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SPIN-LATTICE RELAXATION TIME FOR A $3d^5$ ION IN T_d SYMMETRY IN THE RAMAN REGION

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Résumé. — On a calculé, pour un ion $3d^5$ en symétrie T_d , le temps de relaxation spin-réseau dû au processus Raman, en tenant compte du terme linéaire en rotation $\mathcal{U}_{1R}$ et du terme quadratique en vibration $\mathcal{U}_{2V}$. Les coefficients $\mathcal{U}_{\alpha\beta}$ ont été déterminés pour un ion $3d^n$. Une estimation pour l'ion Mn^{2+} dans ZnS cubique montre que la valeur de $1/T_1$ est 1,2 fois plus grande que celle obtenue en négligeant les termes précédents. On montre aussi qu'il n'y a que deux probabilités de transition indépendantes pour un ion $3d^5$.

Abstract. — The spin-lattice relaxation time for the Raman process has been calculated for a $3d^5$ ion in T_d symmetry. Both $\mathcal{U}_{1R}$ and $\mathcal{U}_{2V}$, the rotational linear and vibrational quadratic terms have been accounted for. The $\mathcal{U}_{\alpha\beta}$ coefficients have been determined for a $3d^n$ ion. An estimate for the Mn^{2+} ion in cubic ZnS shows that the value of $1/T_1$ is 1.2 times greater than that obtained neglecting $\mathcal{U}_{1R}$ and $\mathcal{U}_{2V}$. We also show that there are two independent transitions probabilities for a $3d^5$ ion.

1. **Introduction.** — The determination of the spin-lattice relaxation time T_1 for a paramagnetic ion in a diamagnetic crystal is generally made using Van Vleck's model [1]. The magnetic ion is submitted to the crystal field of the nearest neighbours only, and these ions are considered as constituting a molecule. The displacements of the atoms transform according to a reducible representation D :

$$D = D_V \oplus D_R \oplus D_T$$

where D_V , D_R and D_T correspond respectively to the vibrational, rotational and translational modes.

The spin-lattice interaction is written :

$$\mathcal{U} = \mathcal{U}_1 + \mathcal{U}_2 + \dots = \sum_{\alpha} \mathcal{U}_{\alpha} Q_{\alpha} + \sum_{\alpha, \beta} \mathcal{U}_{\alpha\beta} Q_{\alpha} Q_{\beta} + \dots,$$

Q_{α} being a normal coordinate.

Generally one considers only the vibrational modes in the calculation of T_1 . Moreover, for the Raman process, the quadratic term $\mathcal{U}_2$ is neglected. A calculation of T_1 in the Raman region for Mn^{2+} in cubic ZnS has been made previously [2] with the above simplifications. These may be responsible for the discrepancy between experimental and calculated values of T_1 .

The vibrational and rotational normal coordinates are respectively functions of

$$\varepsilon_{ij} = \frac{1}{2} \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right)$$

with $i, j, k = x, y, z$, and

$$\omega_{ij} = \frac{1}{2} \left(\frac{\partial u_i}{\partial x_j} - \frac{\partial u_j}{\partial x_i} \right) = \pm \theta_k, \quad k \neq i \text{ and } j;$$

+ if i, j, k in cyclic order. The $\{u_i\}$ are the displacement components of the point with coordinates $\{x_i\}$. The linear operator $\mathcal{U}_1$ is the sum of a vibrational term $\mathcal{U}_{1V}$ and a rotational one $\mathcal{U}_{1R}$.

A. Abragam *et al.* [3] have calculated $\mathcal{U}_{1R}$ using the expression :

$$\mathcal{U}_{1R} = \sum_k -i\theta_k [L_k, V_c]$$

L_k is the k th component of the electronic orbital momentum of the ion and V_c is the crystal field operator. The contribution of $\mathcal{U}_{1R}$ to T_1 in ZnS : Mn^{2+} will be studied in section 2.

K. W. H. Stevens has estimated ρ , the ratio of the probabilities induced by $\mathcal{U}_{1V}$ and $\mathcal{U}_{2V}$ [4] :

$$\rho = \frac{|\langle \mathcal{U}_{\alpha V} \rangle|^2 |\langle \mathcal{U}_{\beta V} \rangle|^2}{\Delta^2} : |\langle \mathcal{U}_{\alpha\beta V} \rangle|^2$$

(*) E.R.A. n° 375.

$\langle \mathcal{U}_{\alpha V} \rangle$ and $\langle \mathcal{U}_{\alpha \beta V} \rangle$ are matrix elements of $\mathcal{U}_{\alpha V}$ and $\mathcal{U}_{\alpha \beta V}$, Δ is the energy separation between the ground and intermediate states. Stevens points out that when Δ is a crystal field splitting

$$R \langle \mathcal{U}_{\alpha V} \rangle \sim R^2 \langle \mathcal{U}_{\alpha \beta V} \rangle \sim \Delta$$

(R distance between magnetic ion and ligand). The two contributions are then of the same magnitude. He observes that in numerous iron-group ions, the crystal field leads to an orbital degeneracy of the ground state. This degeneracy is split by the low symmetry component of the crystal and/or by the spin-orbit coupling. In these cases, $\Delta \ll R \langle \mathcal{U}_{\alpha V} \rangle$ and $R^2 \langle \mathcal{U}_{\alpha \beta V} \rangle$, it is then reasonable to neglect the quadratic term. The previous argument does not apply to the $3d^5$ ions (Mn^{2+} , Fe^{3+} , Co^{2+}), which possess an S ground state, so for these ions we may expect $\rho \sim 1$. In section 3, we determine the $\mathcal{U}_{\alpha \beta V}$ coefficients and the spin-lattice transition probabilities for a $3d^5$ ion (T_d symmetry), and make a numerical estimate of T_1 for $\text{ZnS} : \text{Mn}^{2+}$.

In both cases we take the applied magnetic field $\mathbf{H} \parallel [001]$.

2. Contribution of the rotational term. — In the case of four nearest-neighbours with T_d symmetry, D_V is reducible :

$$D_V = A_1 \oplus E \oplus 2 T_2 \quad (1)$$

and D_R has T_1 symmetry. We choose the basis for T_2 representations in such a way that for a homogeneous deformation of the molecule around the paramagnetic ion, the symmetry coordinate of one T_2 representation be zero. The expression of the normal coordinates with this choice and using a real basis for the non-zero T_2 representation has been given previously [2]. We determine the transition probability W for a $3d^5$ ion. We use for the states and energies the notations of [2]. The operator $\mathcal{U}_1$ cannot induce transitions between $|^6A_1, M_S\rangle$ and $|^6A_1, M_{S-K}\rangle$. We must consider the perturbed wave functions $|^6A'_1, M_{S-K}\rangle$ which contain an admixture of the $|^4T_{1i}\rangle$ excited states through the spin-orbit interaction. Since $\mathcal{U}$ does not change the spin multiplicity, the intermediate states to be considered are the $|^4T_1, M_T\rangle$ states. The calculation is made using a Debye model (velocities V_L and V_T) and the fact that the two angular frequencies ω and ω' occurring in the Raman process are such that :

$$g\beta H \ll \omega, \omega' \ll E(^4T_1) - E(^6A'_1).$$

Because of the orthogonality of the normal coordinates, W breaks into three terms : W_{VV} and W_{RR} which are the probabilities obtained neglecting $\mathcal{U}_{1R}$ or $\mathcal{U}_{1V}$; and W_{VR} which corresponds to the cross

product of $\mathcal{U}_{1V}$ and $\mathcal{U}_{1R}$. The following integrals occur frequently in the calculations :

$$\int \frac{d\Omega}{4\pi} |\langle N_i + 1 | \mathcal{A} | N_i \rangle|^2 = (N_i + 1) \left(\frac{\hbar}{2 M \omega_{ks}} \right) k_s^2 \bar{f}_{s,\mathcal{A}} \quad (2)$$

M is the crystal mass.

If $\mathcal{A}$ is a vibrational normal coordinate :

$$\bar{f}_L = \frac{8}{45} R^2, \quad \bar{f}_{T_1} + \bar{f}_{T_2} = \frac{3}{2} \bar{f}_L \quad (3a)$$

except for Q_{A_1} , where

$$\bar{f}_L = \frac{4}{9} R^2, \quad \bar{f}_{T_1} + \bar{f}_{T_2} = 0 \quad (3b)$$

Since the relaxation is dominated by the transitions involving transverse phonons, we have neglected this mode.

If

$$\mathcal{A} = \theta_k, \quad \bar{f}_L = 0, \quad \bar{f}_{T_1} + \bar{f}_{T_2} = \frac{1}{6}. \quad (3c)$$

Straightforward calculations lead to :

$$W_{5/2 \rightarrow 3/2} = 10 \xi^4 C [g_1 p^2 + g_2 p q + g_3 q^2] \quad (4)$$

where

$$C = \left(\frac{kT}{\hbar} \right)^7 \frac{I_6(\theta_D/T)}{4 \pi^3 \rho^2}$$

I_6 is the Debye integral of sixth order, ρ the crystal density and ξ the spin-orbit coupling constant :

$$p = \left(\frac{1}{V_L^5} + \frac{3}{2} \frac{1}{V_T^5} \right) \frac{8 R^2}{45} \quad \text{and} \quad q = \frac{1}{6 V_T^5}$$

$W_{5/2 \rightarrow 1/2}$ is obtained from (4) by replacing 10 by 5/2 and g_1, g_2, g_3 by g'_1, g'_2, g'_3 ; g_1 and g'_1 are given in [2], the others are expressed in appendix.

Detailed calculations lead to the following relations for the three probabilities W_{VV} , W_{RR} and W_{VR} .

$$\begin{aligned} W_{3/2 \rightarrow 1/2} &= \frac{2}{5} W_{5/2 \rightarrow 3/2} & W_{3/2 \rightarrow -1/2} &= \frac{9}{5} W_{5/2 \rightarrow 1/2} \\ W_{M_S \rightarrow M_S - K} &= W_{-M_S + K \rightarrow -M_S} \\ W_{1/2 \rightarrow -1/2} &= 0 \quad (\text{Van Vleck's cancellation}). \end{aligned} \quad (5)$$

We have made a numerical estimate of the W 's for Mn^{2+} in cubic ZnS , using for the constants the values given in [2]. We obtain :

$$\begin{aligned} W_{5/2 \rightarrow 3/2} &= 6.6 \times 10^{-11} T^7 I_6(\theta_D/T) = \\ &= 2.1 W_{5/2 \rightarrow 1/2}. \end{aligned} \quad (6a)$$

Assuming a spin-temperature we find

$$\frac{1}{T_1} = 5.2 \times 10^{-11} T^7 I_6(\theta_D/T). \quad (6b)$$

These values are 1.2 times greater than these obtained neglecting the rotational operator $\mathcal{V}_{1R}$ and still shorter than the experimental value :

$$\frac{1}{T_1} = 8.8 \times 10^{-10} T^7 I_6(168/T) (T_{1\text{sec}}, TK).$$

3. Determination of the contribution of $\mathcal{V}_{2V}$ to T_1 . — The results of section 2 suggest that the contribution of the rotational quadratic term $\mathcal{V}_{2R}$ should be negligible compared to that of the vibrational quadratic term $\mathcal{V}_{2V}$. We first determine the operator $\mathcal{V}_{2V}$, and then its contribution to the transition probability. Because of the orthogonality of the normal coordinates, $\mathcal{V}_{2V}$ leads to a change in W_{VV} only.

We wish to determine

$$\mathcal{V}_{\alpha\beta} = \frac{1}{2} \sum_i \left(\frac{\partial^2 V(i)}{\partial Q_\alpha \partial Q_\beta} \right)_0 = \sum_i \mathcal{V}_{\alpha\beta}(i)$$

where the derivatives are taken at the equilibrium positions of the atoms, $V(i)$ is the potential energy of a 3d electron in the crystal field, the summation is over the 3d electrons, and the subscript V has been omitted for sake of brevity. We use for E and T₂ a real basis $\{ Q_e, Q_\theta, Q_{T_{2\epsilon}}, Q_{T_{2\eta}}, Q_{T_{2\zeta}} \}$.

If $\{ Q_\alpha Q_\beta \}$ is a set of $Q_\alpha Q_\beta$ products transforming according to $\Gamma_a \otimes \Gamma_b$, the corresponding operators $\mathcal{V}_{\alpha\beta}$ transform according to $\Gamma_a^* \otimes \Gamma_b^*$, which in our case is identical with $\Gamma_a \otimes \Gamma_b$. Since $\mathcal{V}_{\alpha\beta} = \mathcal{V}_{\beta\alpha}$, the operators which do not respect this symmetry do not appear in the decomposition of $\Gamma_a \otimes \Gamma_b$ into irreducible representations of T_d . There is therefore, no A_2 operator in the decomposition of $E \otimes E$, nor T_1 in the decomposition of $T_2 \otimes T_2$. For instance, we need only determine $\mathcal{V}_{ee}, \mathcal{V}_{\theta\eta}, \mathcal{V}_{\zeta\zeta}, \mathcal{V}_{\zeta\eta}$; the other operators will then be easily determined using Clebsch-Gordan coefficients given by Griffith [5]. We have

$$V(i) = \sum_j V(i, j)$$

$$V(i, j) = ee_{\text{eff}} [(X_0 + x - \alpha_j - X_j)^2 + (Y_0 + y - \beta_j - Y_j)^2 + (Z_0 + z - \gamma_j - Z_j)^2]^{-1/2}. \quad (7)$$

The charges of the electron and of the ligand, e and e_{eff} , are algebraic quantities. The coordinates of the nuclei at their equilibrium positions are (0, 0, 0) for the paramagnetic atom, and $(\alpha_j, \beta_j, \gamma_j)$ for ligand j . The components of the displacement of the nuclei are X_0, Y_0, Z_0 for the central atom and X_j, Y_j, Z_j for ligand j . The second derivatives $\frac{\partial^2 V(i)}{\partial Q_\alpha \partial Q_\beta}$ are obtained making use of the following properties :

— The symmetry coordinates are linear functions of the displacements and are related to them by a unitary real matrix.

— The coordinates of E and T₂ types are not functions of X_0, Y_0, Z_0 .

— $V(i)$ is a sum of one ligand operators $V(i, j)$:

$$\frac{\partial^2 V(i)}{\partial Q_\alpha \partial Q_\beta} = \sum_{j=1}^4 \left[\frac{\partial^2 V(i, j)}{\partial X_j^2} \frac{\partial X_j}{\partial Q_\alpha} \frac{\partial X_j}{\partial Q_\beta} + \dots \right] + \left[\frac{\partial^2 V(i, j)}{\partial X_j \partial Y_j} \left(\frac{\partial X_j}{\partial Q_\alpha} \frac{\partial Y_j}{\partial Q_\beta} + \frac{\partial Y_j}{\partial Q_\alpha} \frac{\partial X_j}{\partial Q_\beta} \right) + \dots \right]. \quad (8)$$

In expression (8), α and β may be distinct or not, and the dots indicate similar terms in Y_j^2 and Z_j^2 , and in $Y_j Z_j$ and $Z_j X_j$.

We determined the values of the derivatives versus the atomic displacements, at the equilibrium positions, with the method used by Hutchings [6] in the crystal field problem.

The operators $\mathcal{V}_{\alpha\beta}(i)$ thus obtained are then expressed in terms of the operators

$$D_q^{(k)}(i) = \sqrt{\frac{4\pi}{2k+1}} Y_l^m(\theta_i, \Phi_i) r_i^k$$

where θ_i, Φ_i, r_i are the coordinates of electron i and Y_l^m is a spherical harmonic (we chose the phase convention prescribed by Condon and Shortley [7]). The operators $\mathcal{V}_{\alpha\beta}$ are deduced from the $\mathcal{V}_{\alpha\beta}(i)$, replacing the operators $D_q^{(k)}(i)$ by $D_q^{(k)} = \sum_i D_q^{(k)}(i)$,

where the sum is over the 3d electrons. For a 3dⁿ ion in T_d symmetry :

$$\begin{aligned} \mathcal{V}_{ee} &= -\frac{ee_{\text{eff}}}{2R^3} A_1^{(0)} - 6\alpha' E_\theta^{(2)} + \\ &\quad + 5\sqrt{21}\beta' A_1^{(4)} + 4\sqrt{15}\beta' E_\theta^{(4)} \\ \mathcal{V}_{\theta\eta} &= 6\sqrt{2}\alpha'(T_{21}^{(2)} + T_{2-1}^{(2)}) - \frac{3\sqrt{30}}{4}\beta' \times \\ &\quad \times [-\sqrt{7}(T_{11}^{(4)} + T_{1-1}^{(4)}) + (T_{21}^{(4)} + T_{2-1}^{(4)})] \end{aligned} \quad (9)$$

$$\begin{aligned} \mathcal{V}_{\zeta\zeta} &= \frac{ee_{\text{eff}}}{2R^3} A_1^{(0)} + 34\alpha' E^{(2)} - \\ &\quad - \beta'[5\sqrt{21}A_1^{(4)} - 4\sqrt{15}E_\theta^{(4)}] \\ \mathcal{V}_{\zeta\eta} &= -\frac{i74}{\sqrt{3}}\alpha' T_{20}^{(2)} - i8\sqrt{5}\beta' T_{20}^{(4)} \end{aligned}$$

where

$$\alpha' = \frac{ee_{\text{eff}}}{12R^5}, \quad \beta' = \frac{ee_{\text{eff}}}{6R^7}.$$

The symmetry adapted operators $A_1^{(0)}, A_1^{(k)}, E_\theta^{(k)}, T_{1i}^{(k)}, T_{2i}^{(k)}$ ($i = 1, 0, -1; k = 2, 4$) are obtained replacing $|k, q\rangle$ by $D_q^{(k)}$ in the expressions given in table A.19 of ref. [5].

Under the same assumptions as made in section 2,

the transition probabilities $W_{5/2 \rightarrow 3/2_{VV}}$ and $W_{5/2 \rightarrow 1/2_{VV}}$ are now :

$$W_{5/2 \rightarrow 3/2_{VV}} = 10 \xi^4 C[h_1^2 + h_2^2] p^2 \quad (10a)$$

$$W_{5/2 \rightarrow 1/2_{VV}} = \frac{5}{2} \xi^4 C[2(h_3^2 + h_4^2) + h_5^2 + h_1^2] p^2 \quad (10b)$$

the expressions of the h_i are given in appendix.

The relations (5) still hold for W_{VV} because the total contribution of the operators with T_1 symmetry vanishes.

The numerical values of $W_{5/2 \rightarrow 3/2_{VV}}$ and $W_{5/2 \rightarrow 1/2_{VV}}$ for Mn^{2+} in cubic ZnS are :

$$\begin{aligned} W_{5/2 \rightarrow 3/2_{VV}} &= 6.1 \times 10^{-11} T^7 I_6(\theta_D/T) = \\ &= 2.3 W_{5/2 \rightarrow 1/2_{VV}}. \end{aligned} \quad (11)$$

Finally, the values of $W_{5/2 \rightarrow 3/2}$, $W_{5/2 \rightarrow 1/2}$, $1/T_1$ are respectively 8 %, 1 % and 2 % greater than those obtained neglecting the quadratic operator $\mathcal{U}_{2V}$.

4. Conclusion. — In this paper, an attempt has been made to obtain a better agreement between experimental and theoretical values of the relaxation

time T_1 for Mn^{2+} in cubic ZnS in the Raman region. In the expansion of the spin-lattice interaction $\mathcal{U}$ into normal coordinates, we have considered both $\mathcal{U}_{1R}$ (rotational linear term) and $\mathcal{U}_{2V}$ (vibrational quadratic term). The method of Abragam *et al.* allowed the determination of the matrix elements of $\mathcal{U}_{1R}$. We have found the $\mathcal{U}_{\alpha\beta}$ operators, the coefficients occurring in $\mathcal{U}_{2V}$ for a $3d^n$ ion in T_d symmetry. The decomposition of $\mathcal{U}_{\alpha\beta}$ into irreducible operators does respect the relation $\mathcal{U}_{\alpha\beta} = \mathcal{U}_{\beta\alpha}$.

For ZnS : Mn^{2+} , the contribution of $\mathcal{U}_{1R}$ and $\mathcal{U}_{2V}$ is minor, T_1 being shorter by a factor 1.2 and still longer than the experimental value. This difference may come from the crudeness of the point charge model and the Debye approximation.

We found relations between transition probabilities $W_{M_S \rightarrow M_S - K}$ which are the same for both the linear and quadratic terms. These relations still hold for the direct process (though we used the dynamic spin Hamiltonian) [2]. This suggests that this property comes from the symmetry of the problem. The fact that there are only two independent probabilities could help in the interpretation of further continuous saturation measurements.

Appendix. — The three eigenstates transforming as T_1 and T_2 are written :

$$\begin{aligned} |^4T_{1i}, M_T\rangle &= \alpha_i |^4P^4T_1, M_T\rangle + \beta_i |^4F^4T_1, M_T\rangle + \gamma_i |^4G^4T_1, M_T\rangle \\ |^4T_{2i}, M_T\rangle &= \alpha'_i |^4D^4T_2, M_T\rangle + \beta'_i |^4F^4T_2, M_T\rangle + \gamma'_i |^4G^4T_2, M_T\rangle \end{aligned}$$

where $M = 1, 0, -1$, $i = 1, 2, 3$,

$$\Delta_i = E(^4T_{1i}) - E(^6A'_1), \quad \Delta'_i = E(^4T_{2i}) - E(^6A'_1), \quad \Delta_G = E(G^4E) - E(^6A'_1)$$

We put

$$p_{\alpha\beta} = \sum_i \frac{\alpha_i \beta_i}{\Delta_i}, \quad k_{\alpha\beta} = \sum_i \alpha_i \beta_i \Delta_i, \quad k'_{\alpha\beta} = \sum_i \alpha'_i \beta'_i \Delta'_i$$

We make the correspondence $\alpha\alpha, \beta\beta, \gamma\gamma, \beta\gamma, \gamma\alpha, \alpha\beta \rightarrow 1 \dots 6$.

The g values are following :

$$\begin{aligned} g_2 &= p_5^2 \left\{ \left[\frac{\delta' r^4}{3} (14 p_1 + 8 p_6) \right]^2 + \frac{4}{15} \left[\frac{30}{7} \alpha r^2 p_6 + \beta r^4 \left(p_1 - \frac{11}{7} p_6 \right) \right]^2 + \right. \\ &\quad \left. + \frac{4}{49} \left[\sqrt{30} \delta r^2 p_6 + \delta' r^4 \left(7 p_1 + \frac{2}{3} p_6 \right) \right]^2 + \frac{1}{5} \left[\frac{15}{7} \alpha r^2 p_6 + \beta r^4 \left(\frac{4}{3} p_1 - \frac{8}{7} p_6 \right) \right]^2 \right\} \\ g_3 &= \left[p_1 - p_1^2 k_1 - \frac{9}{4} p_6^2 k_2 + \frac{1}{4} p_5^2 k_3 + 3 p_1 p_6 k_6 - p_1 p_5 k_5 + \frac{3}{2} p_5 p_6 k_4 + \right. \\ &\quad \left. + \frac{15}{4} p_6^2 k'_2 + \frac{\sqrt{105}}{2} p_5 p_6 k'_4 + \frac{7}{4} p_5^2 k'_3 + 2 p_5^2 \Delta_G \right] \\ g'_2 &= 4 p_5^2 \left\{ \left[\frac{\sqrt{30}}{14} \delta r^2 p_6 - \delta' r^4 \left(3 p_1 - \frac{2}{7} p_6 \right) \right]^2 + \left[\frac{\sqrt{15}}{7} \alpha r^2 p_6 + \beta r^4 \left(\frac{2}{\sqrt{15}} p_1 - \frac{22}{7 \sqrt{15}} p_6 \right) \right]^2 + \right. \\ &\quad \left. + \left[\frac{\sqrt{30}}{7} \delta r^2 p_6 + \frac{2}{3} \delta' r^4 (p_1 + 2 p_6) \right]^2 + \left[\frac{\sqrt{30}}{14} \delta r^2 p_6 + \frac{5}{3} \delta' r^4 \left(p_1 + \frac{10}{7} p_6 \right) \right]^2 \right\} \\ g'_3 &= 2 \left\{ \left[\frac{15}{4} p_6^2 k'_2 + 7 p_5^2 \left(\frac{k'_3}{4} - \Delta_G \right) \right]^2 + (9 p_5^2 \Delta_G)^2 \right\}. \end{aligned}$$

The reduced matrix elements $\langle {}^4T_1 \parallel \mathcal{V}_F^{(l)} \parallel {}^4T_1 \rangle$, where $\mathcal{V}_F^{(l)}$ is a symmetry-adapted operator occurring in (9), are related through the Clebsch-Gordan coefficients to the following quantities :

$$\begin{aligned} N_{1ij} &= \langle T_{10}^i | T_{1-1}^{(4)} | T_{11}^j \rangle = \left[\frac{1}{6\sqrt{7}} (\gamma_i \alpha_j - \alpha_i \gamma_j) - \frac{1}{3\sqrt{7}} (\beta_i \gamma_j - \beta_j \gamma_i) \right] \overline{r^4} \\ N_{2ij} &= \langle T_{10}^i | T_{21}^{(2)} | T_{11}^j \rangle = -\frac{\sqrt{15}}{14} (\beta_i \gamma_j + \gamma_i \beta_j) \overline{r^2} \\ N_{3ij} &= \langle T_{10}^i | T_{21}^{(4)} | T_{11}^j \rangle = \frac{1}{6} \left[(\alpha_i \gamma_j + \gamma_i \alpha_j) + \frac{4}{7} (\beta_i \gamma_j + \gamma_i \beta_j) \right] \overline{r^4} \\ N_{4ij} &= \langle T_{1-1}^i | E_e^{(4)} | T_{11}^j \rangle = \frac{1}{6} \left[2(\alpha_i \gamma_j + \gamma_i \alpha_j) - (\beta_i \gamma_j + \gamma_i \beta_j) \right] \overline{r^4} \\ N_{5ij} &= \langle T_{1-1}^i | E_e^{(2)} | T_{11}^j \rangle = 0. \end{aligned}$$

The D_m are defined by :

$$\begin{aligned} D_m &= \sum_{i,j} \frac{\alpha_i \alpha_j}{\Delta_i \Delta_j} N_{mij} \quad m = 1, \dots, 5 \\ D_1 &= D_5 = 0, \quad D_2 = -\frac{\sqrt{15}}{7} p_{\alpha\beta} p_{\alpha\gamma} \overline{r^2} \\ D_3 &= \frac{1}{3} p_{\alpha\gamma} \left(p_{\alpha\alpha} + \frac{4}{7} p_{\alpha\beta} \right) \overline{r^4}, \quad D_4 = \frac{1}{3} p_{\alpha\gamma} (2 p_{\alpha\alpha} - p_{\alpha\beta}) \overline{r^4}. \\ h_1 &= (C_1 - \sqrt{3} C_2) - (c'_2 D_2 + c'_4 D_3) \\ h_2 &= \left(C_3 - C_4 + C_5 - \frac{C_6}{2} \right) - \frac{1}{\sqrt{2}} (c_2 D_2 + c_4 D_3) \\ h_3 &= \left(-\frac{3}{4} C_6 + C_3 \right) + \frac{1}{\sqrt{2}} (b_4 D_4 - c_2 D_2 - c_4 D_3) \\ h_4 &= \left(C_5 - \frac{1}{4} C_6 + C_4 \right) + \frac{1}{\sqrt{2}} (b_4 D_4 + c_2 D_2 + c_4 D_3) \\ h_5 &= \frac{\sqrt{3}}{2} (-C_7 + C_8) + \frac{b'_4}{\sqrt{2}} D_4 \\ c_2 &= \frac{-74\sqrt{6}}{3} \alpha' \quad b_4 = -6\sqrt{10} \beta' \quad c_4 = -8\sqrt{10} \beta' \\ c'_2 &= -24 \alpha' \quad b'_4 = 4\sqrt{30} \beta' \quad c'_4 = 3\sqrt{15} \beta' \end{aligned}$$

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