

Theoretical study of the electron paramagnetic resonance parameters and local structure for the tetragonal Ir^{2+} centre in NaCl

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MS received 7 July 2009; accepted 24 November 2009

Abstract. The electron paramagnetic resonance (EPR) parameters (the g factors, hyperfine structure constants and the superhyperfine parameters) for the tetragonal Ir^{2+} centre in NaCl are theoretically investigated from the perturbation formulas of these parameters for a $5d^7$ ion in tetragonally elongated octahedra. This impurity centre is attributed to the substitutional $[\text{IrCl}_6]^{4-}$ cluster on host Na^+ site, associated with the 4% relative elongation along the C_4 -axis due to the Jahn–Teller effect. Despite the ionicity of host NaCl, the $[\text{IrCl}_6]^{4-}$ cluster still exhibits moderate covalency and then the ligand orbital and spin-orbit coupling contributions should be taken into account. In addition, the theoretical EPR parameters based on the Jahn–Teller elongation show good agreement with the observed values.

Keywords. Electron paramagnetic resonance; crystal- and ligand-field theory; Ir^{2+} ; NaCl.

PACS Nos 76.30.He; 71.70.Ch; 75.10.Dg; 71.70.Ej

1. Introduction

Sodium chloride (NaCl) single crystal, which can be successfully grown from both the melt and solution state, is usually regarded as a model system to study the structural properties of transition-metal dopants. Particularly, NaCl crystals containing iridium exhibit unique optical [1,2] and catalytic [3] properties and hot corrosion resistance [4]. Generally, these properties are closely related to the local structures and electronic states of the dopants in this material, which can be conveniently investigated by means of electron paramagnetic resonance (EPR). In general, EPR studies of transition-metal ions in NaCl are largely confined to the first ($3d^n$) and second ($4d^n$) groups [5–7], while those on the third group ($5d^n$)

transition-metal ions in this material are relatively fewer. For example, EPR and electron nuclear double resonance (ENDOR) studies were carried out on iridium-doped solution and melt-grown NaCl single crystals after X-ray irradiation at 77 K [8,9], and the EPR parameters (the anisotropic g factors, the hyperfine structure constants and the superhyperfine parameters) were measured for the tetragonal Ir^{2+} centre [8,9]. Up to now, however, the above experimental data have not been theoretically interpreted, and information about the local structure of this impurity centre was not obtained. Normally, such information about defect structure and electronic properties of paramagnetic impurities would be useful to understand the optical properties of NaCl (and other similar halides) doped with transition-metal ions. Even though the host NaCl is a typical ionic crystal, Ir^{2+} in NaCl can exhibit moderate covalency and then the contributions from the ligand orbital and spin-orbit coupling interactions can no longer be neglected, unlike to $3d^n$ ions in NaCl with little covalency. Unlike the conventional $3d^7$ (e.g., Fe^+ , Co^{2+}) ions of high spin ($S = 3/2$) case under weak or intermediate crystal fields in NaCl [10], $\text{Ir}^{2+}(5d^7)$ belongs to the low spin case ($S = 1/2$) under strong crystal fields and may exhibit novel microscopic mechanisms of the EPR spectra. In addition, the Jahn–Teller ion Ir^{2+} can experience the Jahn–Teller effect by means of vibration interaction, and the local lattice (elongation) distortion may strongly affect the local structure of this impurity centre.

Therefore, theoretical investigations on the EPR spectra and the defect structure for the tetragonal Ir^{2+} centre in NaCl are of fundamental and practical significance. In this work, the EPR parameters and the local structure for $\text{NaCl}:\text{Ir}^{2+}$ are quantitatively studied using the perturbation formulas of these parameters for a $5d^7$ ion in tetragonally elongated octahedra. In the calculations, the ligand orbital and spin-orbit coupling contributions as well as the local lattice distortion due to the Jahn–Teller effect are taken into account from the cluster approach in a uniform way.

2. Theory and formulas

In iridium-doped NaCl, a substitutional Ir^{3+} (in K_3IrCl_6) ion on Na^+ site can trap an electron during X-ray irradiation and transform to a paramagnetic Ir^{2+} ion, forming an octahedral $[\text{IrCl}_6]^{4-}$ cluster when charge compensation is far from the impurity centre [8]. For the Jahn–Teller ion Ir^{2+} , the $[\text{IrCl}_6]^{4-}$ cluster may experience Jahn–Teller effect by stretching two $\text{Ir}^{2+}\text{--Cl}^-$ bonds along $[100]$ (or C_4) axis and thus reduce the original ideal octahedron (O_h) to a tetragonally (D_{4h}) elongated one. Interestingly, similar tetragonal elongations of Jahn–Teller nature for the ligand octahedra were also reported for Ir^{2+} in MgO and CaO [11] and the isoelectronic $[\text{RhCl}_6]^{4-}$ clusters in AgCl and NaCl [12,13]. So, the local structure of the studied Ir^{2+} centre can be described as having a relative tetragonal elongation ratio τ along the C_4 -axis.

As regards the $3d^7$ (e.g., Co^{2+} and Fe^+) ions in alike halides, the systems belong to the weak or intermediate crystal fields, with the ground orbital triplet ${}^4T_{1g}(t_{2g}^4e_g^3)$ of high spin $S = 3/2$ [10,14]. An $\text{Ir}^{2+}(5d^7)$ ion in NaCl, however, suffers very strong crystal fields, with the ground orbital doublet ${}^2E_g(t_{2g}^6e_g)$ of low spin $S = 1/2$ (which

can be described as an unpaired electron in e_g state). When the ligand octahedron is tetragonally elongated, the ground 2E_g is separated into two orbital singlets θ (${}^2A_{1g}$) and ε (${}^2B_{1g}$), with the former lying lowest [14–16].

The perturbation formulas of the EPR parameters (g factors and the hyperfine structure constants) for a d^7 ion in tetragonally elongated octahedra were established by considering the metal orbital and spin-orbit coupling contributions [17]. Nevertheless, the contributions from the low symmetrical (tetragonal) crystal fields and the ligand orbitals and spin-orbit coupling coefficient were not taken into account. Thus, the previous work [17] failed to involve the local structure (low symmetrical distortion) and the impurity–ligand orbital admixtures in the calculations of the EPR parameters, which would be no longer suitable for the tetragonal Ir^{2+} centre with moderate covalency. In order to improve the previous studies, the above contributions are included here from the cluster approach. Applying the perturbation procedure similar to that in ref. [17], the formulas of the EPR parameters for a tetragonally elongated $5d^7$ cluster can be expressed as

$$\begin{aligned} g_{\parallel} &= g_s \cos 2\phi + 2k^2 \sin^2 \phi, \\ g_{\perp} &= g_s \cos^2 \phi + \sqrt{6}k^2 \sin 2\phi, \\ A_{\parallel} &= P[-\kappa + 4N/7 - \sqrt{6} \sin 2\phi/7 + 8 \sin^2 \phi/7], \\ A_{\perp} &= P[-\kappa - 2N/7 + 15\sqrt{6} \sin 2\phi/14 - 4 \sin^2 \phi/7], \end{aligned} \quad (1)$$

with

$$tg2\phi = [\sqrt{6}\zeta'/(\zeta/2 - \Delta E)]/2. \quad (2)$$

Here g_s ($=2.0023$) is the spin-only value. P and κ are the dipolar hyperfine structure parameter and the core polarization constant, respectively. ΔE ($= 10Dq - Ds - 10Dt$) is the energy separation between the ground ${}^2A_{1g}$ and the excited 2E_g states. Here Dq is the cubic field parameter and Ds and Dt the tetragonal ones. N is the average covalency factor, characteristic of the covalency of the system. ζ (and ζ') are the spin-orbit coupling coefficients, denoting the anisotropic contributions of the effective spin-orbit coupling operator for the studied $5d^7$ cluster. Similarly, k (and k') are the orbital reduction factors arising from the anisotropic interactions of the orbital angular momentum operator. From the cluster approach, the spin-orbit coupling coefficients and the orbital reduction factors may be explicitly described as the diagonal and off-diagonal elements for the spin-orbit coupling and orbital angular momentum operators within the cubic irreducible representations γ ($= t_{2g}$ and e_g , labelled as t and e, respectively, hereafter). They are determined as follows [18]:

$$\begin{aligned} \zeta &= N_t(\zeta_d^0 + \lambda_t^2 \zeta_p^0/2), \quad \zeta' = (N_t N_e)^{1/2}(\zeta_d^0 - \lambda_t \lambda_e \zeta_p^0/2), \\ k &= N_t(1 + \lambda_t^2/2), \quad k' = (N_t N_e)^{1/2}[1 - \lambda_t(\lambda_e + \lambda_s A)/2], \end{aligned} \quad (3)$$

where ζ_d^0 and ζ_p^0 are the spin-orbit coupling coefficients of the free $5d^7$ and ligand ions, respectively. N_γ and λ_γ (or λ_s) are, respectively, the normalization factors and the orbital admixture coefficients. A stands for the integral $R\langle ns|\partial/\partial y|np_y\rangle$ and R is the impurity–ligand (or reference) distance in the studied Ir^{2+} centre.

The molecular orbital coefficients N_γ and λ_γ (or λ_s) are usually obtained from the normalization conditions [18]

$$\begin{aligned} N_t(1 - 2\lambda_t S_{dpt} + \lambda_t^2) &= 1, \\ N_e(1 - 2\lambda_e S_{dpe} - 2\lambda_s S_{ds} + \lambda_e^2 + \lambda_s^2) &= 1 \end{aligned} \quad (4)$$

and the approximate relationships [18]

$$\begin{aligned} N^2 &= N_t^2[1 + \lambda_t^2 S_{dpt}^2 - 2\lambda_t S_{dpt}], \\ N^2 &= N_e^2[1 + \lambda_e^2 S_{dpe}^2 + \lambda_s^2 S_{ds}^2 - 2\lambda_e S_{dpe} - 2\lambda_s S_{ds}]. \end{aligned} \quad (5)$$

Here $S_{dp\gamma}$ (and S_{ds}) are the group overlap integrals between the impurity and ligand orbitals with the same γ irreducible representations. In general, the orbital admixture coefficients increase with increasing group overlap integrals, and we can reasonably use the proportional relationship $\rho\lambda_e/S_{dpe} \approx \lambda_s/S_{ds}$ for the same irreducible representation e_g . Here the proportionality factor ρ is usually taken as an adjustable parameter.

Compared to g factors and hyperfine structure constants, the superhyperfine parameters are relatively less investigated. Since superhyperfine parameters arise from the interactions between the unpaired electrons of a paramagnetic ion and the nuclear spin of ligands, study of these parameters can reveal useful information for spin states and electronic structures of paramagnetic impurities in crystals. In the previous study on superhyperfine parameters for low spin d^7 (e.g., Rh^{2+} with the $4d^7$ configuration) ions in crystals [19], the ligand unpaired spin densities were usually obtained by fitting the experimental superhyperfine parameters and failed to correlate with the covalency (or impurity–ligand orbital admixture) of the systems. In addition, the contributions from the ligand $p\sigma$ orbitals and the dipole–dipole interactions were not sufficiently considered. Thus, the previous calculations of the superhyperfine parameters may be improved here by applying the cluster approach and including the above contributions. The formulas of the superhyperfine parameters for an elongated $5d^7$ cluster can be expressed as follows:

$$\begin{aligned} A' &= A_s + 2A_\sigma + 2(1 - \lambda_e^2) \left[1 + \frac{12\langle r^2 \rangle}{(7R^2)} + \frac{30\langle r^4 \rangle}{(7R^4)} \right] A_D, \\ B' &= A_s - A_\sigma - (1 - \lambda_e^2) \left[1 + \frac{12\langle r^2 \rangle}{(7R^2)} + \frac{30\langle r^4 \rangle}{(7R^4)} \right] A_D. \end{aligned} \quad (6)$$

Here A_s denotes the isotropic contributions arising from the ligand $3s$ orbitals. A_σ and A_D stand for the anisotropic contributions due to the admixture between the impurity $5d$ and ligand $3p$ orbitals and the dipole–dipole interactions between the metal electron and ligand nucleus, respectively. $\langle r^n \rangle$ ($n = 2, 4$) are the expectation values of the square and the quartic of the $Ir^{2+} 5d^7$ radial wave function. With the proportionality factor ρ , the unpaired spin densities are determined from the relevant molecular orbital coefficients based on the cluster approach:

$$f_s \approx \alpha \frac{(1 - \mu^2)}{4}, \quad f_\sigma \approx \frac{\alpha\mu^2}{4}. \quad (7)$$

Here $\mu = S_{\text{dpe}}/(S_{\text{dpe}}^2 + \rho^2 S_{\text{ds}}^2)^{1/2}$ is characteristic of the ligand p-s hybridization and $\alpha = N_e^{1/2} \lambda_e / \mu$ denotes mainly the influence of the covalency effect.

The isotropic and anisotropic parts of the superhyperfine parameters can be further expressed as follows [20]:

$$A_s = f_s A_s^0, \quad A_\sigma = f_\sigma A_p^0, \quad A_D = \frac{g\beta g_n \beta_n}{R^3}. \quad (8)$$

Here f_s and f_σ are the unpaired spin densities for the ligand 3s and 3p σ orbitals, respectively. $A_s^0 = (8\pi/3)g_s\mu_B g_n \mu_n |\phi(0)|^2$ and $A_p^0 = g_s\mu_B g_n \mu_n \langle r^{-3} \rangle_{3p}$ are the related nuclear parameters for the Cl⁻ ligand. Here g_n is the nuclear g value. μ_B and μ_n are the electron Bohr magneton and nuclear magneton. $\phi(0)$ is the wave function of the chlorine 3s orbital at the nucleus. $\langle r^{-3} \rangle_{3p}$ is the expectation value of the inverse cube of the chlorine 3p radial wave function. For the dipole-dipole interaction term, the g factor is usually taken as the average $[(g_{\parallel} + 2g_{\perp})/3]$ of those in eq. (1).

The tetragonal field parameters can be determined from the superposition model [21] and the local geometry of the [IrCl₆]⁴⁻ cluster in terms of the Jahn-Teller elongation ratio τ :

$$Ds \approx (4/7)\bar{A}_2[(1 - \tau)^{-t_2} - (1 + 2\tau)^{-t_2}], \\ Dt \approx (16/21)\bar{A}_4[(1 - \tau)^{-t_4} - (1 + 2\tau)^{-t_4}]. \quad (9)$$

Here t_2 (≈ 3) and t_4 (≈ 5) are the power-law exponents [21]. \bar{A}_2 and \bar{A}_4 are the intrinsic parameters. For transition-metal ions in octahedra, the relationships $\bar{A}_4 \approx (3/4)Dq$ and $\bar{A}_2 \approx 10.8\bar{A}_4$ have been proved as valid rules in many crystals [21-23] and are reasonably applied here. Equation (9) reveals that the EPR parameters, particularly the anisotropy Δg ($= g_{\perp} - g_{\parallel}$), are connected with the tetragonal field parameters and hence with the local structure of the impurity centre.

Considering the difference between the ionic radius r_i (≈ 0.97 Å, extrapolated from those for Ir⁴⁺ and Ir³⁺ [24]) of the impurity Ir²⁺ and the radius r_h (≈ 1.16 Å [24]) of the host Na⁺, the reference distance R can be unlike the host cation-anion distance R_H (≈ 2.82 Å [25]) in pure NaCl. Utilizing the empirical relationship $R \approx R_H + (r_i - r_h)/2$ for an impurity ion in crystals [26], the reference distance $R \approx 2.725$ Å is calculated for NaCl:Ir²⁺ here. From the optical spectra for Ir²⁺ in chlorides [27,28], $Dq \approx 2030$ and $N \approx 0.825$ may be determined for NaCl:Ir²⁺. From the distance R and the Slater-type self-consistent field (SCF) wave functions [29,30], the group overlap integrals $S_{\text{dpt}} \approx 0.0054$, $S_{\text{dpe}} \approx 0.0202$, $S_{\text{ds}} \approx 0.0098$ and $A \approx 1.3766$ are obtained. Thus, the molecular orbital coefficients can be determined from eqs (4) and (5), provided the proportionality factor ρ is known. Using the free-ion values $\zeta_d^0 \approx 4056$ cm⁻¹ [31] for Ir²⁺ and $\zeta_p^0 \approx 587$ cm⁻¹ [32] for Cl⁻, the spin-orbit coupling coefficients and the orbital reduction factors can be acquired from eq. (3). The dipolar hyperfine structure parameter $P \approx -35.7 \times 10^{-4}$ cm⁻¹ for Ir²⁺ [33]. The core polarization constant is usually obtained from the relationship $\kappa = -2\chi/(3\langle r^{-3} \rangle)$ [17]. Here χ is characteristic of the density of unpaired spins at the nucleus of the central ion, and $\langle r^{-3} \rangle$ is the expectation value of the inverse cube of the Ir²⁺ 5d radial wave function in crystals (which can be expressed as the corresponding free-ion value $\langle r^{-3} \rangle_0$ multiplying the covalency factor N). Thus, the

Table 1. The g factors, the hyperfine structure constants and the superhyperfine parameters (in 10^{-4} cm^{-1}) for the tetragonal Ir^{2+} centre in NaCl.

	g_{\parallel}	g_{\perp}	A_{\parallel}	A_{\perp}	A'	B'
Cal. ^a	1.838	2.683	56.2	78.4	–	–
Cal. ^b	1.860	2.864	56.2	78.0	27.2	12.1
Expt. [8,9]	1.867; 1.866(1)	2.866; 2.868(1)	51.0; 48.4	81.1; 82.4	27.0; 28.0	12.0; 12.0

^aCalculations of the g factors and the hyperfine structure constants based on omission of the ligand contributions (similar to those in the previous work [17]).

^bCalculations based on the improved formulas (eqs (1) and (6)) considering the ligand orbital and spin-orbit coupling contributions from the cluster approach.

value $\kappa \approx 1.2$ is obtained for $\text{NaCl}:\text{Ir}^{2+}$ from $\langle r^{-3} \rangle_0 \approx 10.5$ a.u. [33] for Ir^{2+} and $\chi \approx -15$ a.u. [17] for $5d^n$ ions. In the calculations of the superhyperfine parameters, the expectation values $\langle r^2 \rangle$ and $\langle r^4 \rangle$ for Ir^{2+} are 2.890 and 14.416 a.u., respectively [31]. The nuclear parameters are $A_s^0 \approx 1555.7 \times 10^{-4}$ and $A_p^0 \approx 46.7 \times 10^{-4} \text{ cm}^{-1}$ for the Cl^- ligand [34].

There are only two unknown parameters (the relative tetragonal elongation ratio τ and the proportionality factor ρ) in the formulas of the EPR parameters. Substituting the related values into eqs (1) and (6) and matching the theoretical results to the experimental data, one can obtain

$$\tau \approx 4\%, \quad \rho \approx 0.72. \quad (10)$$

The corresponding results (Cal.^b) are given in table 1. The related molecular orbital coefficients are $N_t \approx 0.827$, $N_e \approx 0.834$, $\lambda_t \approx 0.463$, $\lambda_e \approx 0.422$ and $\lambda_s \approx 0.148$. The spin-orbit coupling coefficients $\zeta \approx 3407 \text{ cm}^{-1}$, $\zeta' \approx 3321 \text{ cm}^{-1}$ and the orbital reduction factors $k \approx 0.916$ and $k' \approx 0.710$ can also be obtained. In order to analyse the importance of the covalency (ligand contributions), the calculated g factors and the hyperfine structure constants (Cal.^a) based on omission of the ligand contributions are listed in table 1.

3. Discussion

Table 1 reveals that the theoretical results (Cal.^b) based on the relative tetragonal elongation ratio τ show good agreement with the experimental data, suggesting that the model and formulas as well as the related parameters adopted in this work can be regarded as reasonable. Meanwhile, the information about the impurity local structure is also obtained for $\text{NaCl}:\text{Ir}^{2+}$, i.e., the tetragonal elongation ratio (4%) due to the Jahn–Teller nature.

(1) The relative tetragonal elongation ratio τ ($\approx 4\%$) due to the Jahn–Teller effect attributes the dominant contribution to the low symmetrical distortion of the impurity centre, corresponding to the large anisotropy Δg (~ 1). Similar tetragonal

elongations of the ligand octahedra due to the Jahn–Teller effect were also reported for Ir^{2+} in MgO and CaO [11] and the isoelectronic Rh^{2+} in AgCl and NaCl [12,13]. It seems that Ir^{2+} prefers to experience tetragonal elongation distortion of the Jahn–Teller nature and exhibits positive Δg in octahedra. Moreover, the relative elongation ratio τ ($\approx 4\%$) for Ir^{2+} in NaCl is close to but slightly larger than that ($\approx 3\%$) for the isoelectronic Rh^{2+} centres in NaCl [13] and LiH [35] and can be regarded as suitable. In detail, the relaxation of 0.22 \AA for the parallel $\text{Ir}^{2+}\text{--Cl}^-$ bonds (related to the reference distance R) in $\text{NaCl}:\text{Ir}^{2+}$ obtained in this work is comparable with but larger than that ($\approx 0.15 \text{ \AA}$, with $R \approx 2.532 \text{ \AA}$ [13]) in $\text{NaCl}:\text{Rh}^{2+}$. This can be ascribed to the longer reference distance ($\approx 2.725 \text{ \AA}$) and hence weaker bonding (or lower force constant) in the former. Therefore, the Ir^{2+} centre in NaCl assigned to a tetragonally elongated octahedron due to the Jahn–Teller effect is theoretically verified in the present study. In addition, the charge compensation (e.g., cation vacancy) is regarded as far from the impurity centre, and its influence on the local structure around Ir^{2+} in NaCl may be negligible.

(2) The g factors and the hyperfine structure constants (Cal.^b) based on the ligand orbital and spin-orbit coupling contributions are in better agreement with the experimental data than those (Cal.^a) based on omission of these contributions. From eqs (1) and (3), when the ligand contributions are neglected, the theoretical g factors, the anisotropy Δg and the average of the g factors are smaller than the experimental data and cannot be simultaneously compensated by fitting the relative tetragonal elongation ratio τ . According to eqs (1) and (9), modification of the tetragonal field parameters based on τ has influence only on Δg , whereas the magnitudes or average of the g factors are insensitive to the tetragonal distortion. The importance of the ligand contributions depends mainly upon the moderate covalency (impurity–ligand orbital admixture) in $\text{NaCl}:\text{Ir}^{2+}$, characterized as the covalency factor N ($\approx 0.825 < 1$) and the orbital admixture coefficients ($\approx 0.15\text{--}0.46$) based on the cluster approach. Therefore, the formulas of the g factors including the ligand contributions in the present work seem more applicable to $5d^7$ ions in crystals. In contrast, the hyperfine structure constants are almost irrelevant to the covalency or ligand contributions, since they originate mainly from the dominant isotropic contributions due to the core polarization constant κ (see eq. (1)).

(3) Based on the calculations, the proportionality factor ρ ($\approx 0.72 < 1$) suggests a decrease by 30% for the ratio λ_s/S_s as compared with λ_e/S_e . In fact, the admixture of the Ir^{2+} $5d$ orbital with the Cl^- $3s$ orbital should be less than that with the Cl^- $3p$ orbital, since the $3s$ orbital is normally more compact than the $3p$ orbital for the same ligand. Thus, the above decrease in the $5d\text{--}3s$ orbital admixture can be understood. On the other hand, the present treatments on the superhyperfine parameters based on the proportionality factor ρ are also more convenient than the previous studies based on fitting the experimental data with three adjustable molecular orbital coefficients [19].

4. Summary

The EPR parameters and the local structure for the tetragonal Ir^{2+} centre in NaCl are theoretically studied from the perturbation formulas based on the cluster

approach. The $[\text{IrCl}_6]^{4-}$ cluster is found to experience 4% relative elongation along the C_4 -axis due to the Jahn–Teller effect. The ligand orbital and spin-orbit coupling contributions should be taken into account in view of the moderate covalency of the system.

Acknowledgement

This work was supported by the Support Program for Academic Excellence of UESTC.

References

- [1] F Callens, H Vrielinck and P Matthys, *Radiat. Eff. Def. Sol.* **158**, 11 (2003)
- [2] K Sabbe, H Vrielinck, F Callens and D V Broucke, *J. Phys.: Condens. Matter* **12**, 10611 (2000)
- [3] G Rupprechter, K Hayek and M Jose-Yacamann, *Thin Solid Films* **206**, 148 (1995)
- [4] Y N Wu and A Yamaguchi, *Mater. Trans.* **47**, 1981 (2006)
- [5] M Zdravkova, H Vrielinck, F Callens and E Boesman, *J. Appl. Phys.* **82**, 2476 (1997)
- [6] F Callens, H Vrielinck and P Matthys, *J. Appl. Phys.* **84**, 422 (1998)
- [7] H Vercammen, D Schoemaker, H Kass, E Goovaerts and A Bouwen, *J. Appl. Phys.* **84**, 428 (1998)
- [8] N V Vugman and N M Pinhal, *Mol. Phys.* **38**, 1999 (1979)
- [9] M Zdravkova, K Sabbe, F Callens, E Dobbeleir and P Matthys, *Imag. Sci. J.* **47**, 63 (1999)
- [10] M Narayana, V S Sivasankar and S Radhakrishna, *Phys. Status Solidi* **B105**, 11 (1981)
- [11] J T Suss, A Raizman and W Low, *Phys. Rev.* **15**, 5184 (1977)
- [12] H Vrielinck, K Sabbe, F Callens, P Matthys and D Vandebroucke, *Spectrochim. Acta* **A6**, 319 (2000)
- [13] M T Barriuso, P G Fernandez, J A Aramburu and M Moreno, *Solid State Commun.* **120**, 1 (2001)
- [14] A Abragam and B Bleaney, *Electron paramagnetic resonance of transition ions* (Oxford University Press, London, 1970)
- [15] R Lacroix, U Hochli and K A Muller, *Helv. Phys. Acta* **37**, 627 (1964)
- [16] Y Tanabe and S Sugano, *J. Phys. Soc. Jpn* **9**, 753 (1954)
- [17] B R McGarvey, *J. Phys. Chem.* **71**, 51 (1967)
- [18] J S Yao, S Y Wu, X Y Gao and H M Zhang, *Hyperfine Interact.* **174**, 103 (2007)
- [19] R S Eachus and R E Graves, *J. Chem. Phys.* **65**, 1530 (1976)
- [20] J Owen and J H M Thornley, *Rep. Prog. Phys.* **29**, 675 (1966)
- [21] D J Newman and B Ng, *Rep. Prog. Phys.* **52**, 699 (1989)
- [22] D J Newman, D C Pryce and W A Runciman, *Am. Mineral.* **63**, 1278 (1978)
- [23] Z Y Yang, C Rudowicz and Y Y Yeung, *Physica* **B348**, 151 (2004)
- [24] R D Shannon, *Acta Crystallogr.* **A32**, 751 (1976)
- [25] R C Weast, *CRC handbook of chemistry and physics* (CRC Press, Boca Raton, 1989), p. B196
- [26] M Moreno, M T Barriuso and J A Aramburu, *Appl. Magn. Reson.* **3**, 283 (1992)

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- [27] C K Jorgensen, *Absorption spectra and chemical bonding in complexes*, 2nd ed. (Pergamon Press, Oxford, 1964)
- [28] C K Jorgensen, private communications
- [29] E Clementi and D L Raimondi, *J. Chem. Phys.* **38**, 2686 (1963)
- [30] E Clementi, D L Raimondi and W P Reinhardt, *J. Chem. Phys.* **47**, 1300 (1967)
- [31] C A Morrison, *Crystal field for transition metal ions in laser host materials* (Springer, Berlin, 1992)
- [32] G L McPerson, R C Kach and G D Stucky, *J. Chem. Phys.* **60**, 1424 (1974)
- [33] J A McMillan and T Halpern, *Adv. Inorg. Chem. Radiochem.* **13**, 135 (1970)
- [34] R S Eachus and R E Graves, *J. Chem. Phys.* **61**, 2860 (1974); **65**, 1530 (1976)
- [35] G C Abell and R C Bowman Jr, *J. Chem. Phys.* **70**, 2611 (1979)