a theoretical study of the fine structure of multiplets and EPR parameters of the transition metal at the D_{2h} site symmetry as Ni^{2+} ion doped in MgF_2 conveniently, a new coordinate symmetry different from the conventional one is needed. In the conventional coordinate symmetry, the in-plane symmetry axes are chosen to be in coincide with transition-metal ion site-ligand axes [11], while for

---

[*] Corresponding author. Tel.: +86 23 6502 3914.
E-mail address: mailfangwang@163.com (W. Fang).

0921-4526/$ - see front matter © 2014 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.physb.2013.12.047

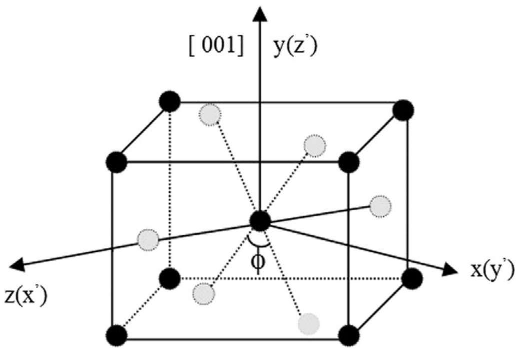

Fig. 1. Rutile-type crystal structure of MgF_2. ● for Mg^{2+} ion and ○ for F^- ion.

the Ni^{2+} at the D_{2h} site symmetry, the axes x and y are chosen to bisect the central-ion-ligand, as shown in Fig. 1. This coordinate symmetry is obtained by a 45° rotation around the Z axis from the conventional undistorted octahedral coordinate axes [9] and the method to construct new wave functions in this new coordinate symmetry and to calculate the CF parameters has been discussed in previously published paper [12,13]. The total Hamiltonian for transition-metal ion at this D_{2h} site symmetry is [14,15]

$$\hat{H}=\hat{H}_1(10Dq)+\hat{H}_2(B,C)+\hat{H}_3(Ds,Dt,D\xi,D\eta)+\hat{H}_4(\zeta,\zeta'), \tag{1}$$

in which $\hat{H}_1(10Dq)$ is the cubic CF, $\hat{H}_2(B,C)$ is the electrostatic Coulomb interaction term, B and C are the Racah parameters in crystal, $\hat{H}_3(Ds,Dt,D\xi,D\eta)$ is the lower CF part, $\hat{H}_4(\zeta,\zeta')$ is the SOC term, respectively. To construct the secular energy matrix of the Hamiltonian in Eq. (1) for $3d^8$, the wave function of $3d^2$ ion in the cubic CF (taken to be zero-order unperturbed wavefunctions [13]) and the relation between the matrix elements of the N-electron systems and their complementary states(10-N)-electron is used [11], namely, the energy matrix of the total Hamiltonian in Eq. (1) for d^8 ions are calculated from the energy matrix of the $3d^2$ ions by the complementary relation [11].

In the energy matrix, the tetragonal CF parameters Ds, Dt and orthorhombic components $D\xi$, $D\eta$ have been defined and discussed in previously published paper [12,13] using the superposition model [16,17], and have the following form

$$\begin{aligned}
Ds&=\frac{4}{7}\overline{A}_2(R_0)\left[\left(\frac{R_0}{R_1}\right)^{t_2}-\left(\frac{R_0}{R_2}\right)^{t_2}\right],\\
Dt&=-\frac{4}{21}\overline{A}_4(R_0)\left[3\left(\frac{R_0}{R_1}\right)^{t_4}+4\left(\frac{R_0}{R_2}\right)^{t_4}+7\cos 2\phi\left(\frac{R_0}{R_1}\right)^{t_4}\right],\\
D\xi&=-\frac{4}{7}\overline{A}_2(R_0)\cos\phi\left(\frac{R_0}{R_1}\right)^{t_2},\\
D\eta&=-\frac{20}{21}\overline{A}_4(R_0)\cos\phi\left(\frac{R_0}{R_1}\right)^{t_4},
\end{aligned} \tag{2}$$

where R_1 is the in-plane Ni^{2+}–F^- bond length (xy plane in Fig. 1), R_2 is the out-plane Ni^{2+}–F^- bond length(along [1 1 0] direction), ϕ bond angle (illustrated in Fig. 1), and the power-law $t_2\approx 3$ and $t_4\approx 5$ [17]. $\overline{A}_4(R_0)$ and $\overline{A}_2(R_0)$ in Eq. (2) are intrinsic parameters with reference distance R_0 which is usually taken as the mean value of R_i $(i=1, 2)$ [12,18], and are usually expressed as Ref. [16]

$$\overline{A}_n(R_0)=-\frac{eq\langle r^n\rangle}{R_0^{(n+1)}}S_n \tag{3}$$

where, $n=2$ or 4, $\langle r^n\rangle$ is the mean values of r^n for Ni^{2+} ion in crystal, $S_2=1/2$ and $S_4=1/8$, q is charge of the ligands, for F^-, q is taken to be $-e$ $(e>0)$ here. From Eq. (3), the relation

$$\frac{\overline{A}_2(R_0)}{\overline{A}_4(R_0)}=4R_0^2\frac{\langle r^2\rangle}{\langle r^4\rangle}, \tag{4}$$

can be where $\langle r^n\rangle$ and $\langle r^n\rangle_0$ $(n=2, 4)$ have following relation [19]

$$\frac{\langle r^2\rangle}{\langle r^2\rangle_0}=\left[\frac{\langle r^4\rangle}{\langle r^4\rangle_0}\right]^{1/2}, \tag{5}$$

where $\langle r^n\rangle_0$ are the values of radial averages for free ion. For Ni^{2+} ion, they can be calculated using Watson's SCF function [20], and have the following values [12],

$$\langle r^2\rangle_0=1.155\ \text{a.u.},\quad \langle r^4\rangle_0=3.134\ \text{a.u.} \tag{6}$$

For $3d^n$ ions in octahedral clusters, $\overline{A_4}(R_0)\approx 3/4Dq$ [21,22] and Dq is the cubic CF parameter. Obviously, if the Dq, bond distances R_1 and R_2, and bond angles ϕ are determined, we can calculate $\langle r^4\rangle$ from $Dq=-eq\langle r^4\rangle/6R_0^5$ and then $\langle r^2\rangle$ and $\overline{A_2}(R_0)$ from Eqs. (5) and (6) sequentially, and then Ds, Dt, $D\xi$, $D\eta$ in Eq. (2) can be obtained, finally.

The SOC parameters ζ, ζ' in the energy matrix have the following forms [11]

$$\begin{aligned}
\zeta&=(N_t^a)^{-1}[\zeta_d+(\lambda_\pi)^2\zeta_p/2],\\
\zeta'&=(N_t^aN_e^a)^{-1/2}[\zeta_d-\lambda_\pi\lambda_\sigma\zeta_p/2]
\end{aligned} \tag{7}$$

where ζ_d and ζ_p are the SOC parameters of the free $3d^n$ ion and the ligands, respectively. For Ni^{2+}, $\zeta_d\approx 649\ cm^{-1}$ [23] and for F^-, $\zeta_p\approx 220\ cm^{-1}$ [11]. The N_i^a, λ_i are liner combination of atomic orbits (LCAO) coefficients which are usually determined by Lohr approximation [24]

$$f_{i\gamma}=\frac{\int(\Psi_i^a)^2(e^2/r_{12})(\Psi_i^a)^2}{\int d_i^2(e^2/r_{12})d_i^2}, \tag{8}$$

and the expressions

$$\begin{aligned}
f_{e\gamma}&=(N_e^a)^{-2}[1-2\lambda_\sigma S_\sigma+(\lambda_\sigma S_\sigma)^2-2\lambda_sS_s+(\lambda_sS_s)^2],\\
f_{t\gamma}&=(N_t^a)^{-2}[1-2\lambda_\pi S_\pi+(\lambda_\pi S_\pi)^2],
\end{aligned} \tag{9}$$

can be obtained from Eq. (8) for the LCAO MO Ψ_i^a $(i=t$ and $e)$

$$\begin{aligned}
\psi_{\mathrm{t}}^a&=(N_t^a)^{-1/2}(\varphi_t-\lambda_\pi\chi_\pi),\\
\psi_{\mathrm{e}}^a&=(N_e^a)^{-1/2}(\varphi_e-\lambda_s\chi_s-\lambda_\sigma\chi_\sigma),
\end{aligned} \tag{10}$$

The approximate relation $f_{e\gamma}=f_{t\gamma}\approx((B/B_0)+(C/C_0))/2$ are often taken [25], where B_0 and C_0 are Racah parameters for free ion. For Ni^{2+} ion, $B_0=1030\ cm^{-1}$ and $C_0=4850\ cm^{-1}$ [11]. The LCAO normalization relations of the orbits in Eq. (10) are

$$\begin{aligned}
N_e^a&=[1-2\lambda_\sigma S_\sigma-2\lambda_sS_s+(\lambda_\sigma)^2+(\lambda_s)^2],\\
N_t^a&=1-2\lambda_\pi S_\pi+\lambda_\pi^2,
\end{aligned} \tag{11}$$

where the coefficients λ_s can be determined by $\lambda_s=cS_s$ and $A_s=(1/3)\lambda_s^2(A_{2s}^0/2S)$ [26], where A_s is superhyperfine constant and $A_{2s}^0=1.503\ cm^{-1}$ for F^- [27]. For Ni^{2+} ion coordinated by six ligands, $S=1$ for the ground state $^3A_{2g}$. The c is usually a constant for a given cluster [26], and for $[NiF_6]^{4-}$ the c is calculated to be 1.427 from the values of A_s [27] and S_s [28]. $S_s=\langle\phi_e|\chi_s\rangle$, $S_\sigma=\langle\phi_e|\chi_\sigma\rangle$, $S_\pi=\langle\phi_t|\chi_\pi\rangle$ are the group overlap integrals which can be calculated by the method given in Ref. [29]. Thus, the energy matrix can be constructed and the ground-state splitting and the fine structure of multiplets can be obtained by the CDM of the energy matrix.

In addition, the ground-state splitting can also be calculate by the PTM, together with the EPR parameters D, E and g-factors (g_x, g_y and g_z) by the high-order perturbation formulas derived previously [13]. In those formulas the orbital reduction factors k and k' are defined as Ref. [11]

$$k=(N_t^a)^{-1}[1-2\lambda_tS_\pi+(\lambda_\pi)^2/2],$$