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Spin-lattice relaxation of Fe^{3+} in ZnS ; experimental evidence for optical phonons

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Résumé. — Nous avons étudié la relaxation spin-réseau de l'ion Fe^{3+} dans ZnS cubique, entre 1,3 et 300 K, en utilisant une impulsion saturante, la saturation progressive et l'élargissement de la raie R.P.E. Dans ZnS, l'ion Fe^{3+} est plus fortement couplé au réseau que l'ion isoélectronique Mn^{2+} . Pour $T > 50$ K, les phonons optiques contribuent à la relaxation, et sont responsables d'un fort élargissement de la raie à 300 K.

Abstract. — The spin-lattice relaxation of the Fe^{3+} ion in cubic ZnS has been studied between 1.3 and 300 K by pulse saturation, progressive saturation and broadening of the E.P.R. line. In ZnS, the Fe^{3+} ion is more strongly coupled to the lattice than the isoelectronic ion Mn^{2+} . For $T > 50$ K, the optical phonons contribute to the relaxation, and are responsible for a strong line broadening at 300 K.

1. Introduction. — We have examined the spin-lattice (S. L.) relaxation of Mn^{2+} in cubic ZnS ($3d^5$ ion, S ground state), both experimentally and theoretically, in previous papers [1, 2, 3]. Uniaxial stress experiments [4, 5] have shown that the static S.L. coefficients are different for the isoelectronic ions Mn^{2+} and Fe^{3+} in ZnS. This fact suggested a comparison of their relaxation behaviour. We present here the results obtained for ZnS : Fe^{3+} . The Fe^{3+} ion must be generated by U.V. irradiation. The sample and apparatus used are described in section 2. The strong variation of the S.L. coupling in the temperature measurement range (1.3-300 K) imposed the use of several experimental methods, which are explained in section 3. The experimental results are given and discussed in sect. 4 and 5. We compare the experimental time measured in the direct process region with that calculated from stress results. The contributions of the acoustic and optical phonons are established. The differences between Mn^{2+} and Fe^{3+} are discussed.

2. Sample and apparatus. — The studied sample was a synthetic cubic crystal of ZnS doped with Fe^{2+} . Under U.V. irradiation an electron can be ejected; conversely Fe^{3+} is transformed back to Fe^{2+} under I.R. light. The U.V. irradiation was produced by a high-pressure mercury lamp (Philips SP 500). The Fe^{3+} concentration was estimated to be approximately 10^{-5} Fe^{3+}/Zn site.

The experiments were performed on an X band spectrometer equipped for pulse measurements and previously described [6, 1]. It uses a superheterodyne detection ($f_{\text{IF}} = 30$ MHz) followed by a synchronous detection (shortest rise time available after filtering : 0.1 μs) and a single klystron (Varian V58, 0.5 W). The klystron frequency was stabilized to within 1 part in 10^6 for periods of the order of an hour. For the lowest temperatures ($1.3 \text{ K} \leq T \leq 4.2 \text{ K}$), we used a rectangular cavity ($Q_u = 1\,500$) immersed in liquid helium; a quartz light pipe was used to irradiate the sample. For higher temperatures ($5.5 \text{ K} \leq T \leq 300 \text{ K}$), we used a gas-flow system (Helitron-Air Product). We were able to focus the exciting light directly onto the sample, located in a cylindrical TE_{011} cavity ($Q_u = 13\,000$). The temperature was measured with an AsGa diode; the sample and the diode were both mounted on a teflon rod, 1 mm apart from one another.

3. Experimental method. — In cubic symmetry, the E.P.R. spectrum of the Fe^{3+} ion ($3d^5$ configuration, 6A_1 ground state) can be described by the following spin-Hamiltonian [7] :

$$\mathcal{H} = g\beta\mathbf{H}\mathbf{S} + \frac{a}{6} \left(S_x^4 + S_y^4 + S_z^4 - \frac{707}{16} \right) \quad (1)$$

with $g = 2.019$, $a = (124.4 \pm 0.5) 10^{-4} \text{ cm}^{-1}$, X , Y , Z are the cubic axes of the crystal. Since the Zeeman energy $\gg a$, S can be taken as a good quantum number, and the E.P.R. transitions are $|M_S\rangle \rightarrow |M_S \pm 1\rangle$.

(*) E.R.A. N° 375.

We chose $\mathbf{H} \parallel [001]$ and studied the

$$|1/2\rangle \rightarrow |-1/2\rangle$$

transition. For $T \leq 30$ K, we saturated the transition with a 0.1 W rf pulse and observed the recovery of the E.P.R. signal with a power low enough to be in the linear region ($P = 10^{-8}$ W at 4.2 K). The recovery signal was fed into a multichannel analyser. When we deal with a multilevel spin system with $2S + 1$ spin sublevels, if the system does not acquire an internal equilibrium before the spin-lattice relaxation takes place, the recovery signal is not exponential (existence of at the most $2S$ distinct time constants). For our system, where the values of the energies are well approximated by the Zeeman term, and the high temperature approximation is valid, Andrew's and Tunstall's arguments [8] can be used and show that there are only three distinct time constants; the corresponding amplitudes depend upon the initial conditions. We observed only two time-constants, both temperature dependent, the longest one is designated hereafter T_1 .

When $T > 30$ K, the signal-to-noise ratio for the recovery signal was poor and did not allow an accurate determination of T_1 . Thus, for $30 \text{ K} \leq T \leq 100$ K, we progressively saturated the $|1/2\rangle \rightarrow |-1/2\rangle$ transition and plotted the ratio

$$\beta = \left[\frac{d\chi''(\omega, H_1)}{dH} \right]_M / \left[\frac{d\chi''(\omega, 0)}{dH} \right]_M$$

for increasing values of the r.f. field $2H_1 \cos \omega t$ present on the sample; $[d\chi''(\omega, H_1)/dH]_M$ is the amplitude of the absorption line derivative (the frequency of modulation used was 22 Hz). Since we observe an inhomogeneous Lorentzian line shape, we adapted Portis model to our case [1, 2]; we consider that the experimental line is made up of independent spin packets, each having a Lorentzian shape (width $\Delta\omega$) [9], distributed according to a Lorentzian law $h(\omega - \omega_0)$ (width $\Delta\omega^*$). The expression for β is then [3] :

$$\beta = \frac{(1+x)^2}{(1+s'^2)^{1/2} [x + (1+s'^2)^{1/2}]^2} \quad x = \frac{\Delta\omega^*}{\Delta\omega} \quad (2a)$$

$$s'^2 = 9(\gamma H_1)^2 \frac{k}{\Delta\omega}, \quad (2b)$$

k , which has the dimension of time, is proportional to T_1 : $k = \alpha T_1$. In order to evaluate α , we made measurements of T_1 by pulse saturation, and of k by progressive saturation, in the same temperature range (20-30 K).

For $T \geq 100$ K, the broadening of the spin-packets by spin-lattice coupling is great enough to lead to a measurable variation of the experimental linewidth. As we have two uncorrelated sources of broadening of the spin-packets, both described by a Lorentzian

line shape [9, 10], the linewidth of the spin-packets is the sum of the two contributions; the linewidth of the absorption signal (we measured its derivative) is then :

$$\Delta H_{\text{exp}} = \Delta H_0 + \Delta H_{\text{SL}},$$

where ΔH_0 is the low temperature value of ΔH_{exp} , and ΔH_{SL} the spin lattice contribution. The spin-lattice relaxation time T_1 is obtained through the relation $T_1 = 2/\gamma \Delta H_{\text{SL}}$. We verified that progressive saturation and line-broadening methods led to the same T_1 value at 100 K.

4. Experimental results. — The variation of the two time constants with temperature, between 1.2 and 30 K, is shown in figure 1. We observed a dramatic increase in the time constants for $T \leq 2.2$ K. This

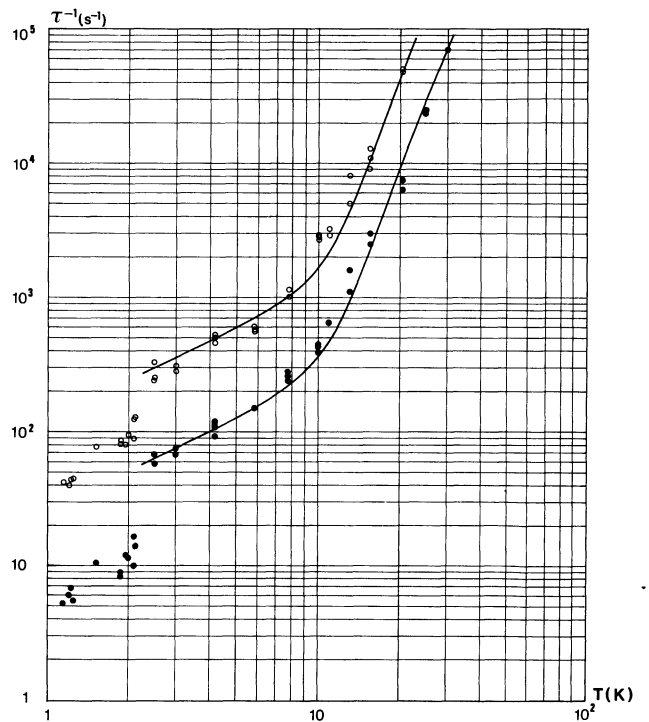


Fig. 1. — Variation of the two relaxation rates with T for Fe^{3+} in cubic ZnS in the temperature range $1.2 \text{ K} < T < 30 \text{ K}$.

($\mathbf{H} \parallel [001]$, $|1/2\rangle \rightarrow |-1/2\rangle$ transition) ;

the lower continuous curve corresponds to

$$\tau^{-1} = T_1^{-1} = 25 T + 12.7 \times 10^{-9} T^7 I_6(168/T),$$

the upper curve to

$$\tau^{-1} = 120 T + 61 \times 10^{-9} T^7 I_6(168/T) \quad (\tau \text{ s, } T \text{ K}).$$

effect is probably not due to the usual phonon-bottleneck for there should not be any discontinuity in these curves. A similar unexplained behaviour has already been observed by Lee and Walsh [11] for Cu^{2+} in lanthanum magnesium nitrate. A direct process was observed between 2 and 8 K; the experimental

results for the largest time constant T_1 are then best fitted by the following expression :

$$T_1 T = 0.040 \quad (T_1, \text{s}; T, \text{K}). \quad (3)$$

The experimental results of the progressive saturation experiments are reported in figure 2, for different temperatures. We used the reduced variable $P/P_{1/2}$, where P is the r.f. power incident on the cavity, $P_{1/2}$ is the power when $\beta = 0.5$. The $\beta(P/P_{1/2})$ curve is temperature independent as long as the spin-packets are not broadened by spin-lattice relaxation. Such a broadening appears when $T > 50$ K. The corresponding T_1 values are reported in figure 3. They were obtained by first fitting the experimental results with the theoretical expression for β : for $T < 50$ K the best fit was obtained with an inhomogeneity factor $x = 100$; for $T > 70$ K, the experimental line begins to broaden : at 100 K, $\Delta H_{\text{exp}} = 8.1 \pm 0.4$ G (for

$T < 70$ K, $\Delta H_{\text{exp}} = 6.7$ G) and $x = 6$. We then determined k knowing $H_1 = 1.64 P^{1/2}$ (Gauss, Watt) ; finally, the method described in section 2 led to $\alpha = 1$, so that $k = T_1$; at 100 K, the T_1 value calculated from progressive saturation is 95 ns, which is in good agreement with the value deduced from line-broadening at the same temperature : $T_1 = 80$ ns.

We had to irradiate the crystal continuously when $T > 100$ K, because of the back transformation $\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$. Furthermore the E.P.R. signal had to be processed through a multichannel analyser ; it should be noticed that the difficulty in detecting the Fe^{3+} ion at 300 K is essentially due to line-broadening : at 300 K the linewidth is $\Delta H_{\text{exp}} = 38$ G ; if the modulation amplitude is kept constant, the amplitude of the derivative is $(38/6.7)^2 \times 3 = 95$ times weaker at 300 K than at 100 K. The T_1 values deduced from line-broadening for $T \geq 100$ K are shown in figure 3.

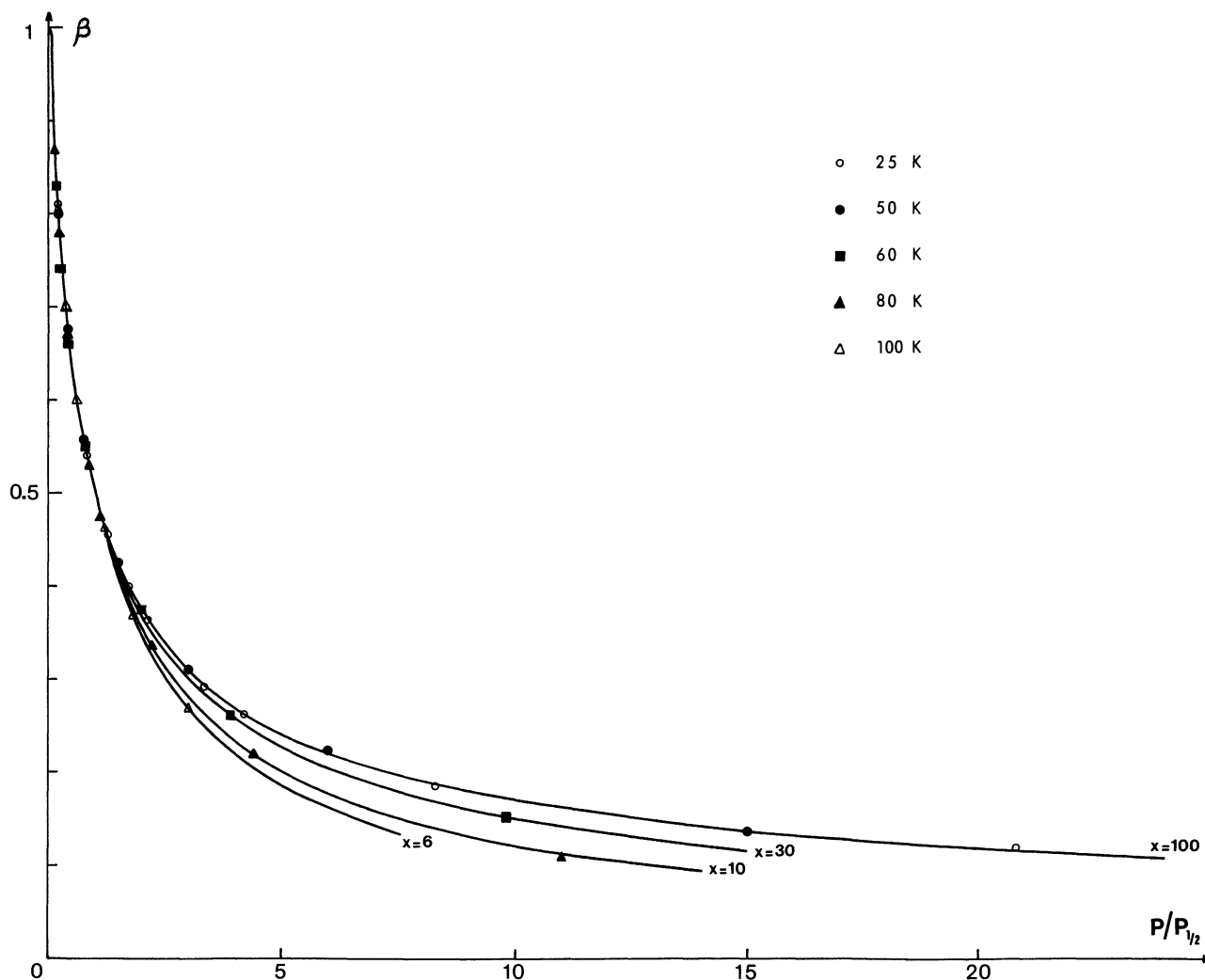


Fig. 2. — Variation of $\beta = \left[\frac{d\chi''(\omega, H_1)}{dH} \right]_{\text{M}} / \left[\frac{d\chi''(\omega, 0)}{dH} \right]_{\text{M}}$ for Fe^{3+} in cubic ZnS , with $P/P_{1/2}$, for some temperatures between 25 K and 100 K ($H \parallel [001]$, $|1/2\rangle \rightarrow |-1/2\rangle$ transition) ; the solid curves were deduced from eq. (2a). The $P_{1/2}$ values for 20-25-30-35-40-45-50-60-70-80-90 and 100 K are respectively 4.5-8.25-17.2-38-86-160-400 μW , 1.53-5-13.6-33-50 mW.

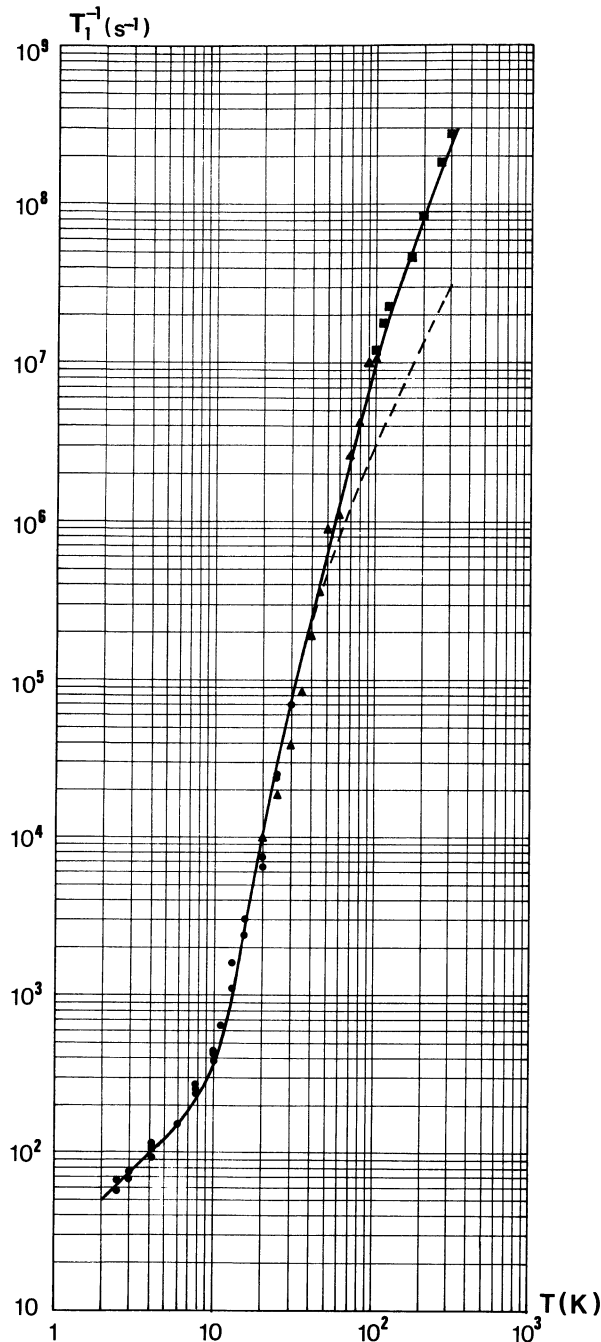


Fig. 3. — Variation of $1/T_1$ with T for Fe^{3+} in cubic ZnS in the temperature range $2 \text{ K} < T < 300 \text{ K}$

($H \parallel [001]$, $|1/2\rangle \rightarrow |-1/2\rangle$ transition)

(● from pulse saturation, ▲ from progressive saturation, ■ from the broadening of the E.P.R. line). The solid curve corresponds to the expression

$$T_1^{-1} = 25 T + 12.7 \times 10^{-9} T^7 I_6(168/T) + 9.6 \times 10^7 \text{Sh}^{-2} 200/T;$$

the dashed curve shows the contribution of the T and T^7 terms.

5. Discussion. — The experimental results between 2.2 and 300 K are best fitted (Fig. 3) by the following analytical expression :

$$\frac{1}{T_1} = 25 T + 12.7 \times 10^{-9} T^7 I_6\left(\frac{168}{T}\right) + 9.6 \times 10^7 \text{Sh}^{-2} \left(\frac{200}{T}\right) \quad (T_1 \text{ s}, T \text{ K}). \quad (4)$$

The first term corresponds to the direct process, the second and third terms to Raman processes through acoustic and optical phonons respectively. We will discuss them successively.

5.1 DIRECT PROCESS. — The S.L. transition probabilities for the direct process can be calculated using a dynamic spin-Hamiltonian $\mathcal{H}_{\text{SL}}$ [12]. For a $3d^5$ ion, the simplest expression for $\mathcal{H}_{\text{SL}}$ is :

$$\mathcal{H}_{\text{SL}} = \sum_{i,j,k,l} G_{ij,kl} S_i S_j \varepsilon_{kl} = \sum_{ij,kl} c_{ij,kl} S_i S_j \sigma_{kl} \quad (5)$$

ε_{kl} and σ_{kl} are respectively the strain and stress tensor components ; $G_{ij,kl}$ and $c_{ij,kl}$ are related to each other through the stiffness tensor components $C_{mn,kl}$:

$$G_{ij,kl} = \sum_{mn} C_{ij,mn} c_{mn,kl}. \quad (6)$$

We suppose that the values of the $G_{ij,kl}$ are constant between 0 and 10 GHz, and determine them from static uniaxial stress experiments [4, 5] :

Using the Voigt notation [13], we obtain for Mn^{2+} and Fe^{3+} in cubic ZnS :

$$\begin{aligned} \text{Mn}^{2+} \quad G_{11} &= -3.6 \times 10^{-18} \text{ erg} \\ &G_{44} = 36 \times 10^{-18} \text{ erg}, \\ \text{Fe}^{3+} \quad G_{11} &= -185 \times 10^{-18} \text{ erg} \\ &G_{44} = 41 \times 10^{-18} \text{ erg}. \end{aligned}$$

In the case of Mn^{2+} , the relaxation was exponential (existence of a spin temperature), and there was a good agreement between the experimental value of T_1 and that calculated using the dynamic spin-Hamiltonian formalism and the values given by the stress experiments.

As the $G_{ij,kl}$ coefficients for Mn^{2+} and Fe^{3+} are very different, it is interesting to know whether there is still such an agreement for Fe^{3+} . The Fe^{3+} spin system does not acquire a spin temperature : knowing the S.L. transition probabilities [1], we solved the secular equation for the populations of the $2S + 1$ levels, and determined the recovery signal $n(t)$ after saturation of the $|1/2\rangle \rightarrow |-1/2\rangle$ transition with a pulse long enough to reach the steady state. At 4.2 K, we find

$$W_{5/2 \rightarrow 3/2} = 1.9 \text{ s}^{-1}, \quad W_{5/2 \rightarrow 1/2} = 24 \text{ s}^{-1} \quad (7a)$$

$$n(t) \propto 1 - 0.94 e^{-t/0.38} - 0.05 e^{-t/0.011} - 0.01 e^{-t/0.038} \quad (t : \text{s}). \quad (7b)$$

Experimentally we get two time-constants, which are respectively 9.5 and 2 ms.

We could imagine that the S.L. relaxation time of Fe^{3+} is shortened by cross-relaxation with a fast relaxing centre. We rejected this possibility because we did not observe any short temperature independent time constant after a short saturating pulse [14], and because we measured the same time constants in different $\text{ZnS} : \text{Fe}^{3+}$ samples. It is thus necessary to discuss the assumptions made in the course of the calculation : first we have neglected the existence of a fine structure in the determination of the transition probabilities. In fact, first order perturbation theory shows that the error made is a few percent at the most. We also assumed that the value of the stiffness tensor components relating the local strain and stress was that of the bulk material. This assumption, which is incorrect for trivalent rare-earth ions with non local charge compensation [15], could still be more questionable for an iron-group ion.

5.2 RAMAN PROCESSES. — In the intermediate temperature range $8 \text{ K} \leq T \leq 50 \text{ K}$, the Raman process takes place through acoustic phonons. Since the spin multiplicity of the ground level is greater than 2, there could be a possibility for a T^5 process as pointed out by Orbach and Blume [16]. The contribution of both Raman processes will be then :

$$AT^5 I_6 \left(\frac{\theta_D}{T} \right) + BT^5 I_4 \left(\frac{\theta_D}{T} \right) \quad (8)$$

θ_D being the Debye temperature. For Fe^{3+} in cubic ZnS , $A/B \sim k^2 \Delta^2 / \zeta^2$, where $\Delta = 20\,000 \text{ cm}^{-1}$ is the energy difference between the ${}^6\text{A}_1$ and ${}^4\text{T}_1$ levels, and $\zeta = 440 \text{ cm}^{-1}$ is the spin-orbit coupling coefficient [17]. Both contributions are equal for

$$T_0 \sim \frac{\zeta^2}{k\Delta} \cdot \frac{1}{\sqrt{30}} = 1.2 \text{ K}.$$

At 8 K, where the relaxation begins to deviate from the direct process, the T^7 contribution is $\sim (8/1.2) = 44$ times greater than that of the T^5 process. In our case, the latter process is thus always hidden and we discarded it from the analytical expression for T_1 . In this discussion, as $\theta_D/T \gg 1$, we used $I_n(\theta_D/T) \sim n!$. In the next paper, we compare the relative contributions of the T^5 and T^7 processes for different ions in several matrices.

The choice of the value $\theta_D = 168 \text{ K}$ in the Debye integral has been suggested by previous experiments on Mn^{2+} in the same matrix [1].

The experimental results begin to deviate from a $T^7 I_6(\theta_D/T)$ law at $T = 50 \text{ K}$. At 300 K, T_1 is 10 times smaller than that predicted by this latter law. The $\text{Sh}^{-2} 200/kT$ temperature dependence in expression (4) has been interpreted by Huang [18] as the contribution of the optical phonons in the relaxation process. This contribution is important at high temperature where the optical phonon branch becomes noticeably populated; the relaxation time should vary as $\text{Sh}^{-2} \hbar\omega_0/2 kT$, where ω_0 is the upper limit of the optical phonon branch; in our case, the value $\omega_0 = 400 \text{ K}$ corresponds to the T_0 optical phonon-branch [19]. Huang restricted himself to the case of Kramers transitions. We have here a multilevel spin system and the $|1/2\rangle \rightarrow |-1/2\rangle$ E.P.R. line is probably broadened mainly by non-Kramers S.L. transitions, which are generally more effective than the Kramers ones. However a calculation similar to Huang's one leads to the same temperature dependence in the case of a non-Kramers transition ⁽¹⁾.

6. Conclusion. — Fe^{3+} is more strongly coupled to the lattice than Mn^{2+} . Because of this more efficient coupling, at low temperature the Fe^{3+} spin system does not acquire a spin-temperature through dipolar interactions, in contrast to what is observed for $\text{ZnS} : \text{Mn}^{2+}$.

In the direct process region, the T_1 values calculated from static uniaxial stress experiments do not agree with spin-lattice relaxation measurements, contrary to what is observed with $\text{ZnS} : \text{Mn}^{2+}$. It could be of interest to determine the local relation between stress and strain, in order to remove the questionable use of bulk coefficients.

At 300 K, the optical phonons are most efficient, in marked contrast with the usual situation, and lead to a strong broadening of the E.P.R. line.

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⁽¹⁾ Footnote : G. Roger, C. More, C. Blanc, have recently observed the contribution of optical phonons in $\text{ZnS} : \text{Mn}^{2+}$, for $T \geq 300 \text{ K}$. We thank them for communicating their results prior to publication.

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