Vol 11 No 9, September 2002
1009-1963/2002/11(09)/0940-04

Chinese Physics

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New expressions for g-factors of the mixed ground state of $3d^9$ ions with a compressional tetragonal symmetry and its application to NaCl:Ni^+(I)*

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(Received 24 October 2001; revised manuscript received 20 April 2002)

We deduce new expressions for g-factors of the $3d^9$ ions with a compressional tetragonal symmetry, in which we consider not only the contribution from the spin-orbit coupling of the central transition metal ion but also that of the ligand orbits as well as the admixture of $^2B_{1g}$ into $^2A_{1g}$ (ground state). By using the new formulae, the electron paramagnetic resonance g-factors for NaCl:Ni^+(I) are studied. Thus, the puzzle that the $g_\parallel$-shift is positive is reasonably explained.

Keywords: double spin-orbit coupling, NaCl:Ni^+(I), electron paramagnetic resonance g-factor
PACC: 7170C, 7630F

1. Introduction

Optical spectra, electromagnetic properties and electron paramagnetic resonance (EPR) parameters can be used in one of the important methods of studying the microstructure of materials. For example, recently some works[1−10] have investigated the relationships among optical spectra, EPR parameters D, E, g-factors and the microstructure of materials. In a tetragonal crystal field, the doublet $^2E_{2g}$ level of a $3d^9$ ion splits into two nondegenerate orbits: namely, $^2B_{1g}=|x^2-y^2\rangle$ and $^2A_{1g}=|3z^2-r^2\rangle$. When the site symmetry is compressional, the EPR $g_\parallel$-factors are smaller than those of the free electrons: namely, the $g_\parallel$-shift $\Delta g_\parallel = g_\parallel - g_e < 0$. The classical crystal field model, which considers only the contribution to the g-factor from the spin-orbit (SO) coupling of the central transition-metal (TM) ions, has given the expressions for the g-factors of the $3d^9$ clusters. For example, the theoretical formulae of EPR g-factors of the ground state $^2A_{1g}$ for the $3d^9$ clusters in the tetragonal crystal field are given by[11]

$$g_\parallel = g_e - 3\left(\frac{\zeta_d}{\Delta}\right)^2,$$

$$g_\perp = g_e - 6\frac{\zeta_d}{\Delta} - 6\left(\frac{\zeta_d}{\Delta}\right)^2. \qquad (1)$$

Here, $g_\parallel$ and $g_\perp$ are the parallel and perpendicular components to the tetragonal axis, respectively; $g_e(=2.0023)$ is the free spin g-value; ζ_d is the SO coupling parameter of d-electron of the $3d^9$ ion; Δ is the zero-order energy separation. It can be seen easily that formula (1) should give the result in which the sign of the $g_\parallel$-shift ($\Delta g_\parallel = g_\parallel - g_e$) is negative.

For NaCl:Ni^+(I), from the EPR spectra, Kuwabara[12] obtained that the sign of the $g_\parallel$-shift is positive (i.e. $\Delta g_\parallel = g_\parallel - g_e = 0.0457 > 0$). This result cannot be explained by formula (1). In this paper, we derive new expressions for g-factors of the $3d^9$ ions with a tetragonal symmetry, in which we consider not only the contribution from the SO coupling of the central TM ion but also that of ligand orbits as well as admixture of the $^2B_{1g}$ into $^2A_{1g}$ (ground state). By using the new formulae, we have studied the EPR g-factors for NaCl:Ni^+(I). The calculated results agree well with the experimental findings. Thus, the puzzle that the $g_\parallel$-shift is positive is reasonably explained.

2. Derivation of formulae

For a $3d^9$ cluster with a tetragonal crystal field, the Hamiltonian can be written as

$$\hat{H} = \hat{H}_0 + \hat{H}_{CF} + \hat{H}_{SO} + \hat{H}_{Ze} = \hat{H}_0 + \hat{H}', \qquad (2)$$

where $\hat{H}_0$ is the zero-order Hamiltonian, i.e. the electrostatic Coulomb term. $\hat{H}_{CF}$ is the tetragonal crystal

*Project supported by the Science Foundation of Sichuan Education Committee (Grant No 143).
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field potential. According to Misetich and Buch,[13] the SO coupling interaction Hamiltonian is given as

$$\hat{H}_{\rm SO} = (\beta e/mc)\left[\sum_i \zeta_c(r_{ic})\hat{l}_{ic}\cdot\hat{S}_i + \sum_{i,L}\zeta_L(r_{iL})\hat{l}_{iL}\cdot\hat{S}_i\right], \tag{3}$$

in which the two kinds of orbital angular momentum operators $\hat{l}_{ic}$ and $\hat{l}_{iL}$ of the ith electron about the central TM ion and the ligand ion L are comprised in this equation. However, the cross matrix elements ($\langle p_r|\hat{l}_{ic}|p_r\rangle$ and $\langle d_r|\hat{l}_{iL}|d_r\rangle$ etc, see the following Eq.(6)) can be neglected. The Zeeman interaction $\hat{H}_{\rm Ze}$ has the form

$$\hat{H}_{\rm Ze} = \mu_{\rm B}B\cdot(\hat{l} + g_{\rm e}\hat{S}). \tag{4}$$

In the compressional tetragonal crystal field, the ground state of the $3d^9$ ions is $^2A_{1g}$. When the $^2B_{1g}$ state admixes into $^2A_{1g}$, the ground state can be constructed in the following form

$$|\Psi_0\rangle = A|3z^2 - r^2\rangle + B|x^2 - y^2\rangle, \tag{5}$$

where A and B ($A^2 + B^2 = 1$) are the mixing coefficients.

In this paper, using the double SO coupling parameter model and considering a linear combination of atomic orbitals (LCAO) molecular orbit, the one-electron irreducible representation basic functions can be written as

$$|\Psi_\gamma\rangle = \sqrt{N_\gamma}(|d_\gamma\rangle - \lambda_\gamma|p_\gamma\rangle). \tag{6}$$

Here, $\gamma = t_{2g}$ or e_g denote the irreducible representation of the O_h group; N_γ and λ_γ are the normalization and mixing coefficients of molecular orbitals, respectively; $|d\rangle$ denotes the d-orbit function of the central TM ion; and $|p\rangle$ denotes the γ type symmetrical orbitals which are the total contributions from the ligands in the first layer and are constructed by these $|p\rangle$ orbits of the ligands. Solving the matrix expression for the perturbation Hamiltonian in Eq.(2), we have

$$g_\parallel = \frac{1}{\mu_{\rm B}B_z}\left[\left\langle\Gamma(0),\frac{1}{2}\middle|\hat{H}_{\rm eff}\middle|\Gamma(0),\frac{1}{2}\right\rangle - \left\langle\Gamma(0),-\frac{1}{2}\middle|\hat{H}_{\rm eff}\middle|\Gamma(0),-\frac{1}{2}\right\rangle\right], \tag{7a}$$

$$g_\perp = \frac{2}{\mu_{\rm B}B_{x(y)}}\left\langle\Gamma(0),\frac{1}{2}\middle|\hat{H}_{\rm eff}\middle|\Gamma(0),-\frac{1}{2}\right\rangle, \tag{7b}$$

where B_z and $B_{x(y)}$ denote the components of the z-direction and $x(y)$-direction of a magnetic field, respectively. $\Gamma(0)$ denotes the mixed ground-state wavefunction constructed from expressions (5) and (6), and $m_s = \pm 1/2$ are the spin quantum numbers. $\hat{H}_{\rm eff}$ denotes the effective perturbation Hamiltonian, and its first-order, second-order and third-order perturbation expressions are

$$\hat{H}^{(1)}_{\rm eff} = \hat{H}', \tag{8a}$$

$$\hat{H}^{(2)}_{\rm eff} = \sum_\alpha \frac{\hat{H}'|\Gamma(\alpha),m_s\rangle\langle\Gamma(\alpha),m_s|\hat{H}'}{\Delta E(\alpha)}, \tag{8b}$$

$$\hat{H}^{(3)}_{\rm eff} = \sum_{\alpha\beta} \frac{\hat{H}'|\Gamma(\alpha),m_s\rangle\langle\Gamma(\alpha),m_s|\hat{H}'|\Gamma(\beta),m_s\rangle\langle\Gamma(\beta),m_s|\hat{H}'}{\Delta E(\alpha)\Delta E(\beta)}, \tag{8c}$$

where $|\Gamma(\alpha),m_s\rangle$ and $|\Gamma(\beta),m_s\rangle$ denote the excited state wavefunctions, and $\Delta E(\alpha)$ and $\Delta E(\beta)$ are the energy separations between the excited state and the ground state, respectively. Then, using Eqs.(5)–(8) and a perturbation-loop method as well as considering all of the perturbation processes, the analytical perturbation formulae for the g-factors of the mixed ground state are obtained

$$\begin{aligned} g_\parallel =& g_{\rm e} + g_\parallel(\zeta_{\rm d}) + g_\parallel(\zeta_{\rm p}) + g_\parallel(\zeta_{\rm d},\zeta_{\rm p}) \\ =& g_{\rm e} - 8B^2\sqrt{N_tN_e}\left(1 - \frac{1}{2}\lambda_t\lambda_e\right)(\zeta^{te}_{\rm d} - \zeta^{te}_{\rm p})/\Delta E(b_{2g}) \\ & - 4B^2\sqrt{N_tN_e}\left(1 - \frac{1}{2}\lambda_t\lambda_e\right)(\zeta^t_{\rm d}\zeta^{te}_{\rm d} - \zeta^t_{\rm d}\zeta^{te}_{\rm p} + \zeta^{te}_{\rm d}\zeta^t_{\rm p} - \zeta^t_{\rm p}\zeta^{te}_{\rm p})/[\Delta E(e_{\rm g})\Delta E(b_{2g})] \\ & - (B^2 + 3A^2)N_t\left(1 + \frac{1}{2}\lambda_t^2\right)(\zeta^{te}_{\rm d} - \zeta^{te}_{\rm p})^2/[\Delta E(e_{\rm g})]^2, \end{aligned} \tag{9a}$$

$$
\begin{aligned}
g_\perp =& g_{\rm e} + g_\perp(\zeta_{\rm d}) + g_\perp(\zeta_{\rm p}) + g_\perp(\zeta_{\rm d},\zeta_{\rm p}) \\
=& g_{\rm e} - (2B^2+6A^2)\sqrt{N_tN_e}\left(1-\frac{1}{2}\lambda_t\lambda_e\right)(\zeta_{\rm d}^{te}-\zeta_{\rm p}^{te})/\Delta E(e_{\rm g}) \\
& - 2B^2\left[\sqrt{N_tN_e}\left(1-\frac{1}{2}\lambda_t\lambda_e\right)(\zeta_{\rm d}^{t}\zeta_{\rm d}^{te}-\zeta_{\rm d}^{t}\zeta_{\rm p}^{te}+\zeta_{\rm d}^{te}\zeta_{\rm p}^{t}-\zeta_{\rm p}^{t}\zeta_{\rm p}^{te})\right. \\
& \left. - N_t\left(1+\frac{1}{2}\lambda_t^2\right)(\zeta_{\rm d}^{te}-\zeta_{\rm p}^{te})^2\right]/[\Delta E(e_{\rm g})\Delta E(b_{2\rm g})] \\
& - (B^2+3A^2)\sqrt{N_tN_e}\left(1-\frac{1}{2}\lambda_t\lambda_e\right)(\zeta_{\rm d}^{t}\zeta_{d}^{te}-\zeta_{\rm d}^{t}\zeta_{\rm p}^{te}+\zeta_{\rm d}^{te}\zeta_{\rm p}^{t}-\zeta_{\rm p}^{t}\zeta_{\rm p}^{te})/[\Delta E(e_{\rm g})]^2, \qquad (9b)
\end{aligned}
$$

with

$$
\begin{aligned}
\zeta_{\rm d}^{t} = N_t\zeta_{\rm d}, \qquad & \zeta_{\rm d}^{te} = (N_tN_e)^{1/2}\zeta_{\rm d}, \\
\zeta_{\rm p}^{t} = N_t\lambda_t^2\zeta_{\rm p}/2, \qquad & \zeta_{\rm p}^{te} = (N_tN_e)^{1/2}\lambda_t\lambda_e\zeta_{\rm p}/2. \qquad (10)
\end{aligned}
$$

3. Application to NaCl:Ni$^+$(I)

The crystal NaCl has an octahedral (O_h) structure with unit cell constant a_0=0.5640nm.[14] The crystals NaCl:Ni$^+$(I) were produced by irradiating the crystals NaCl containing Ni^{2+} with x-rays[12] and the experimental values of the EPR g-factors were given $g_\parallel$=2.048 and $g_\perp$=2.270 (i.e. $\Delta g_\parallel = g_\parallel - g_{\rm e} = 0.0457 > 0$) in the range from 80 to 240K. The local structure of the $(NiCl_6)^{5-}$ cluster is of the axially compressional D_{4h} symmetry that possesses the weaker rhombic distortion caused by a positive ion vacancy lying nearby. Therefore, it is considered that the admixture of B_{1g} into A_{1g} (ground state) might occur through the vibration and the positive ion vacancy lying nearby.

It is difficult to determine the LCAO coefficients N_γ and λ_γ by a molecular orbital calculation. Hence, we use a semi-empirical method instead. We define the group overlap integral as

$$S_{\rm dp}(\gamma) = \langle d_\gamma | p_\gamma \rangle. \qquad (11)$$

We can determine the values of the molecular orbital coefficients N_γ and λ_γ using the approximate relation[15]

$$f_\gamma = N_\gamma^2[1 - 2\lambda_\gamma S_{\rm dp}(\gamma) + \lambda_\gamma^2 S_{\rm dp}^2(\gamma)], \qquad (12)$$

the normalization relation

$$N_\gamma[1 - 2\lambda_\gamma S_{\rm dp}(\gamma) + \lambda_\gamma^2] = 1, \qquad (13)$$

and the relation[16]

$$f_\gamma = \overline{N}^4 = \frac{\zeta_{\rm d}^2}{\zeta_{\rm d0}^2}, \qquad (14)$$

where $\overline{N}$ denotes the average covalency reduction factor, and $\zeta_{\rm d0}$ is the SO coupling parameter of the free d-electron of the $3d^9$ ion. In general, the values of the factors $\overline{N}$ are 0.8–1 for TM $3d^n$ ions in the crystals, and 0.9–1[17] when the ligands are the haloid atoms in the cluster. In this paper, the value of $\overline{N}$=0.95 is reasonably adopted. We use the Slater-type self-consistent field (SCF) orbital[18] to calculate the group overlap integral $S_{\rm dp}(\gamma)$. On the basis of this work, a further calculation has been carried out, and the coefficients N_γ and λ_γ have been obtained. The calculated values for NaCl:Ni$^+$(I) are listed in Table 1. In this paper, the values of the SO coupling parameters $\zeta_{\rm d}$ (Ni^+)=–603cm^{-1} (Ref.[19]) and $\zeta_{\rm p}$ (Cl)=587cm^{-1} (Ref.[15]) are used. Also, the values of the state mixing coefficients A=0.9321 and B=0.3621 are reasonably adopted. Substituting these values into formulae (9) and (10), the g-factors for the NaCl:Ni$^+$(I) can be obtained. The results are compared with the experimental data in Table 2.

Table 1. The group overlap integrals and the molecular orbital coefficients in NaCl:Ni$^+$(I).

$S_{\rm dp}(e_{\rm g})$	$S_{\rm dp}(t_{2\rm g})$	λ_e	λ_t	N_e	N_t
0.0103	0.0025	0.3333	0.3298	0.9056	0.9032

Table 2. Comparison between the calculated and observed g-values in NaCl:Ni^+(I).

	Calculated values*					Observed values[12]	
	$g(\zeta_d)$	$g(\zeta_p)$	$g(\zeta_d,\zeta_p)$	$g=g_e+\sum_i g_i$	$\Delta g_{\parallel(\perp)}$	g	$\Delta g_{\parallel(\perp)}$
$g_\parallel$	0.0439	0.0032	–0.0015	2.0479	0.0456	2.048	0.0457
$g_\perp$	0.3323	0.0185	0.0001	2.3532	0.3509	2.270	0.2677

*$\Delta E(e_g)$=7400cm^{-1} and $\Delta E(b_{2g})$=8100cm^{-1} [12] are used.

4. Discussion

In this paper, we give the new formulae for calculating $g_\parallel$ and $g_\perp$-factors of the $3d^9$ ions with the mixed state of $^2B_{1g}$ and $^2A_{1g}$ (ground state) in a tetragonal crystal field. The formulae should be suitable for a compressional tetragonal crystal field when B=0, and suitable for an elongational one when A=0. In particular, the formulae should coincide with the simple expressions obtained from the classical crystal field approach which includes only the SO coupling (ζ_d) of the central TM ions when ζ_p=0.

In NaCl:Ni^+(I), the local structure of the $(NiCl_6)^{5-}$ cluster is of a compressional tetragonal symmetry. Considering that the admixture occurs through vibration and a weaker rhombic distortion, the calculated results show good agreement with the experimental data (see Table 2). The puzzle that the $g_\parallel$-shift is positive is reasonably explained.

The calculated results show that contributions of the central Ni^+ ions are larger. However, the small contributions from the ligand (Cl) orbits cannot be neglected for calculating g-factors in NaCl:Ni^+(I); $g_\parallel$ (ζ_p) is about 7.3% of $g_\parallel$ (ζ_d), and the ratio of $g_\perp$ (ζ_p) to $g_\perp$ (ζ_d) is about 5.6%. It is worth noting that in the halogen clusters both the covalences and the SO coupling interactions increase from fluorine to iodine. Therefore, the values of $g(\zeta_p)$ from the halogen ligands must be of the order: F(ζ_{2p}=220cm^{-1}) < Cl(ζ_{3p}=587cm^{-1}) < Br(ζ_{4p}=2460cm^{-1}) < I(ζ_{5p}=5060cm^{-1}). Obviously, this suggests that in the calculation of EPR g-factors for TM $3d^n$ ions in some covalent crystals with the ligands, such as Cl, Br and I, which possess the strong SO coupling interactions, we should use the new formulae reported in this paper.

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