Theoretical Study of the Local Lattice Distortion at the Trigonal Cr^{3+} Center in BiI_3

Shao-Yi Wu[a,b], Xiu-Ying Gao[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 Center 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. W.; E-mail: shaoyi_wu@163.com

Z. Naturforsch. **61a,** 78 – 82 (2006); received August 8, 2005

The local lattice distortion at the trigonal Cr^{3+} center in BiI_3 is theoretically studied by the perturbation formulas of the EPR parameters for a $3d^3$ ion in trigonal symmetry, based on the cluster approach. In these formulas the contributions from the s-orbitals of the ligands, which were often ignored, are taken into account. It is found that the local angle β (between the direction of the impurity-ligand bonding R and the C_3 axis) in the impurity center is smaller than the host angle β_H in the pure crystal. The calculated EPR parameters are improved compared to those in absence of the ligand s-orbital contributions. The local lattice distortion obtained in this work is discussed.

Key words: Electron Paramagnetic Resonance; Crystal- and Ligand-Field Theory; Cr^{3+}; BiI_3.

1. Introduction

Belonging to layered-type semiconductors, BiI_3 has widely been studied as to band edge shift, exciton transition, optical properties as well as influence of transition metal ions (e. g., Mn^{2+} and Cr^{3+}) on exciton spectra [1 – 8]. In addition, electron paramagnetic resonance (EPR) experiments were carried out on this material doped with Cr^{3+}, and the EPR parameters (zero-field splitting and g factors) were measured for a trigonal Cr^{3+} impurity center in BiI_3 (and also other halides) [9]. Based on the compact (second-order perturbation) formula of the g factor in cubic approach, the experimental g factors were clearly illustrated by considering the spin-orbit coupling coefficient of the ligand, which contributes significantly to the g factors [9]. However, in the treatments the host metal-ligand angle β_H ($\approx 57.5°$) was adopted, and the local lattice distortion of the impurity center was not taken into account. In fact, since the radius of the impurity Cr^{3+} is much smaller than that of the host Bi^{3+}, the impurity-ligand distance R and bonding angle β in the impurity center may be different from those in the host. Therefore the local lattice distortion due to size mismatch substitution should be considered.

In order to acquire local structure information which may be helpful to understand the properties of this material and to make a satisfactory interpretation of the EPR parameters, in this work the s-orbitals of the ligands are introduced in the single-electron wavefunctions of the octahedral $3d^3$ cluster with trigonal symmetry. Then the improved theoretical model and formulas including the ligand s-orbital contributions based on the cluster approach are applied to the studied BiI_3:Cr^{3+}.

2. Calculations

BiI_3 has a layered-type structure of the space group $R\bar{3}$ [9, 10]. When the impurity Cr^{3+} is doped into the lattice of BiI_3, it may substitute the host Bi^{3+} ion and conserve the local trigonal symmetry. For a Cr^{3+}($3d^3$) ion in octahedral trigonal symmetry, the perturbation formulas of the EPR parameters were obtained, based on the strong cubic field approximation and the cluster approach [11, 12], by means of the Macfarlane perturbation loop method [13, 14]. Thus, the formulas of the zero-field splitting and the g shifts $\Delta g_\parallel$

and $\Delta g_\perp$ are expressed as [12, 15]

$$\begin{aligned} D &= (2/9)\zeta'^2 V(1/E_1{}^2 - 1/E_3{}^2) \\ &\quad - \sqrt{2}\zeta\zeta' V'[2/(3E_1E_4) + 1/(E_2E_3) \\ &\quad + 1/(3E_3E_4) + 1/(E_2E_4) + \sqrt{2}B/(E_1E_4E_5)] \\ &\quad - \sqrt{2}\zeta'^2 B V'[4/(E_3E_4E_5) + 9/(2E_2{}^2E_3)], \\ \Delta g_\parallel &= g_\parallel - g_\mathrm{s} \\ &= -8\zeta' k'/(3E_1) \\ &\quad - 2\zeta(2k'\zeta - k\zeta' + 2g_\mathrm{s}\zeta')/(9E_1{}^2) \\ &\quad + 4\zeta'^2(k - 2g_\mathrm{s})/9E_3{}^2 \\ &\quad - \zeta^2(k + g_\mathrm{s})/(3E_2{}^2) \\ &\quad - 4\zeta\zeta' k'[1/(3E_1E_2) + 1/(9E_1E_3) \\ &\quad + 1/(3E_2E_3)] + 8\zeta' k' V/(9E_1{}^2) \\ &\quad - 4\sqrt{2}(k'\zeta + k\zeta')V'/(3E_1E_4), \\ \Delta g_\perp &= g_\perp - g_\mathrm{s} \\ &= \Delta g_\parallel - \zeta' k' V/(3E_1{}^2) \\ &\quad + \sqrt{2}(2k\zeta' + k'\zeta)V'/(3E_1E_4), \end{aligned} \tag{1}$$

where $g_\mathrm{s} = 2.0023$ is the spin only value. ζ and ζ' are the spin-orbit coupling coefficients, and k and k' are the orbital reduction factors. B (or C) is (are) the Racah parameter(s) for the $3\mathrm{d}^3$ ion in crystals. V and V' are the trigonal field parameters. The energy denominators E_i can be expressed in terms of the cubic field parameter Dq and the Racah parameters [13, 14]:

$$\begin{aligned} &E_1 = 10Dq, && E_2 = 15B + 5C, \\ &E_3 = 10Dq + 9B + 3C, && E_4 = 10Dq + 12B, \\ &E_5 = 20Dq + 3B. && \end{aligned} \tag{2}$$

In the general treatments of the cluster approach, the contributions of the s-orbitals of ligands are often ignored [9, 11 – 15]. To achieve further investigations of the EPR parameters, the above contributions are considered here. Thus, the total single electron wavefunction containing the contributions from the s-orbitals of ligands are expressed as

$$\begin{aligned} \psi_\mathrm{t} &= N_\mathrm{t}{}^{1/2}(\varphi_\mathrm{t} - \lambda_\mathrm{t}\chi_\mathrm{pt}), \\ \psi_\mathrm{e} &= N_\mathrm{e}{}^{1/2}(\varphi_\mathrm{e} - \lambda_\mathrm{e}\chi_\mathrm{pe} - \lambda_\mathrm{s}\chi_\mathrm{s}), \end{aligned} \tag{3}$$

where φ_γ ($\gamma = \mathrm{e}$ and t indicate the irreducible representations of the O_h group) are the d-orbitals of the central $3\mathrm{d}^3$ ion. $\chi_{\mathrm{p}\gamma}$ and χ_s denote the p- and s-orbitals of the ligands. N_γ and λ_γ (or λ_s) are the normalization factors and the orbital admixture coefficients, respectively. Based on the semiempirical method [11, 12], we have the approximate relationships

$$\begin{aligned} f_\mathrm{t} &= N_\mathrm{t}{}^2[1 + \lambda_\mathrm{t}{}^2 S_\mathrm{dpt}{}^2 - 2\lambda_\mathrm{t} S_\mathrm{dpt}], \\ f_\mathrm{e} &= N_\mathrm{e}{}^2[1 + \lambda_\mathrm{e}{}^2 S_\mathrm{dpe}{}^2 + \lambda_\mathrm{s}{}^2 S_\mathrm{ds}{}^2 \\ &\quad - 2\lambda_\mathrm{e} S_\mathrm{dpe} - 2\lambda_\mathrm{s} S_\mathrm{ds}], \end{aligned} \tag{4}$$

and the normalization conditions

$$\begin{aligned} &N_\mathrm{t}(1 - 2\lambda_\mathrm{t} S_\mathrm{dpt} + \lambda_\mathrm{t}{}^2) = 1, \\ &N_\mathrm{e}(1 - 2\lambda_\mathrm{e} S_\mathrm{dpe} - 2\lambda_\mathrm{s} S_\mathrm{ds} + \lambda_\mathrm{e}{}^2 + \lambda_\mathrm{s}{}^2) = 1. \end{aligned} \tag{5}$$

Here $S_{\mathrm{dp}\gamma}$ (and S_ds) are the group overlap integrals. Generally speaking, the admixture coefficients increase with increasing the group overlap integrals, and one can approximately adopt a proportional relationship between the admixture coefficients and the related group overlap integrals, i. e., $\lambda_\mathrm{e}/S_\mathrm{dpe} \approx \lambda_\mathrm{s}/S_\mathrm{ds}$ within the same irreducible representation $\mathrm{e_g}$. The covalency factor f_γ is often determined from the ratio of the Racah parameters for the $3\mathrm{d}^3$ ion in a crystal to those in free state, i. e., $f_\gamma \approx (B/B_0 + C/C_0)/2$.

From the cluster approach including the ligand s-orbital contributions, the spin-orbit coupling coefficients ζ, ζ' and the orbital reduction factors k, k' for the $3\mathrm{d}^3$ octahedral cluster are written as

$$\begin{aligned} \zeta &= N_\mathrm{t}(\zeta_\mathrm{d}{}^0 + \lambda_\mathrm{t}{}^2\zeta_\mathrm{p}{}^0/2), \\ \zeta' &= (N_\mathrm{t}N_\mathrm{e})^{1/2}(\zeta_\mathrm{d}{}^0 - \lambda_\mathrm{t}\lambda_\mathrm{e}\zeta_\mathrm{p}{}^0/2), \\ k &= N_\mathrm{t}(1 + \lambda_\mathrm{t}{}^2/2), \\ k' &= (N_\mathrm{t}N_\mathrm{e})^{1/2}[1 - \lambda_\mathrm{t}(\lambda_\mathrm{e} + \lambda_\mathrm{s}A)/2], \end{aligned} \tag{6}$$

where $\zeta_\mathrm{d}{}^0$ and $\zeta_\mathrm{p}{}^0$ are the spin-orbit coupling coefficients of the free $3\mathrm{d}^3$ and the ligand ions, respectively. A denotes the integral $R\langle n\mathrm{s}|\frac{\partial}{\partial y}|n\mathrm{p}_y\rangle$, where R stands for the impurity-ligand distance in the studied system. Obviously, when taking $S_\mathrm{ds} = \lambda_\mathrm{s} = 0$ and $A = 0$, the ligand s-orbital contributions vanish and then the above formulas are reduced to those in absence of the above contributions [11 – 15].

According to the superposition model [16], the trigonal field parameters V and V' for the Cr^{3+} center in $\mathrm{BiI_3}$ can be written as

$$\begin{aligned} V &= (18/7)\bar{A}_2(R)(3\cos^2\beta - 1) \\ &\quad + (40/21)\bar{A}_4(R)(35\cos^4\beta - 30\cos^2\beta + 3) \\ &\quad + (40\sqrt{2}/3)\bar{A}_4(R)\sin^3\beta\cos\beta, \end{aligned}$$

$$\begin{aligned} V = {} & (-6\sqrt{2/7})\bar{A}_2(R)(3\cos^2\beta - 1) \\ & + (10\sqrt{2/21})\bar{A}_4(R)(35\cos^4\beta - 30\cos^2\beta + 3) \\ & + (20/3)\bar{A}_4(R)\sin^3\beta\cos\beta, \end{aligned} \quad (7)$$

where β is the angle between the impurity-ligand bond and the C_3 axis. The magnitude of trigonal distortion can be characterized by the difference $\delta\beta$ $(= \beta - \beta_0$, where $\beta_0 \approx 54.736°$ is the bonding angle in cubic symmetry). $\bar{A}_2(R)$ and $\bar{A}_4(R)$ are the intrinsic parameters with the reference bonding length or impurity-ligand distance R. For $3d^n$ ions in octahedra, $\bar{A}_4(R) \approx (3/4)Dq$ [16] and $\bar{A}_2(R)/\bar{A}_4(R) \approx 9 \sim 12$ are valid in many crystals [17–19]. Here we take $\bar{A}_2(R) \approx 12\bar{A}_4(R)$. Therefore, the trigonal distortion (or local structure) is related to the trigonal field parameters and hence to the EPR parameters (particularly zero-field splitting) of the studied impurity center.

Since the ionic radius r_i (≈ 0.63 Å [20]) of the impurity Cr^{3+} is much smaller than the radius r_h (≈ 0.95 Å [20]) of the host Bi^{3+}, the impurity-ligand distance R and the impurity-ligand bonding angle β in the impurity center may be dissimilar to the corresponding distance R_H (≈ 3.115 Å [10]) and angle β_H ($\approx 57.5°$ [9]) in the host crystal. The distance R can be approximately calculated from the empirical formula $R \approx R_\mathrm{H} + (r_\mathrm{i} - r_\mathrm{h})/2$ [21, 22]. Thus, we have $R \approx 2.955$ Å. From the distance R and the Slater-type SCF functions [23, 24], the related integrals are obtained, i. e., $S_\mathrm{dpt} \approx 0.0117$, $S_\mathrm{dpe} \approx 0.0415$, $S_\mathrm{ds} \approx 0.0212$, $A \approx 1.1269$.

The spectral parameters Dq, B and C can be acquired from optical spectra of the similar trigonal $[CrI_6]^{3-}$ cluster in $CsMgI_3$ [12]. Thus, we have $Dq \approx 1028$ cm^{-1}, $B \approx 465$ cm^{-1} and $C \approx 1740$ cm^{-1} here. By using (4) and (5) and the free-ion parameters $B_0 \approx 1030$ cm^{-1} and $C_0 \approx 3850$ cm^{-1} [25] for Cr^{3+}, the parameters $f_\gamma \approx 0.452$ and hence $N_\mathrm{t} \approx 0.678$, $N_\mathrm{e} \approx 0.695$, $\lambda_\mathrm{t} \approx 0.702$ and $\lambda_\mathrm{e} \approx 0.633$ can be calculated. From the free-ion values $\zeta_\mathrm{d}{}^0 \approx 273$ cm^{-1} [25] for Cr^{3+} and $\zeta_\mathrm{p}{}^0 \approx 5060$ cm^{-1} for I^- [26], the parameters $\zeta \approx 1029$ cm^{-1}, $\zeta' \approx -583$ cm^{-1}, $k \approx 0.844$ and $k' \approx 0.446$ are calculated from (6).

Table 1. EPR parameters of the trigonal Cr^{3+} center in BiI_3.

	D (10^{-4} cm^{-1})	$\Delta g_\parallel$	$\Delta g_\perp$
Calc.[a]	174490	0.0637	0.0447
Calc.[b]	−567	0.0797	0.0797
Calc.[c]	−500	0.0577	0.0577
Expt. [9]	−500 (20)	0.0557 (100)	0.0557 (100)

[a] Calculations based on the host angle β_H and inclusion of the contributions from the s-orbitals of the ligands.

[b] Calculations based on the local angle β in (8) and neglecting of the contributions from the s-orbitals of the ligands (i. e., similar to the treatments in [11, 12]).

[c] Calculations based on the local angle β in (8) and inclusion of the contributions from the s-orbitals of the ligands.

Substituting these parameters (as well as the host angle β_H) into (1), the EPR parameters for the studied Cr^{3+} center are calculated and given in Table 1. Obviously, these results do not show good agreement with the experimental data, particularly, the theoretical D has the wrong (positive) sign and is about two orders in magnitude larger than the observed value, even in consideration of the significant uncertainty ($\sim 2°$) in β_H [9]. This means that the trigonal distortion based on the host angle β_H is somewhat too large to be suitable for the analysis of the EPR parameters. Therefore, local lattice distortion around the impurity ion in the Cr^{3+} center may be introduced here. By fitting the calculated D to the observed result, one can obtain the local angle

$$\beta \approx 54.73°. \quad (8)$$

Thus, the local angle for the impurity center is much smaller than that in the host, i. e., the corresponding lattice (angular) distortion $\Delta\beta$ $(= \beta - \beta_\mathrm{H})$ is $-2.77°$. The calculated EPR parameters are shown in Table 1. For comparisons, the calculated results based on inclusion of ligand s-orbital contributions and the host angle β_H, and those on the local angle and neglecting of the contributions from the s-orbitals of the ligands (i. e., $S_\mathrm{ds} = \lambda_\mathrm{s} = 0$ and $A = 0$, similar to the treatments in [11, 12]) are also given in Table 1.

3. Discussion

According to Table 1, theoretical EPR parameters for the studied system including the ligand s-orbital contributions and the local lattice (angular) distortion $\Delta\beta$ show better agreement than those in absence of ligand s-orbital contributions or lattice distortion with the observed values. This reveals that the theoretical model and the parameters adopted in this work may be regarded as suitable.

1. The calculated D or g shifts on neglecting the ligand s-orbital contributions are by about 13% or 38% larger than those including these contributions, i. e., the contributions from the spin-orbit coupling of the ligand I^- seem to be overestimated in the former. In fact, inclusion of the s-orbitals of the ligand I^- decreases the parameters N_e and λ_e [see (5)], then reduces the

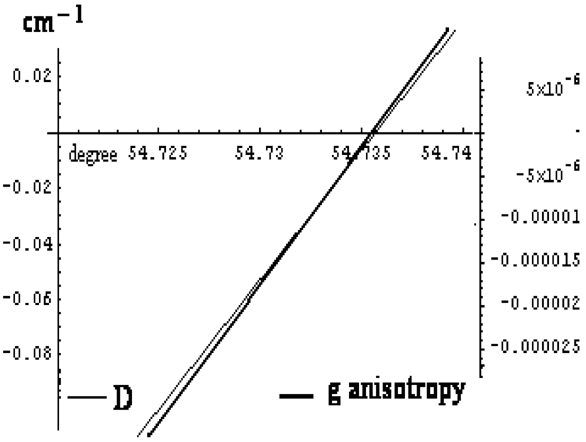

Fig. 1. The Variation of the *D* and *g* anisotropy versus the angle β [around the value in (8)].

magnitudes of k' and ζ' [see (6)], and finally leads to smaller *D* or *g* shifts [see (1)]. Thus, improvement of the calculated zero-field splitting and the *g* factors can be achieved by considering the ligand s-orbital contributions. Meanwhile, the previous assumption that the contributions of the s-orbitals of the ligands are negligible for $3d^n$ ions in octahedra (e. g., $KNiF_3$) [27,28] seems not always suitable for a ligand having a much larger spin-orbit coupling coefficient (e. g., I^-), and then the ligands s-orbital contributions should be considered in studies of zero-field splitting and *g* factors.

2. The local lattice distortion, characterized by $\Delta\beta$, leads to good agreement in the EPR parameters between theory (by including the ligand s-orbital contributions) and experiment. As mentioned before, the impurity-ligand angle β may be different from the host β_H due to the significant discrepancy between the ionic radius (≈ 0.63 Å) of the impurity Cr^{3+} and that (≈ 0.95 Å) of the replaced Bi^{3+}. Thus the local angle β (or decrease $|\Delta\beta|$ in the metal-ligand bonding angle) can be understood, in consideration of (i) the relaxation around the smaller Cr^{3+} replacing the larger Bi^{3+} and (ii) the slight modification of the distance between the sandwich layers which suffer weak van der Waals interactions. Additionally, the angle β dependences of *D* and the *g* anisotropy ($\Delta g_{\parallel} - \Delta g_{\perp}$) can be illustrated in Fig. 1 for the values around 54.73° in (8). It is found that the *D* or *g* anisotropy almost linearly decreases with the decrease of β. Near the value ($\approx 54.73^\circ$, which is close to that of cubic symmetry) in (8), the small trigonal distortion $\delta\beta$ leads to small trigonal field parameters V and V' [see (7)] and hence small *D* or *g* anisotropy [see (1)]. Note that the *g* anisotropies based on the angles around β in (8) are too small to be measured in EPR experiments, and only an isotropic *g* factor was observed within the experimental errors [9]. Interestingly, similar decrease in the metal-ligand bonding angle due to size mismatching substitution is also found in the EPR studies on the trigonal (D_{3d}) Co^{2+} center in $ZnSiF_6 \cdot 6H_2O$ crystal (where the impurity Co^{2+} is also smaller than the replaced Zn^{2+}) [29]. When considering the property of the trigonal distortion, the ligand octahedron changes from compression ($\delta\beta_H = \beta_H - \beta_0 \approx 2.764^\circ > 0$) in the host (even in consideration of the uncertainty 2° in β_H [9]) to slight elongation ($\delta\beta \approx -0.006^\circ \leq 0$) in the impurity center. Therefore, the negative value of zero-field splitting for Cr^{3+} in the elongated octahedron can be understood, in consideration of the negative sign of ζ' due to the much larger spin-orbital coupling coefficient of I^- [see (6)].

3. In the above calculations, only the contributions from the crystal-field (CF) mechanism (related to the CF energy levels) are considered, while those from the charge-transfer (CT) mechanism (related to the CT energy levels) are ignored. Since the CT levels are usually far from the $^4A_2$ ground state, their contributions can be regarded as insignificant. Approximately, the energy separation between the CT levels and the related ground state can be estimated from the expression $E_{CT} \approx 30000\ cm^{-1}[\chi(L) - \chi(M)]$, where $\chi(L)$ and $\chi(M)$ are, respectively, the optical electronegativities of the ligand and the metal ions [28]. In the studied system, $\chi(Cr^{3+}) \approx 1.8$ and $\chi(I^-) \approx 3.0$ [30], yielding $E_{CT} \sim 36000\ cm^{-1}$. Based on the recent CT studies on the *g* factors for $3d^3$ ions [31], the contributions from the CT mechanism are estimated to be about 0.013. Thus the total *g* shifts would be slightly larger than the experimental results, but still better than those in absence of the ligand s-orbital contributions. So, more exact studies of the EPR parameters should be applied to the complete perturbation formulas including both the CF and CT mechanisms. All the same, the theoretical studies on the local lattice distortion and the EPR parameters of $BiI_3{:}Cr^{3+}$ can be regarded as reasonable.

[1] A. M. Ghorayeb, C. C. Coleman, and A. D. Yoffe, J. Phys. C **17**, L715 (1984).
[2] H. Kondo, T. Kawai, and T. Karasawa, Solid State Commun. **94**, 129 (1995).
[3] T. Iida, M. Sakai, T. Karasawa, T. Komatsu, and Y. Kaifu, J. Phys. C **16**, 4719 (1983).
[4] T. Karasawa, T. Iida, M. Sakai, T. Komatsu, and Y. Kaifu, J. Phys. C **18**, 4043 (1985).
[5] G. E. Jellison Jr., J. O. Ramey, and L. A. Boatner, Phys. Rev. B **59**, 9718 (1999).
[6] T. Komatsu, T. Karasawa, I. Akai, and T. Lida, J. Lumin. **70**, 448 (1996).
[7] M. Schluter, M. L. Cohen, S. E. Kohn, and C. Y. Fono, Phys. Status Solidi B **78**, 737 (1976).
[8] V. G. Dorogan, V. O. Zhydkov, and F. V. Motsnyi, Semicond. Phys. Quant. Eletr. Opt. **5**, 417 (2002).
[9] R. W. Bene, Phys. Rev. **178**, 497 (1969).
[10] B. G. Hyde and S. Andersson, Inorganic Crystal Structures, Wiley Interscience, New York 1989.
[11] J. J. Chen, M. L. Du, and J. Qin, Phys. Status Solidi B **174**, K15 (1992).
[12] M. L. Du and C. Rudowicz, Phys. Rev. B **46**, 8974 (1992).
[13] R. M. Macfarlane, J. Chem. Phys. **47**, 2006 (1967).
[14] R. M. Macfarlane, Phys. Rev. B **1**, 989 (1970).
[15] S. Y. Wu, X. Y. Gao, and W. Z. Yan, Z. Naturforsch. **58a**, 503 (2003).
[16] J. D. Newman, D. C. Pryce, and W. A. Runciman, Am. Mineral. **63**, 1278 (1978).
[17] W. L. Yu, X. M. Zhang, L. X. Yang, and B. Q. Zen, Phys. Rev. B **50**, 6756 (1994).
[18] J. D. Newman, D. C. Pryce, and W. A. Runciman, Am. Mineral. **63**, 1278 (1978).
[19] A. Edgar, J. Phys. C **9**, 4303 (1976).
[20] R.C. Weast, CRC Handbook of Chemistry and Physics, CRC Press, Boca Raton 1989, p. F 187.
[21] H. N. Dong and S. Y. Wu, Z. Naturforsch. **58a**, 507 (2003).
[22] S. Y. Wu and H. N. Dong, Z. Naturforsch. **59a**, 235 (2004).
[23] E. Clementi and D. L. Raimondi, J. Chem. Phys. **38**, 2686 (1963).
[24] E. Clementi, D. L. Raimondi, and W. P. Reinhardt, J. Chem. Phys. **47**, 1300 (1967).
[25] J. S. Griffith, The Theory of Transition-metal Ions, Cambridge University Press, London 1964.
[26] G. L. McPerson, R. C. Kach, and G. D. Stucky, J. Chem. Phys. **60**, 1424 (1974).
[27] J. A. Aramburu and M. Moreno, J. Chem. Phys. **83**, 6071 (1985).
[28] A. A. Misetich and T. Bush, J. Chem. Phys. **41**, 2524 (1964).
[29] W. C. Zheng and S. Y. Wu, Spectrochim. Acta A **57**, 1177 (2001).
[30] A. B. P. Lever, Inorganic Electronic Spectroscopy, Elsevier Science Publishers, Amsterdam 1984.
[31] S. Y. Wu and H. N. Dong, Z. Naturforsch. **59a**, 689 (2004).