Theoretical Studies on the Gyromagnetic Factors for Nd^{3+} in Scheelites-Type ABO_4 Compounds

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Z. Naturforsch. **59a,** 947 – 951 (2004); received September 24, 2004

The gyromagnetic factors for Nd^{3+} in scheelite-type ABO_4 compounds (A = Cd, Ca, Pb, Ba; B = Mo, W) are theoretically studied by the perturbation formulas of the anisotropic g factors $g_\parallel$ and $g_\perp$ for a $4f^3$ ion in tetragonal symmetry. In these formulas, the contributions to the g factors due to the second-order perturbation terms and the admixtures of various energy levels are taken into account. The relevant crystal-field parameters are determined by the superposition model and the local geometrical relationship of the A^{2+} sites occupied by the impurity Nd^{3+}. The obtained g factors agree reasonably with the observed values. The discrepancies between theory and experiment are discussed.

Key words: EPR; Crystal-fields and Spin Hamiltonian; Nd^{3+}; Scheelite-type ABO_4 Compounds (A= Cd, Ca, Pb, Ba; B=Mo, W).

1. Introduction

Scheelite-type ABO_4 compounds (A = Cd, Ca, Pb, Ba; B = Mo, W) [1 – 4], doped with rare-earth ions (such as Nd^{3+}, Er^{3+}) have been extensively studied due to their optical and laser properties [5 – 11]. In addition, EPR studies of these systems were carried out [12 – 14]. For example, the anisotropic g factors $g_\parallel$ and $g_\perp$ of Nd^{3+} doped $CdMoO_4$, $CaWO_4$, $PbMoO_4$ and $BaWO_4$ were measured by means of EPR technique [12, 13]. Sattler et. al. [14] attributed the above EPR data to the lowest $\Gamma_{7,8}$ doublet of the $4f^3$ configuration. Until now, however, these EPR results have not been systematically investigated. In order to explanation further these g factors, which may be helpful to understand the optical properties of these materials, in this paper the g factors are theoretically investigated by the perturbation formulas of $g_\parallel$ and $g_\perp$ for a $4f^3$ ion in tetragonal symmetry. In these formulas, the contributions to the g factors due to the second-order perturbation terms and the admixtures of various states are considered.

2. Calculations

In the scheelite-type compounds ABO_4, the impurity Nd^{3+} ions replace the host A^{2+} and form tetragonally distorted $[NdO_8]^{13-}$ clusters [5, 6]. For a $4f^3$ ion in tetragonal symmetry its ground $^4I_{9/2}$ configuration may be split into five Kramers doublets due to the tetragonal crystal-field interaction. According to [14], the relationship

$$16g_\perp{}^2 = 21(-g_\parallel{}^2 + 2g_J g_\parallel + 15g_J{}^2) \qquad (1)$$

exists for the lowest doublet $\Gamma_{5,6}$, where $g_J = 8/11$ is the Lande factor for the ground state $^4I_{9/2}$. Since the measured g factors do not satisfy this relationship [12, 13], the lowest doublet may be attributed to $\Gamma_{7,8}$ instead [14].

In the treatments of the g factors in previous works [15, 16], merely the contributions to the g factors from the first-order perturbation terms were taken into account. Nevertheless, besides the lowest $\Gamma_{7,8}$, the other 10 irreducible representations Γ_x (i.e., six $\Gamma_{5,6}$ and four $\Gamma_{7,8}$) due to the tetragonal splitting of the ground

$^4I_{9/2}$ and the first excited $^4I_{11/2}$ levels would mix with the lowest $\Gamma_{7,8}$ via crystal-field $\hat{H}_{CF}$ and orbital angular momentum $\hat{J}$ interactions, and then result in second-order perturbation contributions to the g factors, as pointed out in our recent works [17–20]. Thus, the second-order perturbation formulas of the EPR g factors for a $4f^3$ ion in tetragonal symmetry can be written as

$$\begin{aligned} g_{\parallel} &= g_{\parallel}{}^{(1)} + g_{\parallel}{}^{(2)}, \\ &\quad g_{\parallel}{}^{(1)} = 2g_J \langle \Gamma\gamma | \hat{J}_Z | \Gamma\gamma \rangle, \\ &\quad g_{\parallel}{}^{(2)} = 2\sum_X{}' \frac{\langle \Gamma\gamma | \hat{H}_{CF} | \Gamma_X \gamma_X \rangle \langle \Gamma_X \gamma_X | \hat{J}_Z | \Gamma\gamma \rangle}{E(\Gamma_X) - E(\Gamma)}, \\ g_{\perp} &= g_{\perp}{}^{(1)} + g_{\perp}{}^{(2)}, \\ &\quad g_{\perp}{}^{(1)} = 2g_J \langle \Gamma\gamma | \hat{J}_X | \Gamma\gamma' \rangle, \\ &\quad g_{\perp}{}^{(2)} = 0. \end{aligned} \qquad (2)$$

Here the diagonal elements g_J of the operator $\hat{J}$ for various states can be obtained from [15, 16]. Note that the nondiagonal elements $g_J{}'$ may occur in the expansions of (2) for interactions between different $^{2S+1}L_J$ configurations. As mentioned in [17–20], the second-order perturbation term $g_{\perp}{}^{(2)}$ vanishes because none of the ten Γ_x has a non-zero matrix element with the lowest $\Gamma_{7,8}$ doublet for both $\hat{H}_{CF}$ and the x or y component of the $\hat{J}$ operators.

For the lowest doublet $\Gamma_{7,8}$, the basic function $\Gamma\gamma^{(\gamma')}$ (where γ and γ' denote the two components of the irreducible representation) should include the admixtures of various states, i. e., the admixture between the ground $^4I_{9/2}$ and the first excited $^4I_{11/2}$ states via crystal-field interaction, the admixture among $^2H_{9/2}$, $^4G_{9/2}$ and $^4I_{9/2}$ and that among $^2I_{11/2}$, $^2H_{11/2}$ and $^4I_{11/2}$ via spin-orbit coupling interaction. Therefore the basic function $\Gamma\gamma^{(\gamma')}$ may be expressed as

$$\begin{aligned} |\Gamma\gamma^{(\gamma')}\rangle = &\sum_{M_{J1}} C(^4I_{9/2}; \Gamma\gamma^{(\gamma')} M_{J1}) N_{9/2} (|^4I_{9/2} M_{J1}\rangle \\ &+ \lambda_H |^2H_{9/2} M_{J1}\rangle + \lambda_G |^4G_{9/2} M_{J1}\rangle) \\ &+ \sum_{M_{J2}} C(^4I_{11/2}; \Gamma\gamma^{(\gamma')} M_{J2}) N_{11/2} (|^4I_{11/2} M_{J2}\rangle \\ &+ \lambda_H{}' |^2H_{11/2} M_{J2}\rangle + \lambda_I |^2I_{11/2} M_{J2}\rangle), \end{aligned} \qquad (3)$$

where M_{J1} and M_{J2} are in the ranges of $-9/2$ to $9/2$ and $-11/2$ to $11/2$, respectively. The coefficients $C(^4I_{9/2}; \Gamma\gamma^{(\gamma')} M_{J1})$ and $C(^4I_{11/2}; \Gamma\gamma^{(\gamma')} M_{J2})$ can be obtained by diagonalizing the 22×22 energy matrix containing $^4I_{9/2}$ and $^4I_{11/2}$ states. N_i and λ_i are, respectively, the normalization factors and the mixing coefficients. They can be determined by using the spin-orbit coupling matrix elements and the perturbation method.

In scheelite-type ABO_4, the A^{2+} ion is coordinated to eight nearest O^{2-} ions which form the edges of a slightly distorted dodecahedron with S_4 point symmetry [21, 22]. However, the D_{2d} symmetry is proved to be a good approximation due to the rather small distortion from D_{2d} to S_4 [21], as treated by many authors for trivalent rare-earth ions in similar scheelite-type $LiYF_4$ [23, 24]. Thus, we still take the D_{2d} approximation here for simplicity. For the $Nd^{3+}(4f^3)$ ion in D_{2d} symmetry, the crystal-field interaction $\hat{H}_{CF}$ in the above formulas can be written in terms of the Stevens equivalent operators as [15, 17–19]

$$\hat{H}_{CF} = B_2^0 O_2^0 + B_4^0 O_4^0 + B_6^0 O_6^0 + B_4^4 O_4^4 + B_6^4 O_6^4. \qquad (4)$$

Here B_k^q ($k = 2$, 4 and 6; $|q| \le k$) are the crystal-field parameters, which can be determined from the superposition model (SPM) [25] and the local geometrical relationship of the studied impurity centers. Thus, we have

$$B_k^q = \sum_{j=1}^{2} \bar{A}_k K_k^q(\theta_j, \phi_j)(R_0/R_j)^{t_k}, \qquad (5)$$

where $K_k^q(\theta_j, \phi_j)$ are the coordination factors [25, 26] obtained from the local structural data of the studied Nd^{3+} centers. The parameters t_k and $\bar{A}_k$ are, respectively, the power-law exponents and the intrinsic parameters (with the reference distance or impurity-ligand distance R_0). In the D_{2d} approximation, four of the eight nearest O^{2-} ions of an A^{2+} site are at the distance $R_1{}^H$ and the angle θ_1, and the other four at the different distance $R_2{}^H$ and angle θ_2, where θ_j are the polar angles of the metal-ligand distances $R_j{}^H$ related to the fourfold axis of the studied systems [22, 27, 28] (see Table 1). Since the ionic radius r_i (≈ 0.995 Å [29]) of the impurity Nd^{3+} is different from the radii r_h of the host A^{2+} ions, we can reasonably estimate the impurity-ligand distances R_j of the impurity centers from the host values $R_j{}^H$ by the empirical relationship [18, 19]

$$R_j \approx R_j{}^H + (r_i - r_h)/2. \qquad (6)$$

The corresponding values of R_j are shown in Table 1.

	r_i (Å)	r_h (Å)	R_1^{H} (Å)	R_2^{H} (Å)	R_1 (Å)	R_2 (Å)	θ_1 (°)	θ_2 (°)
$CdMoO_4$		0.97	2.440	2.400	2.453	2.413	66.69	139.83
$CaWO_4$	0.995	0.99	2.479	2.438	2.484	2.443	66.73	139.88
$PbMoO_4$		1.20	2.632	2.608	2.530	2.506	68.10	141.63
$BaWO_4$		1.34	2.778	2.738	2.606	2.566	69.05	143.00

Table 1. Structural parameters of the A^{2+} sites and those of the Nd^{3+} impurity centers in scheelite-type ABO_4 compounds [22, 27, 28].

	t_2	t_4	t_6	$\bar{A}_2$ (cm^{-1})	$\bar{A}_4$ (cm^{-1})	$\bar{A}_6$ (cm^{-1})
$CdMoO_4$	3.5	6	6	522	90.4	44.6
$CaWO_4$					86.5	39.2
$PbMoO_4$					89.8	45.6
$BaWO_4$					110.8	64.6

Table 2. SPM parameters for the tetragonal Nd^{3+} centers in scheelite-type ABO_4 compounds.

	$g_\parallel$		$g_\perp$		$\Delta g(=g_\perp-g_\parallel)$	
	Calc.	Expt. [12, 13]	Calc.	Expt. [12, 13]	Calc.	Expt. [12, 13]
$CdMoO_4$	2.296	2.302	2.511	2.492	0.215	0.190
$CaWO_4$	2.062	2.035	2.580	2.537	0.518	0.502
$PbMoO_4$	1.556	1.351	2.619	2.592	1.063	1.241
$BaWO_4$	1.332	0.820	2.588	2.563	1.256	1.743

Table 3. EPR g factors for the tetragonal Nd^{3+} centers in scheelite-type ABO_4 compounds.

In view of the admixture (or covalency) between the 4f orbitals of Nd^{3+} and the 2p orbitals of the O^{2-} ions for Nd^{3+} - O^{2-} bonds in ABO_4:Nd^{3+}, the orbital reduction factor $k(\approx 0.9818$ [30]) for the Nd^{3+} - F^- bonds in CaF_2:Nd^{3+} can also be applied here, because of the similarity of the covalency of O^{2-} and F^- [31–33]. The free-ion parameters of the Coulomb repulsion ($F^2 \approx 71090$ cm^{-1}, $F^4 \approx 50917$ cm^{-1} and $F^6 \approx 34173$ cm^{-1}), the two-body interaction parameters ($\alpha \approx 20.8$ cm^{-1}, $\beta \approx -651$ cm^{-1} and $\gamma \approx 1868$ cm^{-1}) and the spin-orbit coupling coefficient ($\zeta_{4\mathrm{f}} \approx 875$ cm^{-1}) were obtained from the similar $[NdO_8]^{13-}$ cluster in YAG:Nd^{3+} [34]. They are approximately adopted here.

According to [22], the power-law exponents $t_2 \approx 3.5$, $t_4 \approx t_6 \approx 6$ and the intrinsic parameters $\bar{A}_2 \approx 522$ cm^{-1}, $\bar{A}_4 \approx 66.3$ cm^{-1} and $\bar{A}_6 \approx 4.1$ cm^{-1} are obtained for the $[NdO_8]^{13-}$ cluster in $CaWO_4$ (with $R_0 \approx 2.466$ Å). These parameters can be approximately adopted here, with only $\bar{A}_4$ and $\bar{A}_6$ adjustable in view of the differences in the Nd^{3+} - O^{2-} bonding lengths and angles for the various $[NdO_8]^{13-}$ clusters.

By fitting the observed g factors of ABO_4:Nd^{3+}, we obtain the values of $\bar{A}_4$ and $\bar{A}_6$, which are shown in Table 2. The corresponding theoretical g factors are given in Table 3. For comparisons, the anisotropies $\Delta g(=g_\perp-g_\parallel)$ for these systems are also calculated and collected in Table 3.

3. Discussions

From Table 3 one can find that the calculated g factors for the ABO_4:Nd^{3+} systems agree reasonably with the observed values, except that the theoretical $g_\parallel$ (or Δg) for $BaWO_4$ and $PbMoO_4$ are larger (or smaller) than the experimental data.

1) According to the calculations we find that the contributions to $g_\parallel$ from the second-order perturbation terms amount to are about 10 $\sim$ 12% of those from the first-order perturbation terms. Thus, in order to interpret the g factors for Nd^{3+} in ABO_4 compounds more exactly, the second-order perturbation contributions should be taken into account. Based on the above studies, the importance of the contributions due to the second-order perturbation terms is related to the tetragonal crystal-fields. Seen from (2), both the numerators and the denominators of $g_\parallel{}^{(2)}$ increase with increasing strength of the crystal-fields. Meanwhile, the contributions due to some irreducible representations Γ_x are very small or cancel one another. As regards the contributions from the admixtures of various states, they amount to about 4%, which is smaller than those from the second-order perturbation terms. Thus, higher excited states (e.g., $^2I_{11/2}$, $^2H_{9/2}$) would even contribute less.

2) On the whole, the calculated g factors based on the perturbation formulas (2) and the SPM parameters in this work are consistent with the observed values, suggesting that the perturbation formulas and the related parameters are suitable. (i) The adjusted SPM parameters $\bar{A}_4$ obtained in this work are comparable with but slightly larger than that (≈ 66.3 cm^{-1}) for $CaWO_4$:Nd^{3+} adopted in [22], while the parameters $\bar{A}_6$ in present work are one order in magnitude larger than that (≈ 4.1 cm^{-1}) in [22]. In addition, the values of $\bar{A}_4$ or $\bar{A}_6$ for the various ABO_4 compounds in this

work are also close to one another and can be regarded as reasonable. (ii) The larger calculated anisotropies Δg of $BaWO_4$ and $PbMoO_4$ are consistent with their larger tetragonal distortions (i. e., larger polar angles θ_j, see Table 1), compared with those of $CdMoO_4$ and $CaWO_4$.

3) There are some errors in the calculations. (i) The larger theoretical $g_\parallel$ (or smaller Δg) for $BaWO_4$ (and $PbMoO_4$) may be due to the considerably size mismatching substitution of the larger Ba^{2+} (and Pb^{2+}) by the smaller Nd^{3+}, which would lead to local relaxation around the impurity. Thus, the angles θ_j may increase by an amount $\Delta\theta$ so as to increase the tetragonal distortion and hence the calculated Δg. Considering this effect, the theoretical results for $BaWO_4$ (and $PbMoO_4$) can be understood. (ii) The free-ion parameters are taken from those for YAG:Nd^{3+} in [34], which may bring some errors. Nevertheless, these errors have only slight influence (no more than 3%) on the energy separations between the ground $^4I_{9/2}$ and the excited $^4I_{11/2}$, $^2H_{9/2}$, $^4G_{9/2}$, et. al. states and lead to still smaller errors (no more than 2%) to the coefficients N_i and λ_i in (3). Since the basic function $\Gamma\gamma$ and the calculated g factors are mainly related to the crystal-field splitting of the ground $^4I_{9/2}$ state, the calculation errors of the g factors due to the approximation of the free-ion parameters are expected to be smaller than 2%. (iii) The errors of the adopted SPM parameters may have some influence on the theoretical g factors. According to the calculations, the errors of the g factors are estimated to be less than 6%, as the parameters $\overline{A}_k$ and t_k change by 10%. These errors are partially absorbed in the adjusted parameters $\overline{A}_4$ and $\overline{A}_6$. (iv) The errors of the orbital reduction factor k may also affect the magnitude of the theoretical g factors. As one adjusts k within the range of $0.9 \sim 1$, the variations of the g factors are no more than 3%. (v) For simplicity, the D_{2d} approximation instead of the exact S_4 symmetry is adopted to describe the crystal-field interaction in (4). Even though one takes the strict S_4 symmetry, the imaginary parts of the rank-4 and rank-6 crystal-field parameters are very small, as stated in [21 – 23]. As a result, their contributions to the coefficient $C(^4I_{9/2};\Gamma\gamma^{(\gamma')}M_{J1})$ or $C(^4I_{11/2};\Gamma\gamma^{(\gamma')}M_{J2})$ in $\Gamma\gamma^{(\gamma')}$ and hence to the final g factors are expected to be smaller than 5%.

Acknowledgement

This work was supported by the Youth Fundation of Science and Technology of UESTC under grant No. JX04022.

[1] B. G. Wang, E. W. Shi, W. Z. Zhong, and Z. W. Yin, J. Inorg. Mater. **13**, 648 (1998).
[2] B. M. Sinelnikov, E. V. Sokolenko, and V. Y. Zvekov, Inorg. Mater. **32**, 999 (1996).
[3] C. Koepke, A. J. Wojtowicz, and A. Lempicki, J. Lumin. **54**, 345 (1993).
[4] A. A. Kaminski, H. J. Eichler, K. Ueda, N. V. Klassen, B. S. Redkin, L. E. Li, J. Findeisen, D. Jaque, J. Garcia-Sole, J. Fernandez, and R. Balda, Appl. Opt. **38**, 4533 (1999).
[5] N. Faure, C. Borel, M. Couchaud, G. Bassett, R. Templier, and C. Wyon, Appl. Phys. B-Lasers Opt. **63**, 593 (1996).
[6] T. T. Baseive, A. A. Sobol, Y. Voronko, and P. G. Zverev, Opt. Mater. **15**, 205 (2000).
[7] P. Cerny, P. G. Zverev, H. Jelinno, and T. T. Basieve, Opt. Commun. **177**, 397 (2000).
[8] P. G. Zvervev, T. T. Basiev, A. A. Sobol, V. V. Shornyakov, L. I. Ivleva, N. M. Polozkiov, and V. V. Osiko, Quantum Electron. **30**, 55 (2000).
[9] M. Gaft, R. Reisfeld, G. Panczer, Ph. Blank, and G. Boulon, Spectrochim. Acta A **54**, 2163 (1998).
[10] M. Nikl, P. Bohacek, E. Mihokova, M. Kobayashi, M. Ishii, Y. Usuki, V. Babin, A. Stolovich, S. Zazubovich, and M. Bacci, J. Lumin. **87-89**, 1136 (2000).
[11] I. S. Minhas, K. K. Sharmia, and J. B. Gruber, Phys. Rev. B **8**, 385 (1973).
[12] I. N. Kurkin, Fiz. Tverd. Tela **8**, 731 (1966) [Sov. Phys. Solid State **8**, 585 (1966)].
[13] D. R. Mason, C. A. Morrison, C. Kikuchi, and R. T. Farrar, Bull. Amer. Phys. Soc. **12**, 468 (1967).
[14] J. P. Sattler and J. Newarich, Phys. Rev. B **4**, 1 (1971).
[15] A. Abragam and B. Bleaney, Electron Paramagnetic Resonance of Transition Ions, Oxford University Press, London 1970.
[16] L. A. Sorin and M. V. Vlasova, Electron Spin Resonance of Paramagnetic Crystals, Translated from Russian by P. Gluck, Plenum Press, New York 1973.
[17] S. Y. Wu and W. C. Zheng, Spectrochim. Acta A **58**, 3179 (2002).
[18] S. Y. Wu, H. N. Dong, and P. Li, Z. Naturforsch. **58a**, 439 (2003).
[19] H. N. Dong and S. Y. Wu, Z. Naturforsch. **58a**, 507 (2003).
[20] H. N. Dong, W. C. Zheng, and S. Y. Wu, Phys. Stat. Sol. B **240**, 120 (2003).

[21] A. Kiel and W. B. Mims, Phys. Rev. B **1**, 2935 (1970).

[22] Vishwamittar and S. P. Puri, J. Chem. Phys. **61**, 3720 (1974).

[23] M. A. Couto dos Santos, E. Antic-Fidancev, J. Y. Gesland, J. C. Krupa, M. Lemaýtre-Blaise, and P. Porcher, J. Alloys & Comp. **275/277**, 435 (1998).

[24] R. Cavellec, S. Hubert, and E. Simoni, J. Solid State Chem. **129**, 189 (1997).

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

[26] C. Rudowicz, J. Phys. C: Solid State Phys. **20**, 6033 (1987).

[27] Y. Abraham, N. A. W. Holzwarth, and R. T. Williams, Phys. Rev. B **62**, 1733 (2000).

[28] M. Daturi, G. Basca, M. M. Borel, A. Leclaire, and P. Paiggio, J. Phys. Chem. B **101**, 4358 (1997).

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

[30] C. A. Freeth and G. D. Jones, J. Phys. C **15**, 6833 (1982).

[31] M. M. Ellis and D. J. Newman, J. Chem. Phys. **49**, 4037 (1968).

[32] D. J. Newman and M. M. Curtis, J. Phys. Chem. Solids **30**, 2731 (1969).

[33] M. M. Curtis and D. J. Newman, J. Chem. Phys. Lett. **9**, 606 (1971).

[34] J. R. Quagliano and F. S. Richardson, J. Alloys Compounds **180**, 131 (1992).