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RELAXATION STUDY OF A $3d^5$ ION IN T_d SYMMETRY : Mn^{2+} in ZnS

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Résumé. — On a étudié la relaxation de l'ion Mn^{2+} dans ZnS cubique entre 1,3 et 135 K, à 9,3 GHz, par une technique d'impulsion saturante. A basse température, la variation du signal de retour à l'équilibre en fonction de la durée de l'impulsion saturante montre que le système acquiert une température de spin avant de relaxer. Le processus de diffusion qui maintient cette température de spin ne dépend pas de la température ; il a une constante de temps $T_D = 0,5$ ms. Des études complémentaires avec une technique de balayage rapide en champ magnétique confirment que l'ensemble des 30 raies R.P.E. acquiert une température de spin. Quand $T < 10$ K, la relaxation est assurée par un processus direct et $T_1 T = 1,18$ Ks. Quand $T_1 > 10$ K, on observe un processus Raman $\left(\frac{1}{T_1} \propto T^7 I_6 \left(\frac{168}{T}\right)\right)$. Dans le cas du processus direct, un hamiltonien dynamique, établi

à partir de mesures sous contrainte uniaxiale, rend bien compte de la relaxation. Une détermination de la contribution Raman à la relaxation a été effectuée avec le modèle des modes normaux de vibration de Van Vleck ; elle fournit une valeur de T_1 qui est d'un ordre de grandeur supérieure à la valeur expérimentale. Dans les deux cas, les phonons transverses sont les plus efficaces.

Abstract. — The relaxation behaviour of Mn^{2+} in cubic ZnS has been studied between 1.3 and 135 K, at 9.3 GHz, with a pulse saturation method. At low temperatures, the variation of the recovery signal with the saturating pulse duration indicates that the system acquires a spin-temperature before relaxing. The diffusion process maintaining the spin-temperature is temperature independent and has a time constant $T_D = 0.5$ ms. Complementary studies using a fast field sweep technique confirm that the whole system of 30 EPR lines acquires a spin temperature. When $T < 10$ K, relaxation takes place via a direct process, and $T_1 T = 1.18$ Ks. When $T_1 > 10$ K, we observe a Raman process $\left(\frac{1}{T_1} \propto T^7 I_6 \left(\frac{168}{T}\right)\right)$. In the case of the direct process, relaxation is well described by a

dynamic hamiltonian deduced from uniaxial stress measurements. A determination of the Raman contribution to relaxation made with Van Vleck's normal mode formalism leads to a T_1 value which is an order of magnitude greater than the experimental value. In both cases transverse phonons are the most efficient.

1. Introduction. — Theoretical studies have shown that several mechanisms may be effective in the relaxation of $3d^5$ ions in an S ground state (Cr^{+} , Mn^{2+} , Fe^{3+}) [1, 2]. Few experimental results are available concerning the relaxation behaviour of Mn^{2+} in cubic ZnS [3]. Some care should be taken when studying this system because stacking faults are often present and give rise to complex E.S.R. spectra [4]. The necessary information about the crystal structure and spin hamiltonian is given in section 2.

In section 3, we describe the experimental devices. We give a brief description of the systems which permit easy variation of the saturating pulse duration and fast field sweeping after saturation of a definite transition. These devices were used to elucidate the relaxation mechanisms.

The experimental results for the relaxation of Mn^{2+} in cubic ZnS in the temperature range 1.3-135 K are given in section 4. The variation of T_1 versus T is reported. Furthermore, we establish the existence of a temperature-independent diffusion process at low temperatures.

In section 5, we make a determination of the spin-

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lattice relaxation time for both the direct and Raman processes. We study the direct process with a dynamic hamiltonian where the spin-lattice coefficients G_{ijkl} are deduced from static measurements. We examine the Raman process according to Van Vleck's normal mode formalism. We discuss theoretical and experimental results.

2. Crystal structure. Spin hamiltonian. — The lattice is f.c.c. The basis contains one Zn atom (0, 0, 0) and one S atom ($a/4, a/4, a/4$ with $a = 5.41 \text{ \AA}$). The crystal may be viewed as resulting from the packing of double layers along the $[111]_w$ direction (packing axis). This is noted $A\alpha B\beta C\gamma$, where A, B, C refer to Zn atoms, α, β, γ to S atoms. Stacking faults are often present in cubic ZnS. They give rise to different Mn^{2+} E.S.R. spectra : if the crystal field is considered to be due to the 1st, 2nd and 3rd nearest neighbours (n.n) only, and if it is remarked that for any sequence of layers the 1st n.n of a Mn^{2+} ion always form a regular tetrahedron, the 2nd n.n form a prism (P) or anti-prism (N), and there is a single (S) or no (N) 3rd n.n on the stacking axis, then only four distinct sites may exist. They are called AN, AS, PN, PS [4]. The symmetry is T_d for AN, C_{3v} for the other sites. Since the substitution of the $B\beta$ layer by $C\gamma$ corresponds to a 180° rotation, which does not belong to T_d nor C_{3v} , two homologous centers are obtained for each site AN, AS, PN, PS. The spin hamiltonian is not invariant under this rotation and a splitting of all E.S.R. lines is observed.

Most experiments were done on a synthetic cubic crystal (Eagle Picher Industries, 10^{-4} atom g Zn per ZnS mole). Because of the existence of stacking faults, relaxation was studied mainly for $\mathbf{H} \parallel [111]_w$, where the two cubic systems of lines coalesce (Fig. 1). The axial lines were much weaker than the cubic lines and in the following the presence of the axial sites will be neglected. Measurements were also made on a natural sample of zinc blende (concentration $\approx 5 \times 10^{-6}$ atom g Zn per ZnS mole) without stacking faults, but cross-relaxation with impurities was then present.

The spin hamiltonian coefficients for the cubic site have been derived by Matarese and Kikuchi [5] and Schneider *et al.* [6]. The spin hamiltonian is written :

$$\mathcal{H} = g\beta\mathbf{H}\mathbf{S} + A\mathbf{I}\mathbf{S} + \frac{a}{6} \left[Sx^4 + Sy^4 + Sz^4 - \frac{707}{16} \right]$$

where $S = \frac{5}{2}$, $I = \frac{5}{2}$, g and A are isotropic,

$$g = 2.0025 \pm 0.0002, A = -68.5 \text{ G}, a = +8.42 \text{ G},$$

x, y, z are the cubic axes of the site. Since Zeeman energy $\gg A \gg a$, the eigenstates may be labelled $|M_S, M_I\rangle$, the EPR transitions are

$$|M_S, M_I\rangle \leftrightarrow |M_S - 1, M_I\rangle,$$

and the EPR spectrum consists of six hyperfine groups of five fine structure lines.

FIG. 1. — Geometry for the two homologous cubic centers in ZnS. The crystallographic axes $[100]'$, $[010]'$ and $[001]'$ of one center are obtained by rotating, around the $[111]_w$ axis, the crystallographic axes of the other centers. The parameter of the spin hamiltonian are identical for the two centers.

3. Experimental conditions. — Experiments were done using an X band spectrometer previously described [7]. It uses a superheterodyne detection ($f_{IF} = 30 \text{ Mc/s}$) and a single klystron (Varian V58, 500 mW). Some elements were added to allow low power and pulse measurements. A block diagram of the device is given in figure 2. Low power measurements (10^{-9} W range) were made possible by the introduction of a Yig filter and a transmission cavity between single side-band modulator (S.S.M.) and mixer to filter out residual waves from the modulator. The spurious I.F. voltage at the mixer output was then less than the voltage obtained from a 10^{-10} W r.f. power incident on the signal input. Pulse measurements were made using two fast switching diodes (Microwave Associates MA 83191 X 20A). The two pulses which controlled the saturating and isolating diodes were locked together (Fig. 3). The saturating pulse (duration τ) was initiated a time τ_1 after the beginning of the isolating pulse. Its trailing edge was used to cut off the isolating pulse after a delay τ_2 . We could take τ_1 and $\tau_2 = 0.2$ or $1 \mu\text{s}$; τ could be varied between 10^{-7} and 1 s . The locking allowed easy studies of the influence of the saturating r.f. pulse

FIG. 2. — Block diagram of the superheterodyne single klystron spectrometer used for spin-lattice relaxation time measurements by a pulse saturation technique.

FIG. 3. — The clock generator triggers the bistable and, after a delay τ_1 , monostable 1. The trailing edge from monostable 2 triggers back the bistable after a delay τ_2 .

upon relaxation (only the single parameter τ had to be varied, the mixer being always protected). Moreover, it was possible to observe the E.S.R. signal recovery 0.2 μ s after a saturating pulse of arbitrary duration, for instance 1 s. The switching times of the diodes were in the nanosecond range and introduced no limitation. A four-stage filter was used at the output of the I.F. synchronous detector to allow good I.F. suppression with fast rise time (0.1 μ s).

During pulse experiments, the klystron was frequency-locked to an auxiliary temperature-stabilized cavity (long term stability better than 10 kc/s) to avoid saturation of the I.F. chain. For spin-lattice relaxation time measurements, a cylindrical TE_{011} cavity with $Q_u = 2\,600$ was used. The sample could be rotated around two perpendicular axes and at low temperatures it was immersed in liquid He. Temperatures were measured with an AsGa diode placed near the sample. Studies above 4.2 K were made by letting the whole cryostat warm up (the passage from 5 to 10 K took 4 hours).

Studies with field sweeping were done using a rectangular TE_{012} cavity. Two Helmholtz coils ($\varnothing$ 20 mm, $L = 60\,\mu$ H, with 50 turns of 0.5 mm copper wire) were placed against the cavity walls. Eddy currents were reduced by cutting a slot in the middle of the large face and bottom (at 10^5 c/s, the

modulating field was attenuated by a factor 2). The coils were fed by an electronic device (Fig. 4) which allowed us to create a single sweep of sine wave form at the end of the saturating pulse. We could thus saturate a definite transition without field sweeping; a sweep of large amplitude was moreover possible with neither cavity warming nor helium boiling.

FIG. 4. — Block diagram of the fast field sweep device.

4. Experimental results. — A 0.1 W r.f. pulse was used to saturate the central line of the $M_I = -\frac{1}{2}$ group ($|\frac{1}{2}, -\frac{1}{2}\rangle \leftrightarrow |-\frac{1}{2}, -\frac{1}{2}\rangle$ transition) with $H \parallel [111]_w$: At 4.2 K the analysis of the recovery was made with $P = 10^{-7}$ W. The result was the same with 10^{-8} W and this point was corroborated by C.W. measurements. The dependence of the recovery signal on the duration τ of the saturating pulse, is indicated in figure 5. When $\tau = 10^{-1}$ s, a single exponential is recorded (time constant $T_1 = 0.27$ s). When $\tau = 10^{-4}$ s, the recovery is faster (time constant $T_D = 0.5$ ms). Treatment of the tail end of the signal with a multichannel analyser shows that a second time constant $T_1 = 0.27$ s is still present. For an intermediate τ value ($\tau = 10^{-2}$ s), the two expo-

Fig. 5. — Recovery signal observed for different saturating pulse durations τ ; $T = 4.2$ K, $H \parallel [111]_w$, $P_{\text{sat}} = 10^{-1}$ W, $P_{\text{anal}} = 10^{-7}$ W, time base 0.1 s per large division. Upper curve $\tau = 10^{-1}$ s, middle curve $\tau = 10^{-2}$ s, lower curve $\tau = 10^{-4}$ s.

nentials are of comparable magnitude. The same measurements were made at 1.34 K and the same observations were made, with $T_D = 0.5$ ms independent of temperature, and $T_1 = 0.88$ s. This suggests that T_D is associated with diffusion of energy via temperature independent interactions (dipolar interactions) and T_1 with spin-lattice relaxation. A field sweep after a saturating pulse gives new information. Figure 6 shows the result obtained when satura-

FIG. 6. — Lower curves : Recording of different M_I groups of absorption lines for two saturating pulse durations; $H \parallel [111]_w$, $T = 4.2$ K. $P_{sat} = 10^{-1}$ W, $P_{anal} = 10^{-7}$ W. The upper curve shows how the lines have been recorded.

ting the $|\frac{1}{2}, -\frac{1}{2}\rangle \leftrightarrow |-\frac{1}{2}, -\frac{1}{2}\rangle$ transition and then observing the $M_I = -\frac{1}{2}, -\frac{3}{2}, \frac{1}{2}$ groups and part of the $M_I = -\frac{5}{2}$ group, with a sine wave of 1 ms duration and of 180 G_{pp} magnitude. It was observed that for a pulse duration of $\tau = 0.1$ s, the intensities of all the observed lines are weaker than when $\tau = 10^{-2}$ s. This indicates that for a long pulse duration the system of the thirty E.P.R. lines is partially saturated, the whole system acquiring a spin temperature during the pulse. Figure 7 was obtained with a shorter sweep (10^{-4} s) around the central line of the $M_I = -\frac{1}{2}$ hyperfine group; when τ increases, one observes first the saturation of the central line then, when $\tau \gg T_D$, the saturation of the other lines. All these experiments show that in the low temperature region (defined by $T_1 < T_D$), relaxation takes place in two steps : establishment of a spin temperature for the whole system of the thirty E.P.R. lines, followed by its relaxation. The recovery of a system with $(2S + 1)$ levels and no diffusion effects would take place through $2S$ exponentials. It was verified that

FIG. 7a. — Recording of different $M_S \rightarrow M_S - 1$ transitions of the $M_I = -\frac{1}{2}$ group for several saturating pulse durations. $H \parallel [111]_w$, $T = 4.2$ K.

FIG. 7b. — Figure 7b shows how the absorption lines have been recorded.

no variation occurred when τ was increased from 0.1 s. All the T_1 measurements were thus made with $\tau = 0.1$ s. When $T_1 \geq 1$ ms the signal-to-noise ratio was improved with a multichannel analyser.

The experimental results are shown in figures 8 and 9.

When $T_1 < 10$ K :

$$T_1 T = 1.18 \text{ Ks} \quad (T_1, \text{s}; T \text{ K}). \quad (1)$$

FIG. 8. — Dependence of the spin-lattice relaxation time of Mn²⁺ in ZnS (T_d symmetry) in the temperature range 1.3 K < T < 10 K, **H** // [111]_w, transition $|\frac{1}{2}, -\frac{1}{2}\rangle \rightarrow |-\frac{1}{2}, -\frac{1}{2}\rangle$. These data show a direct process.

When $T_1 > 10$ K, the experimental results are in good agreement with the expression :

$$\frac{1}{T_1} = \frac{T}{1.18} + 8.8 \times 10^{-10} T^7 \times I_6 \left(\frac{168}{T} \right),$$

(T_1 s ; T K) (2)

where

$$I_6(x_0) = \int_0^{x_0} \frac{e^x x^6 dx}{(e^x - 1)^2}.$$

From the numerical expressions of $I_6(x_0)$ [8], we can distinguish three regions corresponding to different temperature ranges :

x_0	$I_6(x_0)$	T K	1/T ₁ dependence
$x_0 > 12$	const.	$T < 14$ K	$1/T_1 = AT + BT^7$
$10 > x_0 > 5$	$I_6 \propto x_0$	$17 \text{ K} < T < 34 \text{ K}$	$1/T_1 = AT + CT^6$; for $T \geq 25$ K
$x_0 \ll 1$	$I_6 \propto x_0^5$	$T \gg 168$ K	$1/T_1 = DT^2$ the direct process is negligible

In the temperature range where the direct process gives no contribution to the spin-lattice relaxation time ($T \geq 25$ K) we studied for **H** // [111]_w the relaxation time of a line ($|\frac{1}{2}, -\frac{3}{2}\rangle \rightarrow |-\frac{5}{2}, -\frac{1}{2}\rangle$ transition) adjacent to the central one

$$(| + \frac{1}{2}, -\frac{1}{2}\rangle \rightarrow | - \frac{1}{2}, -\frac{1}{2}\rangle \text{ transition}).$$

We find that the T_1 values are the same although there is no diffusion effect as it can be checked by our fast field sweep technique.

FIG. 9. — log-log plot of $1/T_1$ versus T for Mn²⁺ in ZnS (T_d symmetry) in the temperature range 1.3 K < T < 134 K. **H** // [111]_w, transition $|\frac{1}{2}, -\frac{1}{2}\rangle \rightarrow |-\frac{1}{2}, -\frac{1}{2}\rangle$. For $T > 20$ K, relaxation is caused by a Raman process. The overall data are described by the following expression :

$$\frac{1}{T_1} = \frac{T}{1.18} + 8.8 \times 10^{-10} T^7 I_6 \left(\frac{168}{T} \right), (T_1 \text{ s}, T \text{ K}).$$

Moreover we studied the central line for **H** parallel to the principal axis of one of the two cubic systems (**H** // [001], Fig. 1). Within a factor 2 we found the same temperature dependence as the central line (Fig. 10). This allows us to make a theoretical determination of T_1 for the Raman process with **H** // [001], where the calculation is easier (cf. § 5).

5. Interpretation of the results. — We have made a theoretical determination of the spin-lattice relaxation

FIG. 10. — log-log plot of $1/T_1$ versus T for Mn^{2+} in ZnS (T_d symmetry) in the temperature range $20 \text{ K} < T < 50 \text{ K}$.

● Transition $|-\frac{3}{2}, -\frac{1}{2}\rangle \rightarrow |-\frac{5}{2}, -\frac{1}{2}\rangle$ for $\mathbf{H} \parallel [111]$, ○ Transition $|\frac{1}{2}, -\frac{1}{2}\rangle \rightarrow |-\frac{1}{2}, -\frac{1}{2}\rangle$ for $\mathbf{H} \parallel [001]$.

time when the system possesses a spin temperature for both direct and Raman processes.

We describe the system by a dynamic spin hamiltonian and interpret the results in terms of the direct process.

We replace the dynamic spin-lattice coupling coefficients by the values obtained from stress measurements [9]. This approximation is justified because only phonons of low frequency contribute to the relaxation process. In terms of the Raman process. It is assumed that one phonon is absorbed and one is emitted. We keep the linear terms of the dynamic part of the crystalline potential, for the contribution of this term is generally more effective than that of the quadratic terms [10].

We first derive the spin lattice relaxation time when there is a spin temperature.

For our system, in the high-temperature range, the

number $N(M_S, M_I)$ of centers in the state $|M_S, M_I\rangle$ is given by :

$$N(M_S, M_I) = \frac{N}{(2S+1)(2I+1)} [1 - M_S \Delta_S] \quad (3)$$

where N is the total number of spins,

$$\Delta_S = \frac{\hbar \omega_0}{k T_S}, \quad \omega_0 = g \beta H,$$

T_S is the spin temperature.

The energy given up to the lattice per unit time, $\dot{E}_L$, is :

$$\dot{E}_L = \hbar \omega_0 \frac{N}{2S+1} (\Delta - \Delta_S) \sum_{K=1}^{2S+1} \sum_{M_S=S}^{-S+K} \times \\ \times K^2 W_{M_S \rightarrow M_S-K} \quad (4a)$$

where

$$\Delta = \frac{\hbar \omega_0}{k T},$$

T is the lattice temperature, $W_{M_S \rightarrow M_S-K}$ is the relaxation transition probability from state $|M_S, M_I\rangle$ to state $|M_S - K, M_I\rangle$. The variation per unit time of the spin system energy, $\dot{U}$, is

$$\dot{U} = \frac{-N}{2S+1} \hbar \omega_0 \sum_{M_S=S}^{-S} (M_S)^2 \dot{\Delta}_S. \quad (4b)$$

Energy conservation leads to :

$$\dot{\Delta}_S = \frac{\Delta - \Delta_S}{T_1} \quad (5)$$

with

$$\frac{1}{T_1} = \frac{3}{S(S+1)(2S+1)} \sum_K \sum_{M_S=S}^{-S+K} \times \\ \times K^2 W_{M_S \rightarrow M_S-K}. \quad (6)$$

5.1 THE DIRECT PROCESS. — The spin lattice relaxation process is described by the dynamic hamiltonian $\mathcal{H}_{SL}$:

$$\mathcal{H}_{SL} = \sum_{ijkl} G_{ij,kl} S_i S_j \varepsilon_{kl} \quad (7)$$

ε_{kl} and $G_{ij,kl}$ are respectively the strain and spin-lattice tensor components.

When a stress is applied to a crystal containing paramagnetic ions, its effects on the E.S.R. spectrum can be described by the following spin-hamiltonian :

$$\mathcal{H}_{\text{stress}} = \sum_{ijkl} C_{ij,kl} S_i S_j \sigma_{kl} \quad (8)$$

σ_{kl} and $C_{ij,kl}$ are the components of two stress tensors. $G_{ij,kl}$ and $C_{ij,kl}$ have the same symmetry properties

as the photoelastic tensors and they are related to each other by the stiffness tensor c_{mnkl} :

$$G_{ij,kl} = \sum_{mn} C_{ij,mn} c_{mnkl} . \quad (9)$$

G_{11} , G_{12} and G_{44} . The tracelessness of the spin-hamiltonian adds a further condition :

$$G_{11} + 2 G_{12} = 0 . \quad (10)$$

The correspondence between the G 's and C 's is :

$$G_{11} = C_{11}(c_{11} - c_{12}) \quad (11)$$

$$G_{44} = C_{44} c_{44} .$$

In the case of T_d symmetry (and using Voigt notation [11]) there are only three independent coefficients,

The detailed expression of $\mathcal{H}_{SL}$ is [19] :

$$\begin{aligned} \mathcal{H}_{SL} = & \frac{G_{11}}{2} \{ [3 S_x^2 - S(S+1)] \varepsilon_{xx} + [3 S_y^2 - S(S+1)] \varepsilon_{yy} + [3 S_z^2 - S(S+1)] \varepsilon_{zz} \} + \\ & + 2 G_{44} \{ (S_y S_z + S_z S_y) \varepsilon_{yz} + (S_z S_x + S_x S_z) \varepsilon_{zx} + (S_x S_y + S_y S_x) \varepsilon_{xy} \} \end{aligned} \quad (12)$$

where

$$\varepsilon_{ij} = \frac{1}{2} \left[\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right] . \quad (13)$$

The (u_i) are the displacement components of the point with coordinates (x_i) . This displacement is analysed in terms of phonon operators :

$$\mathbf{u}(\mathbf{r}) = \sum_{\mathbf{k},s} \left(\frac{\hbar}{2 M \omega_{ks}} \right)^{1/2} \mathbf{e}(\mathbf{k}, s) [a_{ks} e^{i\mathbf{k}\mathbf{r}} + a_{ks}^+ e^{-i\mathbf{k}\mathbf{r}}] \quad (14)$$

with

$$a_{ks}^+ |n_{ks}\rangle = (n_{ks} + 1)^{1/2} |n_{ks} + 1\rangle \quad (15)$$

$\mathbf{e}(\mathbf{k}, s)$ is the unit vector in the direction of polarization of the mode $(\mathbf{k}, s)$, M is the total mass of the crystal.

The transition probability $W_{M_S \rightarrow M_S - K}$ from the state $|M_S, M_I\rangle$ to $|M_S - K, M_I\rangle$ is given by :

$$W_{M_S \rightarrow M_S - K} = \frac{V}{4 \pi^2 \hbar^2} \left[\int_{\mathbf{k}} \sum_{s=L, T_1, T_2} |\langle M_S - K, n_{ks} + 1 | \mathcal{H}_{SL} | M_S, n_{ks} \rangle|^2 \frac{\omega_{ks}^2}{v_s^3} d\Omega \right]_{\omega_{ks} = K \omega_0} \quad (16)$$

where V is the crystal volume,

$$\omega_{ks} = v_s k .$$

L, T_1, T_2 are the three polarizations (longitudinal, transverse), $d\Omega$ is related to the possible $\mathbf{k}$ directions.

The calculation of $W_{M_S \rightarrow M_S - K}$ requires the knowledge of the following quantities :

$$\langle \varepsilon_{ij} \varepsilon_{kl} \rangle_s = \frac{1}{4 \pi} \int \langle n_{ks} + 1 | \varepsilon_{ij} | n_{ks} \rangle \langle n_{ks} | \varepsilon_{kl} | n_{ks} + 1 \rangle d\Omega = k_s^2 \left(\frac{\hbar}{2 M \omega_{ks}} \right) (n_{ks} + 1) \langle f_{ij} f_{kl} \rangle_s . \quad (17)$$

The non-zero terms are :

$$\begin{aligned} \langle f_{ii}^2 \rangle_L &= \frac{1}{5} & \langle f_{ii}^2 \rangle_{T_1} + \langle f_{ii}^2 \rangle_{T_2} &= \frac{2}{15} \\ \langle f_{ij}^2 \rangle_L &= \frac{1}{15} & \langle f_{ij}^2 \rangle_{T_1} + \langle f_{ij}^2 \rangle_{T_2} &= \frac{1}{10} \\ \langle f_{ii} f_{jj} \rangle_L &= \frac{1}{15} & \langle f_{ii} f_{jj} \rangle_{T_1} + \langle f_{ii} f_{jj} \rangle_{T_2} &= -\frac{1}{15} . \end{aligned} \quad (18)$$

The non-zero probabilities ⁽¹⁾ are :

$$W_{M_S \rightarrow M_S - 1} = \frac{1}{2\pi\rho} \frac{(g\beta H)^2}{\hbar^4} kT \left(\frac{1}{v_L^5} + \frac{3}{2} \frac{1}{v_T^5} \right) \cdot \left(M_S - \frac{1}{2} \right)^2 [S(S+1) - M_S(M_S - 1)] \times \\ \times \left[\frac{3}{5} G_{11}^2 p + \frac{8}{15} G_{44}^2 (1 - 2p) \right] \quad (19a)$$

$$W_{M_S \rightarrow M_S - 2} = \frac{1}{2\pi\rho} \frac{(2g\beta H)^2}{\hbar^4} kT \left(\frac{1}{v_L^5} + \frac{3}{2} \frac{1}{v_T^5} \right) [S(S+1) - M_S(M_S - 1)] [S(S+1) - (M_S - 1)(M_S - 2)] \times \\ \times \left[\frac{3}{80} G_{11}^2 (1 - p) + \frac{1}{15} G_{44}^2 (1 + p) \right] \quad (19b)$$

$$v_{T_1} = v_{T_2} = v_T, \quad p = l^2 m^2 + m^2 n^2 + n^2 l^2 \quad (20)$$

where l, m, n are the direction cosines of the applied field $\mathbf{H}$ with the cristalline axes, ρ is the crystal density.

Putting (19) and (20) into (6) leads to the following expression of the spin-lattice relaxation time T_1 :

$$\frac{1}{T_1} = \frac{3(2S-1)(2S+3)}{25\pi\rho\hbar^4} (g\beta H)^2 kT \left(\frac{1}{v_L^5} + \frac{3}{2} \frac{1}{v_T^5} \right) \left[G_{11}^2 + 2G_{44}^2 + \left(\frac{4}{3} G_{44}^2 - \frac{3}{4} G_{11}^2 \right) p \right] \quad (21)$$

our experiments have been done for $\mathbf{H} \parallel [111]_w$. The experimental function gives us a temperature dependence

$$T_1 T = 1.18 \text{ Ks}.$$

Taking $p = \frac{1}{3}$, $\rho = 4.1 \text{ g/cm}^3$, $H = 3300 \text{ G}$, $v_L = 5.8 \times 10^5 \text{ cm/s}$, $v_T = 2.5 \times 10^5 \text{ cm/s}$, $G_{11} = -3.6 \times 10^{-18} \text{ erg}$, $G_{44} = 3.6 \times 10^{-17} \text{ erg}$ (ref. [9]), we have

$$T_1 T = 1.61 \text{ Ks}. \quad (22)$$

This value agrees with the experimental results.

We see that the G_{44}^2 value is much greater than G_{11}^2 so the angular variation is proportional to

$$G_{44}^2 (1 + \frac{2}{3} p).$$

If we compare our results with those of Wagner *et al.* [3] obtained by an adiabatic fast passage method for $\mathbf{H} \parallel [001]$, we find that

$$\frac{\left(\frac{1}{T_1 T} \right)_{\mathbf{H} \parallel [001]}}{\left(\frac{1}{T_1 T} \right)_{\mathbf{H} \parallel [111]_w}} = 0.87.$$

The theoretical value gives 0.82.

These results show that a spin temperature was established in the spin system studied by Wagner *et al.* Moreover they indicate that our model using static spin-lattice coefficients in the determination of the spin-lattice relaxation time is realistic in the case of the direct process.

It is not possible to use the same procedure as above for the Raman process, since no departure from linearity was observed in uniaxial stress measurements [9].

We have also studied a natural crystal of zinc blende. At 4.2 K we found two time constants

$(5 \pm 2 \text{ ms}$ and $20 \pm 5 \text{ ms})$. These constants were independent of the orientation of the applied field $\mathbf{H}$ with respect to the cristalline axes. These features could be explained by supposing that there is cross-relaxation with fast relaxing impurities.

5.2 THE RAMAN PROCESS. — We make a direct determination of the spin-lattice relaxation time for $\mathbf{H} \parallel [001]$, and under the assumption of a spin temperature. Before outlining the explicit calculation of the transition probability $W_{M_S \rightarrow M_S - K}$ from spin state $|M_S\rangle$ to spin state $|M_S - K\rangle$ with one phonon absorbed and one phonon emitted, we discuss the properties of the first excited states of Mn^{2+} in cubic ZnS ; and we then give the expression for the dynamic part V_{OL} of the cristalline field, and the perturbation scheme used.

The allowed terms for a $3d^5$ configuration are 6S , 4P , 4D , 4F , 4G and doublets. The expressions for the quartet eigenstates are given by Slater J. C. A cristalline field of T_d symmetry may split these terms according to the irreducible representations of T_d :

$$\begin{aligned} ^6S &\rightarrow ^6A_1 \\ ^4P &\rightarrow ^4T_1 \\ ^4D &\rightarrow ^4E \oplus ^4T_2 \\ ^4F &\rightarrow ^4A_2 \oplus ^4T_1 \oplus ^4T_2 \\ ^4G &\rightarrow ^4A_1 \oplus ^4E \oplus ^4T_1 \oplus ^4T_2. \end{aligned}$$

The magnitude of the cubic cristalline field V_c and the relative energies of levels 4P , 4D , 4F , 4G

⁽¹⁾ We must point out that there are mistakes in the W 's expressions for W given by Kondo. The final result giving $1/T_1$ is correct.

are comparable, thus one must diagonalize the ⁴E, three eigenstates of V_c which transform as ⁴T₁ are ⁴T₁ and ⁴T₂ matrices in the presence of V_c. The written :

$$|{}^4T_1^i, M_R\rangle = \alpha_i |P\,{}^4T_1, M_R\rangle + \beta_i |F\,{}^4T_1, M_R\rangle + \gamma_i |G\,{}^4T_1, M_R\rangle \tag{23a}$$

where

$$M_R = 1, 0, -1 \quad i = 1, 2, 3 .$$

The expressions of states such as |P ⁴T₁, M⟩ are given by Griffith (ref. [14], A 19). In the same way :

$$|{}^4T_2^i, M_R\rangle = \alpha'_i |D\,{}^4T_2, M_R\rangle + \beta'_i |F\,{}^4T_2, M_R\rangle + \gamma'_i |G\,{}^4T_2, M_R\rangle , \tag{23b}$$

V_c is diagonal inside the ⁴E representation.

The values for α_i, β_i, γ_i, α'_i, β'_i, γ'_i and for the energies E(⁴T₁ⁱ), E(⁴T₂ⁱ), E(D ⁴E), E(G ⁴E), E(F ⁴A₂) are given in appendix 1.

We must finally note that the spin-orbit interaction couples the ground-state |⁶A₁ M_S⟩ to the excited states |⁴T₁, 1⟩, |⁴T₁, 0⟩, |⁴T₁, -1⟩.

The admixed wave-functions are :

$$|{}^6A_1', M_S\rangle = |{}^6A_1, M_S\rangle - \sum_{i=1}^3 \frac{\alpha_i}{\Delta_i} \zeta [a(M_S) |{}^4T_{11}^{(i)}, M_S - 1\rangle + b(M_S) |{}^4T_{1-1}^{(i)}, M_S + 1\rangle + c(M_S) |{}^4T_{10}^{(i)}, M_S\rangle] . \tag{24}$$

The values for a(M_S), b(M_S), c(M_S) are given in [15]; ζ is the spin orbit coupling constant.

The dynamic part V_{OL} of the cristalline field is described with Van Vleck's normal mode model [16]. The XY₄ system of the Mn²⁺ ion and its four sulfur nearest neighbours is shown in figure 11. This system possesses 9 normal coordinates, which are of symmetry A₁, E, T₂. The coordinate with A₁ symmetry does not contribute to our relaxation process, since it does not change M_S. We choose a linear combination of the displacements in such a way that only one of the two T₂ representations contribute to relaxation. We then obtain :

$$\begin{aligned} Q_\theta &= \frac{1}{2\sqrt{6}} [X_1 + X_2 - X_3 - X_4 + Y_1 - Y_2 - Y_3 + Y_4 - 2(Z_1 - Z_2 + Z_3 - Z_4)] \\ Q_\varepsilon &= \frac{1}{2\sqrt{2}} [-X_1 - X_2 + X_3 + X_4 + Y_1 - Y_2 - Y_3 + Y_4] \\ Q_{T_{2\xi}} &= \frac{1}{2\sqrt{2}} [Y_1 - Y_2 + Y_3 - Y_4 + Z_1 - Z_2 - Z_3 + Z_4] \\ Q_{T_{2\eta}} &= \frac{1}{2\sqrt{2}} [X_1 - X_2 + X_3 - X_4 + Z_1 + Z_2 - Z_3 - Z_4] \\ Q_{T_{2\zeta}} &= \frac{1}{2\sqrt{2}} [X_1 - X_2 - X_3 + X_4 + Y_1 + Y_2 - Y_3 - Y_4] \end{aligned} \tag{25}$$

FIG. 11. — Positions of the nearest neighbours of Mn²⁺ with respect to the crystalline axes.

FIG. 12. — Diagram of the perturbation scheme for the Raman process.

where (X_i, Y_i, Z_i) are the displacements of ion i in figure 11. In the case of a homogeneous deformation (appendix 2), and using a complex basis for easier calculations, we obtain :

$$V_{OL} = \sum_{\Gamma, M_\Gamma} V(\Gamma, M_\Gamma) \cdot Q(\Gamma, M_\Gamma)^* \quad (26)$$

with

$$\begin{aligned} Q_\varepsilon^E &= R \sqrt{\frac{2}{3}} (\varepsilon_{22} - \varepsilon_{11}) \\ Q_\theta^E &= \frac{R \sqrt{2}}{3} (\varepsilon_{11} + \varepsilon_{22} - 2 \varepsilon_{33}) \\ Q_{T_{21}} &= \frac{2R}{\sqrt{3}} (\varepsilon_{13} - i \varepsilon_{23}) \\ Q_{T_{20}} &= \frac{i 2 \sqrt{2}}{\sqrt{3}} R \varepsilon_{12} \\ Q_{T_{2-1}} &= \frac{2R}{\sqrt{3}} (\varepsilon_{13} + i \varepsilon_{23}) . \end{aligned} \quad (27)$$

The expressions of the $V(\Gamma, M_\Gamma)$ are given in appendix 3. The normal coordinates are easily analysed in terms of phonon operators using (13), (14) and (27).

The perturbation scheme used is illustrated in figure 12, where :

N_i is the number of phonons in the mode $(\mathbf{k}, s)$, with $\omega_{\mathbf{k},s} = v_s k$,

N_j is the number of phonons in the mode $(\mathbf{k}', s')$, with $\omega_{\mathbf{k}',s'} = v_{s'} k'$;

energy conservation requires that $K\omega_0 = \omega_{\mathbf{k},s} - \omega_{\mathbf{k}',s'}$.

Since V_{OL} does not act on spin, then only $^4\Gamma$ states must be considered.

We obtain from second order perturbation theory, and noting that $\omega_{\mathbf{k},s}, \omega_{\mathbf{k}',s'} \ll |E(^6A_1) - E(^4\Gamma_i)|$:

$$W_{M_S \rightarrow M_S - K} = \frac{2\pi}{\hbar^2} \sum_{\substack{s,s' \\ \mathbf{k},\mathbf{k}'}} \left[\int |A_{ij} + B_{ij}|^2 \left(\frac{V^2}{8\pi^3} \right)^2 \frac{\omega_{\mathbf{k},s}^2 \omega_{\mathbf{k}',s'}^2}{v_s^3 v_{s'}^3} d\Omega d\Omega' d\omega_{\mathbf{k},s} \right]_{\omega_{\mathbf{k}',s'} = \omega_{\mathbf{k},s} - K\omega_0 \sim \omega_{\mathbf{k},s}} \quad (28)$$

with :

$$A_{ij} = \sum_{^4\Gamma_i, M_{\Gamma_i}} \frac{\langle ^6A_1' M_S - K, N_j - 1 | V_{OL} | ^4\Gamma_i M_{\Gamma_i}, N_j \rangle \langle ^4\Gamma_i M_{\Gamma_i}, N_i + 1 | V_{OL} | ^6A_1' M_S, N_i \rangle}{E(^6A_1') - E(^4\Gamma_i)} \quad (29a)$$

$$B_{ij} = \sum_{^4\Gamma_i, M_{\Gamma_i}} \frac{\langle ^6A_1' M_S - K, N_i + 1 | V_{OL} | ^4\Gamma_i M_{\Gamma_i}, N_i \rangle \langle ^4\Gamma_i M_{\Gamma_i}, N_j - 1 | V_{OL} | ^6A_1' M_S, N_j \rangle}{E(^6A_1') - E(^4\Gamma_i)} \quad (29b)$$

$d\Omega$ and $d\Omega'$ are related to the possible $\mathbf{k}$, and $\mathbf{k}'$ directions respectively.

The following integrals occur frequently in the calculation,

$$\int \frac{d\Omega}{4\pi} |\langle N_i + 1 | Q_{\Gamma, M_\Gamma} | N_i \rangle|^2 = (N_i + 1) \left(\frac{\hbar}{2 M \omega_{\mathbf{k},s}} \right) k_s^2 \bar{f}_{s, \Gamma, M_\Gamma} \quad (30)$$

where for any Q_{Γ, M_Γ} :

$$\bar{f}_L = \frac{8}{45} R^2 \quad \bar{f}_{T_1} + \bar{f}_{T_2} = \frac{3}{2} \bar{f}_L . \quad (31)$$

Straightforward calculations lead to the following non zero probabilities :

$$W_{5/2 \rightarrow 3/2} = \left[\zeta^2 c\left(\frac{3}{2}\right) a\left(\frac{5}{2}\right) \right]^2 \left[(C_1 - \sqrt{3} C_2)^2 + \left(C_3 - C_4 + C_5 - \frac{1}{2} C_6 \right)^2 \right] \cdot A \quad (32a)$$

where

$$A = \frac{1}{4\pi^3 \rho^2} \left(\frac{1}{v_L^5} + \frac{3}{2} \frac{1}{v_T^5} \right)^2 \left(\frac{8}{45} R^2 \right)^2 \left(\frac{kT}{\hbar} \right)^7 I_6 \left(\frac{\theta_D}{T} \right) \quad (32b)$$

with

$$I_6(x_0) = \int_0^{x_0} \frac{e^x x^6}{(e^x - 1)^2} dx, \quad v_T = v_{T_1} = v_{T_2},$$

θ_D is the Debye temperature ($\theta_D \ll |E(^6A_1) - E(^4T_1)|$) :

$$W_{5/2 \rightarrow 1/2} = \left[\zeta^2 b\left(\frac{1}{2}\right) a\left(\frac{5}{2}\right) \right]^2 \left\{ (C_1 - \sqrt{3} C_2)^2 + \frac{3}{4} (C_7 - C_8)^2 + \right. \\ \left. + 2 \left[\left(\frac{3}{4} C_6 - C_3 \right)^2 + \left(\frac{1}{4} C_6 - C_5 - C_4 \right)^2 \right] \right\} \cdot A \quad (32c)$$

$$W_{3/2 \rightarrow 1/2} = \frac{2}{5} W_{5/2 \rightarrow 3/2} \quad W_{3/2 \rightarrow -1/2} = \frac{9}{5} W_{5/2 \rightarrow 1/2} \quad W_{M_S \rightarrow M_S - K} = W_{-M_S + K \rightarrow -M_S} \quad W_{1/2 \rightarrow -1/2} = 0$$

(Van Vleck's cancellation ; the T^9 dependence is neglected).

The quantities C_1 to C_8 are related to the matrix elements of the $V(I, M_I)$. Their expression is given in appendix 4.

Using (6) and (32c) we obtain in the spin-temperature range :

$$\frac{1}{T_1} = \frac{4}{25} [W_{5/2 \rightarrow 3/2} + 8 W_{5/2 \rightarrow 1/2}]. \quad (33)$$

This expression is, strictly speaking, only valid when $T_1 < T_D$. However, when T increases and T_1 becomes greater than T_D , the gradual variation of the coefficients in the linear combination given by (33), is hidden by the far more important variation of the transition probabilities with temperature.

In our case

$$\zeta = 300 \text{ cm}^{-1}, \quad c\left(\frac{3}{2}\right) a\left(\frac{5}{2}\right) = \sqrt{10}, \\ b\left(\frac{1}{2}\right) a\left(\frac{5}{2}\right) = \frac{\sqrt{10}}{2}, \quad R = 2.34 \text{ Å}, \\ 10 D_q = 4200 \text{ cm}^{-1} [17];$$

we take

$$\frac{\langle r^4 \rangle}{\langle r^2 \rangle} = 5 a_0^2 \quad \text{with} \quad a_0 = 0.528 \text{ Å} [18].$$

After a numerical calculation of the C_i we obtain with the previous values for ρ , v_L , v_T :

$$W_{5/2 \rightarrow 3/2} = 5.6 \times 10^{-11} T^7 I_6 \left(\frac{\theta_D}{T} \right) = \\ = 2.1 W_{5/2 \rightarrow 1/2}, \quad (34)$$

$$\frac{1}{T_1} = 4.3 \times 10^{-11} T^7 I_6 \left(\frac{\theta_D}{T} \right) \quad (T_1 \text{ s}, T \text{ K}). \quad (35)$$

Remembering the complexity of the problem, which compels us to several approximations (point-charge model, linear dispersion law, use of two mean velocities v_L and v_T) we may conclude that the theoretical and experimental results are in fairly good

agreement. Our treatment also shows that the relaxation process is mainly due to transverse phonons ($v_T^{-5} \gg v_L^{-5}$). K. Kunc in his thesis [19] shows that the density of states of cubic ZnS for acoustic transverse phonon modes falls off in the vicinity of $T = 170$ K. This temperature compares favourably with the value of 168 K which occurs in the I_6 integral.

We must finally note that Orbach and Blume [21] have shown that for an ion with a quenched orbital moment, a Raman process can take place between states of the ground level. In that case the relaxation rate follows a T^5 temperature dependence. This process is more effective than the T^7 Raman one when the temperature is such that $kT < \zeta^2/\Delta$ (Δ is the energy of the first excited state). In our case ($\zeta = 300 \text{ cm}^{-1}$, $\Delta = 18000 \text{ cm}^{-1}$), this condition is satisfied when $T < 7$ K. We have not observed such a law experimentally in this temperature range because the main contribution comes from the direct process.

6. Conclusion. — Our experiments show that at low temperatures ($T < 20$ K), the whole system acquires a spin-temperature through a temperature independent diffusion process. When $T < 10$ K, the relaxation takes place via a direct process. When $T > 10$ K, we have a Raman process

$$\left(\frac{1}{T_1} \propto T^7 I_6 \left(\frac{168}{T} \right) \right),$$

with slight orientation dependence. Use of the static spin-lattice coefficients instead of the dynamic ones for the direct process is satisfactory. The calculation of the Raman process from first principles gives a value which is an order of magnitude greater than the experimental one. In both case transverse phonons are the most efficient.

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Appendix 1. — [20].

α_i	β_i	γ_i	$\Delta_i = E(^4T_1) - E(^6A_1) \text{ cm}^{-1}$	α'_i	β'_i	γ'_i	$\Delta'_i = E(^4T_2) - E(^6A_1) \text{ cm}^{-1}$
-0.60	0.09	0.79	18 420	-0.14	0.22	0.97	20 870
-0.05	0.99	-0.15	35 180	0.28	0.94	-0.17	36 360
0.80	0.13	0.59	26 150	0.95	-0.25	0.19	25 040
$\Delta_D = E(D^4E) - E(^6A_1) = 25\,880 \text{ cm}^{-1}$				$\Delta_F = E(F^4A_2) - E(^6A_1) = 34\,890 \text{ cm}^{-1}$			
$\Delta_G = E(G^4E) - E(^6A_1) = 21\,500 \text{ cm}^{-1}$							

Appendix 2. — For a homogenous deformation :

$$X_i = \varepsilon_{xx} x_i + \varepsilon_{xy} y_i + \varepsilon_{xz} z_i ,$$

$$Y_i = \varepsilon_{xy} x_i + \varepsilon_{yy} y_i + \varepsilon_{zy} z_i ,$$

$$Z_i = \varepsilon_{xz} x_i + \varepsilon_{yz} y_i + \varepsilon_{zz} z_i ,$$

(x_i, y_i, z_i) are the coordinates of atom i at its equilibrium position ;

(X_i, Y_i, Z_i) are the coordinates of its displacement from this position.

Appendix 3. — Taking into account the first neighbours only, and using Van Vleck's point charge model, we get

$$V(\Gamma, M_\Gamma) = \sum_i V_i(\Gamma, M_\Gamma)$$

(the sum is over the electrons), where :

$$\begin{aligned}
 V_i(E, \theta) &= \alpha D_0^{(2)} + \beta \left[\frac{\sqrt{7}}{\sqrt{10}} (D_{-4}^{(4)} + D_4^{(4)}) - D_0^{(4)} \right] \\
 V_i(E, \varepsilon) &= \frac{\alpha}{\sqrt{2}} [D_{-2}^{(2)} + D_2^{(2)}] + \frac{\sqrt{6}}{\sqrt{5}} \beta [D_{-2}^{(4)} + D_2^{(4)}] \\
 V_i(T_{21}) &= \sqrt{2} \delta D_{-1}^{(2)} + \sqrt{2} \delta' [D_{-1}^{(4)} - \sqrt{7} D_3^{(4)}] \\
 V_i(T_{20}) &= \delta [D_2^{(2)} - D_{-2}^{(2)}] + 2 \sqrt{2} \delta' [D_{-2}^{(4)} - D_2^{(4)}] \\
 V_i(T_{2-1}) &= -\sqrt{2} \delta D_1^{(2)} + \sqrt{2} \delta' [\sqrt{7} D_{-3}^{(4)} - D_1^{(4)}] \\
 \alpha &= -\frac{2\sqrt{2} |ee_{\text{eff}}|}{R^4}, \quad \beta = -\frac{10\sqrt{2} |ee_{\text{eff}}|}{9 R^6} \\
 \delta &= -\frac{4 |ee_{\text{eff}}|}{3 R^4}, \quad \delta' = \frac{5\sqrt{5} |ee_{\text{eff}}|}{3\sqrt{6} R^6} \\
 10 D_q &= -\frac{20 |ee_{\text{eff}}|}{27 R^5} \langle r^4 \rangle, \quad D_q^{(k)} = \sqrt{4 \Pi/2 k + 1} r_i^k Y_k^q(\theta_i, \varphi_i).
 \end{aligned}$$

Appendix 4. — In the calculation (Raman process) use is made of the reduced matrix elements

$$\langle {}^4\Gamma_i | V_R | {}^4\Gamma_j \rangle ,$$

which are related through the Clebsch-Gordan coefficients (ref. [14], A 20) to the following quantities :

$$\begin{aligned}
 M_{1ij} &= \langle T_{10}^{(i)} | V(E, \theta) | T_{10}^{(j)} \rangle = \frac{-2\beta \langle r^4 \rangle}{3\sqrt{5}} [2(\alpha_i \gamma_j + \gamma_i \alpha_j) - (\beta_i \gamma_j + \gamma_i \beta_j)] \\
 M_{2ij} &= \langle T_{10}^{(i)} | V(E, \varepsilon) | T_{20}^{(j)} \rangle = -\frac{2\alpha \langle r^2 \rangle}{7\sqrt{35}} [7\alpha_i \alpha'_j + 4\beta_i \alpha'_j + 5\sqrt{3}\beta_i \gamma'_j + \sqrt{35}\gamma_i \beta'_j] - \\
 &\quad - \frac{2\beta \langle r^4 \rangle}{7\sqrt{105}} [14\alpha_i \gamma'_j + 10\sqrt{3}\beta_i \alpha'_j + 13\beta_i \gamma'_j - \sqrt{105}\gamma_i \beta'_j] \\
 M_{3ij} &= \langle {}^4A_2 | V(T_{20}) | T_{10}^{(i)} \rangle = \frac{2\sqrt{2}}{7} \delta \gamma_i \langle r^2 \rangle + \frac{4}{7} \sqrt{\frac{5}{3}} \delta' \gamma_i \langle r^4 \rangle
 \end{aligned}$$

$$\begin{aligned}
M_{4i} &= \langle E_g(D) | V(T_{20}) | T_{10}^{(i)} \rangle = -\frac{2\sqrt{2}\delta\langle r^2 \rangle}{\sqrt{35}} \left(\alpha_i + \frac{4}{7}\beta_i \right) + \frac{40}{7\sqrt{21}} \beta_i \delta' \langle r^4 \rangle \\
M_{5i} &= \langle E_g(G) | V(T_{20}) | T_{10}^{(i)} \rangle = -\frac{2}{7} \sqrt{\frac{30}{7}} \delta \langle r^2 \rangle \beta_i + \frac{4\delta' \langle r^4 \rangle}{3\sqrt{7}} \left(2\alpha_i + \frac{13}{7}\beta_i \right) \\
M_{6ij} &= \langle T_{1-1}^{(i)} | V(T_{20}) | T_{11}^{(j)} \rangle = \frac{\sqrt{15}\delta\langle r^2 \rangle}{7\sqrt{2}} (\beta_i \gamma_j + \gamma_i \beta_j) + \frac{2\delta' \langle r^4 \rangle}{3} \left[(\alpha_i \gamma_j + \gamma_i \alpha_j) + \frac{4}{7} (\beta_i \gamma_j + \gamma_i \beta_j) \right] \\
M_{7ij} &= \langle T_{2,1}^{(i)} | V(T_{20}) | T_{1,1}^{(j)} \rangle = \delta \langle r^2 \rangle \left[\sqrt{\frac{2}{35}} \alpha'_i \left(-\alpha_j + \frac{16}{7}\beta_j \right) - \frac{3}{7\sqrt{2}} \beta'_i \gamma_j + \frac{\sqrt{15}}{7\sqrt{14}} \gamma'_i \beta_j \right] + \\
&\quad + \delta' \langle r^4 \rangle \left[-\frac{10}{7\sqrt{21}} \alpha'_i \beta_j + \frac{4\sqrt{5}}{7\sqrt{3}} \beta'_i \gamma_j - \frac{10}{3\sqrt{7}} \gamma'_i \left(\alpha_j + \frac{2}{7}\beta_j \right) \right].
\end{aligned}$$

In the following definition of the C_i , there occurs the quantity $a_{ik} = \alpha_i \alpha_k / \Delta_i \Delta_k$:

$$\begin{aligned}
C_1 &= \sum_{ijk} \frac{M_{6ij} M_{1jk}}{\Delta_j} a_{ik} & C_2 &= \sum_{ijk} \frac{M_{7ji} M_{2kj}}{\Delta'_j} a_{ik} \\
C_3 &= \sum_{ijk} \frac{M_{6ij} M_{6jk}}{\Delta_j} a_{ik} & C_4 &= \sum_{ijk} \frac{M_{7ij} M_{7jk}}{\Delta'_j} a_{ik} \\
C_5 &= \frac{1}{\Delta_F} \sum_{i,k} M_{3i} M_{3k} a_{ik} & C_6 &= \sum_{i,k} \left[\frac{M_{4i} M_{4k}}{\Delta_D} + \frac{M_{5i} M_{5k}}{\Delta_G} \right] a_{ik} \\
C_7 &= \sum_{ijk} \frac{M_{1ij} M_{1jk}}{\Delta_j} a_{ik} & C_8 &= \sum_{ijk} \frac{M_{2ij} M_{2kj}}{\Delta'_j} a_{ik}.
\end{aligned}$$

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