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# Magnetic field dependence of spin-lattice relaxation in three iron group salts

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An extension is proposed to the iron group of the Orbach-Huang theory outlined for the relaxation field dependence in rare-earth salts. The general equation $T_1^{-1} = T_{10}^{-1}(H^2 + \frac{1}{2}\mu' H_{\text{dip}}^2 + \mu H_n^2)/(H^2 + \frac{1}{2} H_{\text{dip}}^2 + H_n^2)$ remains valid, but new expressions are given for $\mu'$ and $T_{10}^{-1}$ (if exchange predominates $\mu_1'$ and $H_{\text{exch}}$ replace $\mu'$ and $H_{\text{dip}}$). They are used to compute the coefficients in three salts selected as permitting calculation in CrK alum, CuK double sulfate, and FeK alum. The internal field is typically dipolar in the first and the third while it is due to exchange in the second; furthermore, the third ion is in a $S$ state. The parameters at 77 K have also been measured at frequencies of 0.2, 0.7, 4 and from 8.2 to 12.4 GHz by the resonant modulation method, investigating the field dependence of $T_1$. The agreement between theory and experiment is good in iron alum, in spite of complex calculations in this salt. It is excellent in copper double sulfate and rather moderate in chromium alum. There is a careful discussion of all the assumptions used in computation. To determine $T_{10}$, the temperature dependence of $T_1$ has also been measured, $T$ ranging from 50 to 150 K. Calculation and experiment are in good agreement, adopting for the upper limit of the $I_8$ Van Vleck integral a value close to the Debye temperature in chromium alum, but higher by a factor 1.6 in copper double sulfate and 2 in iron alum.

## I. INTRODUCTION

Electron spin-lattice relaxation is usually investigated by measuring the temperature dependence of the relaxation rate.[1-5] Information about the nature of the relaxation process and the existence of particular phenomena such as a phonon bottleneck[1,6] can be obtained. The influence of other parameters such as paramagnetic centers concentration,[7-11] monocrystalline sample orientation,[2,4] and magnetic field[12-19] has been also investigated. The concentration dependence informs us about dipolar and exchange interactions and possible cross relaxation. The orientation dependence has provided evidence of some considerable anisotropies.[4,20] The magnetic field dependence completes information found from other dependences and informs us about the internal fields within the sample. It has been extensively investigated by nonresonant techniques.[12,13,16,18,21] In contrast, very few determinations have been found using resonant methods because they need several spectrometers operating at different microwave frequencies.

Brons[22] suggested the first phenomenological equation to describe this dependence. Van Vleck[23] gave the first refined theoretical support to it. Orbach[24] developed a very complete theory of the temperature and field dependences for rare-earth ethylsulfates in which the internal field is due to dipolar and hyperfine interactions. Huang[25] extended the Orbach theory to the case of a predominant contribution of exchange in the internal field. The Brons equation has been thoroughly verified using nonresonant experiments. Only two sets of the Orbach-Huang theory have been reported.[18,26] They concern neodymium and dysprosium ethylsulfates. So, we have thought it would be interesting to obtain a precise verification of this theory in other salts. Besides, to complete information, we have extended the theory to iron group and used $3d$ salts for the experimental test. The choice of samples for calculation and experiment have been governed by the following requirements:

(i) The crystalline parameters and the matrix elements of the crystalline potential were known.

(ii) The symmetry was high making calculations possible. Three salts have been adopted corresponding to three different physical situations, chromium potassium alum in which the internal field is essentially dipolar, copper potassium double sulfate (Tutton salt) in which exchange predominates, and iron potassium alum, an $S$-state salt with a dipolar internal field. For the experimental test of our calculations, we have chosen the 60 to 150 K temperature range as ensuring the Raman process to be predominant. This required us to measure very short $T_1$ ($10^{-6}$ to $10^{-8}$ s) with precision and to use a broad range of magnetic field values. Measurements have been performed using four different modulation spectrometers. They used a resonant technique developed by Hervé and Pescia[27] and Pescia,[28] and improved by Gourdon *et al.*,[29] and Ablart.[30] In addition to the adequacy of the method for short $T_1$ measurements, it seemed interesting to carry out experiments by a resonant method making possible comparison with nonresonant data.

In the next section, the Orbach-Huang theory is outlined and the extension to $3d$ ions is presented. The parameters of the field dependence are computed in Sec. III for the investigated salts and the experimental technique is described in Sec. IV. The experimental data are given in Sec. V and discussed with theoretical results in Sec. VI.

## II. THE OUTLINE OF THE ORBACH-HUANG THEORY EXTENSION TO 3*d* IONS

### A. The Hamiltonian

The spin system of a $3d$ ion is governed by the Hamiltonian

$$\mathcal{H}=\mathcal{H}_{\text{fi}}+\mathcal{H}_{\text{c}}+\mathcal{H}_{LS}+\mathcal{H}_{Z} \ , \tag{1}$$

where $\mathcal{H}_{\text{fi}}$ is the free ion energy, $\mathcal{H}_{\text{c}}$ is the static crystalline-field potential, $\mathcal{H}_{LS}$ is the spin-orbit coupling, and $\mathcal{H}_Z$ is the Zeeman energy. For an iron group salt, the crystalline potential can be written with standard notation and using an expansion in spherical harmonics

$$\mathcal{H}_{\text{c}}=\sum_{nm} V_n^m=\sum_{nm} B_n^m\langle r^n\rangle\, Y_n^m(\theta,\phi) \ . \tag{2}$$

The mechanism of relaxation is the modulation of $\mathcal{H}_{\text{c}}$ by the thermal vibrations. So we can expand $B_n^m$ in a Taylor series with the lattice strain $\epsilon$. If $\zeta$ designates a coordinate of an ion producing the crystalline field

$$B_n^m(\zeta)=B_n^m(\zeta_0)+\epsilon\zeta\frac{\partial B_n^m}{\partial\zeta}+\tfrac{1}{2}\epsilon\epsilon'\zeta\zeta'\frac{\partial^2 B_n^m}{\partial\zeta\partial\zeta'} \ . \tag{3}$$

Raman spin-lattice relaxation arises in first order from the term $\partial^2 B_n^m/\partial\zeta\partial\zeta'$ which cannot be directly found from experiment. Consequently, two models in which the dynamic terms are replaced by the static ones are commonly used: (i) *The Orbach scheme*[24] in which the dynamic crystal-field parameters are supposed to be equal to the static ones. (ii) *The Scott and Jeffries scheme*[1] in which the dynamic crystal-field parameters are related to the static ones by relations of the form

$$(B_n^m)_{\text{dyn}}=(B_n^m)_{\text{stat}}g_n^{|m|} \ . \tag{4}$$

### B. Temperature dependence

Now, we suppose the magnetic field is much greater than internal fields. The relaxation rate is then written $T_{10}^{-1}$. For a Kramers salt, it can be expressed as [25,31]

$$T_{10}^{-1}=(9\hbar^2/\pi^3\rho^2 v^{10}\Delta^4)I_8\left|\sum_{nmq,n'm'}\langle p',+|V_n^m|q,\pm\rangle\langle q,\pm|V_{n'}^{m'}|p',-\rangle\right|^2 \ . \tag{5}$$

In Eq. (5), the temperature dependence is due to the $I_8$ coefficient. At temperatures well under $\Theta_D$ the Debye temperature[23]

$$I_8\propto T^9 \ . \tag{6}$$

At temperatures $T\gg\Theta_D$

$$I_8\propto T^2 \ . \tag{7}$$

In intermediate cases,[32]

$$I_8\propto\int_0^{\Theta_D}\frac{\theta^8 e^{\theta/T}}{(e^{\theta/T}-1)^2}\,d\theta\propto T^n \ , \tag{8}$$

$n$ ranging from 9 to 2 when $T$ is varied from $T\ll\Theta_D$ to $T\gg\Theta_D$. At temperatures $T\ll\Theta_D$, the Raman relaxation rate is more correctly expressed as

$$T_{10}^{-1}=AT^9+BH^2T^7 \ . \tag{9}$$

($A$ and $B$ being two temperature-independent constants.) The second term is generally negligible. But, if an admixture between the excited states produced from the ground multiplet takes place, the second term is no more negligible and a $T^7$ dependence may be observed.[19,32]

### C. Field dependence

When the magnetic field is larger than internal fields, the Raman relaxation rate is generally independent of $H$, except is the term $H^2T^7$ of Eq. (9) is no more negligible. Such a dependence has been observed.[19,32,33] When the magnetic field and internal fields are of the same order, another field dependence of the relaxation rate may be observed. It obeys the very general Brons equation[22]

$$T_1^{-1}=T_{10}^{-1}\frac{H^2+\lambda}{H^2+\phi} \ , \tag{10}$$

where $\lambda$ and $\phi$ are two field-independent constants. Orbach[24] has outlined a complete theory of the field dependence in rare-earth ethylsulfates. He has obtained an expression much more detailed and informative than Eq. (10). Under an approximate form remaining valid for $3d$ ions, it is written

$$T_1^{-1}=T_{10}^{-1}\frac{H^2+\mu H_n^2+\frac{1}{2}\mu' H_{\text{dip}}^2}{H^2+H_n^2+\frac{1}{2}H_{\text{dip}}^2}\ , \tag{11}$$

with

$$\mu=\frac{1+g_\perp^2 M^2/2g_\parallel^2}{1+2g_\perp^2/g_\parallel^2} \tag{12}$$

and

$$\mu'=(\alpha_1+\beta_1 M^2)/\gamma_1\ . \tag{13}$$

The detailed expressions of $\alpha_1$, $\beta_1$, $\gamma_1$, and $M^2$ are given in Refs. 18 and 31.

The expression of $M^2$ given by Orbach[24] must be modified for $3d$ ions because the matrix elements of the crystalline field, connecting different spin states, cancel in first order. So, we adopt

$$M^2=\left|\frac{\left|\sum\limits_{nmq}\langle p',-|V_n^m|q,\pm\rangle\right|^2-\left|\sum\limits_{n'm'q}\langle q,\pm|V_{n'}^{m'}|p',+\rangle\right|^2}{\sum\limits_{n'm'q,nm}\langle p',-|V_n^m|q,\pm\rangle\langle q,\pm|V_{n'}^{m'}|p',+\rangle}\right|^2\ , \tag{14}$$

where $|p'\rangle$ represents the ground-state wave function perturbed by the spin-orbit coupling and $|q\rangle$ the excited wave functions. Huang[25] has extended the Orbach theory to the case of an exchange interaction predominant in the internal field. He has obtained

$$T_1^{-1}=T_{10}^{-1}\frac{H^2+\mu H_n^2+\frac{1}{2}\mu_1' H_{\text{exch}}^2}{H^2+H_n^2+\frac{1}{2}H_{\text{exch}}^2}\ , \tag{15}$$

with

$$\mu_1'=\frac{N}{D} \tag{16}$$

(the expressions of $N$ and $D$ are given in Ref. 25). The expression (14) for $M^2$ remains valid here.

## III. CALCULATION OF $\mu'$ OR $\mu_1'$, $T_{10}^{-1}$, $H_{\text{dip}}$, OR $H_{\text{exch}}$ FOR THREE IRON GROUP SALTS

### A. Chromium potassium alum

The ground state of $Cr^{3+}$ ions is $^4F$. In alum, the ion is submitted to a crystalline potential which is almost octahedral, with a tetragonal distortion.[34–36] The internal field is essentially dipolar,[36] hyperfine interaction being negligible. Now, we go to develop the calculation of three parameters of Eq. (10) $\mu'$, $H_{\text{dip}}$, and $T_{10}^{-1}$. Using the data of Ref. 35, we find $\alpha_1=600$; $\beta_1=250$; $\gamma_1=1400$. The expression of $M^2$ [Eq. (14)] involves matrix elements of the dynamic crystalline potential. Following the schemes given in Sec. I, they can be evaluated from those of the static potential known by experiment. The static potential can be written in alum

$$\mathcal{H}_c=V_{\text{cub}}+V_{\text{tetra}} \tag{17}$$

but $V_{\text{tetra}}/V_{\text{cub}}\sim 6.5\times 10^{-2}$ and $V_{\text{tetra}}$ is negligible here.[34] The eigenstates of $\mathcal{H}_c$ are

$$\begin{aligned}
(\tfrac{3}{8})^{1/2}|-1,M_S\rangle &+(\tfrac{5}{8})^{1/2}|\ 3,M_S\rangle=|h\rangle\ ,\\
(\tfrac{3}{8})^{1/2}|1,M_S\rangle &+(\tfrac{5}{8})^{1/2}|-3,M_S\rangle=|f\rangle\ ,\\
|0,M_S\rangle &=|e\rangle\ ,\\
(\tfrac{5}{8})^{1/2}|-1,M_S\rangle &-(\tfrac{3}{8})^{1/2}|\ 3,M_S\rangle=|d\rangle\ ,\\
(\tfrac{5}{8})^{1/2}|1,M_S\rangle &-(\tfrac{3}{8})^{1/2}|-3,M_S\rangle=|c\rangle\ ,\\
1/\sqrt{2}\ |2,M_S\rangle &+\ 1/\sqrt{2}|-2,M_S\rangle=|b\rangle\ ,\\
1/\sqrt{2}\ |2,M_S\rangle &-\ 1/\sqrt{2}|-2,M_S\rangle=|a\rangle\ .
\end{aligned} \tag{18}$$

To compute $M^2$ we have to use the following suggestion, made by Scott and Jeffries[1] and Singh and Sapp.[18] Matrix elements are of comparable amplitude and the relative signs of the parameters of the dynamic crystal field are unknown. Then the best approximation may be to add incoherently each term into the sums of Eq. (14). In the expression of $M^2$ we use the following eigenstates perturbed by spin-orbit coupling:

$$\begin{aligned}
|a,\tfrac{3}{2}\rangle' &=|a,\tfrac{3}{2}\rangle-3\lambda/\Delta|b,\tfrac{3}{2}\rangle+\sqrt{6}\lambda/\Delta|d,\tfrac{1}{2}\rangle\ ,\\
|a,\tfrac{1}{2}\rangle' &=|a,\tfrac{1}{2}\rangle-\lambda/\Delta|b,\tfrac{1}{2}\rangle+2\sqrt{2}\lambda/\Delta|d,-\tfrac{1}{2}\rangle-\sqrt{6}\lambda/\Delta|c,-\tfrac{3}{2}\rangle\ ,\\
|a,-\tfrac{1}{2}\rangle' &=|a,-\tfrac{1}{2}\rangle+\lambda/\Delta|b,-\tfrac{1}{2}\rangle-2\sqrt{2}\lambda/\Delta|c,\tfrac{1}{2}\rangle+\sqrt{6}\lambda/\Delta|d,-\tfrac{3}{2}\rangle\ ,\\
|a,-\tfrac{3}{2}\rangle' &=|a,-\tfrac{3}{2}\rangle+3\lambda/\Delta|b,-\tfrac{3}{2}\rangle-\sqrt{6}\lambda/\Delta|c,-\tfrac{1}{2}\rangle\ .
\end{aligned}$$

Then the numerator of $M^2$ is written

$$\sum_{nmq} (\lambda/\Delta)\langle p,\pm|V_n^m|q,\pm\rangle[18\langle b,\pm|V_n^m|q,\pm\rangle-6\sqrt{6}(\langle c,\pm|V_n^m|q,\pm\rangle-\langle q,\pm|V_n^m|d,\pm\rangle)]\ , \tag{19}$$

the sums being on all the excited states. The denominator of $M^2$ is

$$\sum_{nmq} 2\sqrt{2}(1+\sqrt{3})\langle p,\pm|V_n^m|q,\pm\rangle(\langle q,\pm|V_n^m|d,\pm\rangle-\langle q,\pm|V_n^m|c,\pm\rangle)\ .$$

So, we obtain $\mu' \sim 6$. The calculation of $\mu'$ seems to be the first concerning a $3d$ ion.

The dipolar field can be obtained from thermodynamic parameters,[13] using the relation $H_{\text{dip}}=(2b/C)^{1/2}$, with $b=C_0T^2$ and $C=\zeta\mu_B^2S(S+1)/3k$. So, we find $H_{\text{dip}}=1140$ Oe. This estimation seems to be doubtful with $S>\frac{1}{2}$ because the Stark and dipolar splittings get mixed together and the magnetic specific-heat tail contains Shottky and dipolar contributions mixed together in a nonadditive fashion. Hence, we use the expression[34] $H_{\text{dip}}=(14.4)^{1/2}g\mu_B\zeta[S(S+1)]^{1/2}$, which gives $H_{\text{dip}}=300$ Oe. It can be also estimated from the Anderson relation[37]

$$H_{\text{dip}}=2.3\zeta g\mu_B[S(S+1)]^{1/2}\ , \tag{20}$$

where $\zeta$ represents the spin density. Adopting for chromium alum,[23] $g\sim 2$, $S=\frac{3}{2}$, and $\zeta=2.2\times10^{21}$ spins/cm$^3$, we obtain $H_{\text{dip}}=190$ Oe. To compute $T^{-1}$ at 77 K, we apply Eq. (5) with[23,38] $\rho=1.7\times10^3$ kg/m$^3$, $v=2.3\times10^3$ m/s, and $\Delta=1.4\times10^4$ cm$^{-1}$. $I_8$ is calculated from Eq. (8) adopting[23] $\Theta_D=330$ K. We obtain $I_8=1.3\times10^{20}$ s$^{-9}$. We calculate matrix elements in Eq. (5) as for $\mu'$ with the Orbach scheme. We find $T_{10}^{-1}\sim10^6$ s$^{-1}$. Using the Scott and Jeffries scheme [Eq. (4)] we obtain $T_{10}^{-1}\sim10^9$ s$^{-1}$.

### B. Copper potassium double sulfate

The ground state of Cu$^{2+}$ ion is $^2D$. In double sulfate the ion is submitted to an octahedral crystalline potential showing a small tetragonal distortion.[39] The internal field is due to exchange, dipolar,[40] and hyperfine interactions appearing as negligible. In this salt, there are two Cu$^{++}$ ions per unit cell. They show different orientations with respect to the magnetic field. But, the Raman spin-lattice relaxation is isotropic in Copper Tutton salt[21] and no particular effect is observed. Now we present some assumptions for simplifying the expression (16) of $\mu_1'$. Suppose the existence of long-wavelength phonons and an isotropic exchange interaction.

These two assumptions, though very useful for calculation, have to be considered as rather rough. However, they lead to a good fit between the calculated and measured values of $\mu_1'$. So, we obtain

$$\mu_1'=(\tfrac{1}{8}M^2\Lambda^2)[\tfrac{1}{8}(g_\parallel^4/g_\perp^4)+1]^{-1}\ . \tag{21}$$

Now we must compute the $M^2$ term. Using spherical harmonics, the crystalline-field potential $V$ is written[39]

$$V=\mathcal{H}_c=B_2^0\langle r^2\rangle 0_2^0+B_4^0\langle r^4\rangle 0_4^0+B_4^{\pm4}\langle r^4\rangle 0_4^{\pm4}\ . \tag{22}$$

The values of the different terms (in cm$^{-1}$) are

$$B_2^0\langle r^2\rangle=-12\,360\ ,$$

$$B_4^0\langle r^4\rangle=3000\ ,$$

$$B_4^{\pm4}\langle r^4\rangle=29\,200\ .$$

The eigenstates and eigenvalues (in cm$^{-1}$) are

$$|p,\pm\rangle=1/\sqrt{2}(|2,\pm\rangle+|-2,\pm\rangle),\quad E_p=0\ ,$$

$$|q,\pm\rangle=|0,\pm\rangle,\quad E_q=19\,393,$$

$$|r,\pm\rangle=1/\sqrt{2}(|2,\pm\rangle-|-2,\pm\rangle),\quad E_r=22\,200\ ,$$

$$\left.\begin{array}{l}|s,\pm\rangle=|+1,\pm\rangle\\ |t,\pm\rangle=|-1,\pm\rangle\end{array}\right\},\quad E_s=E_t=27\,293\ .$$

As above, the dynamic crystal-field parameters are computed using either the Orbach or the Scott and Jeffries scheme. At first order, the numerator of $M^2$ vanishes. Spin-orbit coupling avoids the $M^2$ cancellation and the perturbed ground state is written

$$|p',+\rangle=|p,+\rangle-\lambda/(E_p-E_r)|r,+\rangle-\lambda/\sqrt{2}(E_p-E_t)|t,-\rangle\ ,$$

$$|p',-\rangle=|p,-\rangle+\lambda/(E_p-E_r)|r,-\rangle+\lambda/\sqrt{2}(E_p-E_s)|s,+\rangle\ .$$

In the same manner as for Cr$^{3+}$ alum, we find $M^2=4$. Adopting[41] $g_\parallel=2.43$ and $g_\perp=2.05$ we obtain $\mu_1'=1.6$. Here again, the exchange field can be found from thermodynamic parameters.[13] We obtain

$H_{\text{exch}}=490$ Oe. The Anderson relation[37] is written

$$H_{\text{exch}}=[(\tfrac{8}{3})^{1/2}/g\mu_B]\{3kT_N/2[zS(S+1)]^{1/2}\}\ , \tag{23}$$

where $T_N$ represents the Néel temperature and $z$ the number of next nearest neighbors. Taking[42] $T_N\sim 0.05$ K, $S=\frac{1}{2}$, and $g\sim 2$ we find $H_{\text{exch}}\sim 430$ Oe.

To compute $T_{10}^{-1}$ at 77 K, we adopt[38,39,43] $\rho=2.25$ g/cm$^3$, $v=2.5\times 10^3$ m/s (average speed of sound), and $\Delta_q=27\,300$ cm$^{-1}=E_p-E_t$ $\lambda\sim 800$ cm$^{-1}$. $I_8$ is calculated from Eq. (8). Taking either[44,45] $\Theta_D=106$ or 180 K we find either $I_8=1.06\times 10^{17}$ or $4.23\times 10^{18}$ s$^{-9}$. The matrix elements are computed as for Cr$^{3+}$ alum. Using the Orbach scheme, we obtain $T_{10}^{-1}=1.9\times 10^3$ s$^{-1}$ with $\Theta_D=105$ K, and $T_{10}^{-1}=7.4\times 10^3$ s$^{-1}$ with $\Theta_D=180$ K. With the Scott and Jeffries model we find $T_{10}^{-1}=7.4\times 10^5$ s$^{-1}$ with $\Theta_D=180$ K.

### C. Iron potassium alum

The Fe$^{3+}$ ion is in the $^6S$ ground state. Within the alum, the crystalline potential is octahedral with a small tetragonal distortion. The internal field is typically dipolar. The orbital angular momentum of the ground state is quite quenched. To obtain, nonzero matrix elements for the orbit-lattice interaction, it is necessary to mix the ground state with the excited states presenting nonzero angular momentum. $\alpha_1$, $\beta_1$, $\gamma_1$, and the lattice parameters are the same as for chromium alum but $M^2$ has to be modified. Accounting for the excited states.

$$M^2=\left|\frac{\left|\sum_{nmQ}\langle 0',M_S|V_n^m|Q,M_S\rangle\right|^2-\left|\sum_{n'm'Q}\langle Q,M_S|V_{n'}^{m'}|0',M_S+1\rangle\right|^2}{\sum_{nm,n'm'Q}\langle 0',M_S|V_m^m|Q,M_S\rangle\langle Q,M_S|V_{n'}^{m'}|0,M_S+1\rangle}\right|^2\ , \tag{14'}$$

where $|0',M_S\rangle$ is the ground state perturbed by the spin-orbit coupling and $|Q,M_S\rangle$ are the excited states. The cubic crystalline field produces a splitting of the same order as the energy difference between the different excited states. So, as Blume and Orbach[46] pointed out, the cubic crystalline field admixes the three $^4\Gamma$ levels into one another and gives the following states:

$${}_i^4\Gamma_4=\delta_i|^4P\rangle+\theta_i|^F\rangle+\nu_i|^4G\rangle\ , \tag{24}$$

$\delta_i$, $\theta_i$, $\nu_i$ are coefficients determined from the secular determinant of $\mathcal{H}_c$, and $|^4P\rangle$, $|^4F\rangle$, $|^4G\rangle$ are the free ion excited states. Only the states with $M_L=0,\pm 1$ (i.e., containing the $^4P$ state) can be mixed in the ground state by the spin-orbit coupling.

The states presenting the $^4\Gamma$ character are the following[38]:

$$4_P\begin{cases}|1\rangle\\|0\rangle\\|-1\rangle\end{cases},\quad 4_F\begin{cases}(\frac{3}{8})^{1/2}|F,1\rangle+(\frac{5}{8})^{1/2}|F,-3\rangle\\|-0\rangle\\(\frac{3}{8})^{1/2}|F,-1\rangle+(\frac{5}{8})^{1/2}|F,3\rangle\end{cases},$$
$$4_G\begin{cases}-(\frac{7}{8})^{1/2}|G,1\rangle-(\frac{1}{8})^{1/2}|G,-3\rangle\\1/\sqrt{2}|G,4\rangle-1/\sqrt{2}|G,-4\rangle\\(\frac{7}{8})^{1/2}|G,-1\rangle+(\frac{1}{8})^{1/2}|G,3\rangle\end{cases}. \tag{25}$$

The various states ${}_i^4\Gamma_4$ and the $\delta_i$, $\theta_i$, $\nu_i$ coefficients are determined by diagonalizing the matrix in presence of the cubic crystalline potential

$$\mathcal{H}_c=B_4^0\langle r^4\rangle[O_4^0+(\tfrac{5}{14})^{1/2}(O_4^4+O_4^{-4})]\ . \tag{26}$$

The matrix element of $\mathcal{H}_c$ have been computed from Racach general expansions[47–49]

$$\langle l^n\alpha'SL'M_SM_{L'}|C_\tau^\sigma|l^n\alpha SLM_SM_L\rangle=\begin{pmatrix}L'&\sigma&L\\-M_{L'}&\tau&M_L\end{pmatrix}n(2l+1)[(2L+1)(2L'+1)]^{1/2}\begin{pmatrix}l&\sigma&l\\0&0&0\end{pmatrix}$$
$$\times\sum(-1)^{L+L_1}\langle l^n\alpha'SL'(|l^{n-1}\alpha_1S_1L_1\rangle\langle l^{n-1}\alpha_1S_1L_1|)l^n\alpha SL\rangle\begin{Bmatrix}L&\sigma&L\\l&l_1&l\end{Bmatrix}\ , \tag{27}$$

where ( ) and { }, respectively, represent the $3j$ and $6j$ coefficients of Wigner[48,50] and $|1^{n-1}\alpha_1SL_1\rangle$ are the fractional parentage coefficients. The only values are 0 and 4 for $\sigma$, and 0 and $\pm 4$ for $\tau$ concerning a $3d$ ion in

TABLE I. Matrix of the crystalline potential Hamiltonian for iron potassium alum. The numbers are given in units of $\mathrm{cm}^{-1}$.

| | $^4G$ | $^4F$ | $^4P$ |
|---|---|---|---|
| $^4G$ | 33 377 | 7146 | −14 291 |
| $^4F$ | 7146 | 53 150 | 0 |
| $^4P$ | −14 291 | 0 | 36 421 |

TABLE II. Numerical values of the coefficients $\delta_i$, $\theta_i$, $\nu_i$, accounting for the mixing of three $_i^4\Gamma$ levels in FeK alum at energies $\Delta_i(\mathrm{cm}^{-1})$.

| $i$ | $\delta_i$ | $\theta_i$ | $\nu_i$ | $\Delta_i$ |
|---|---|---|---|---|
| 1 | 0.664 | −0.156 | 0.732 | 16 375 |
| 2 | 0.704 | 0.515 | −0.489 | 43 082 |
| 3 | 0.310 | −0.841 | −0.444 | 53 624 |

an octahedral lattice. The energy levels for the free $\mathrm{Fe}^{3+}$ ion[51] (in $\mathrm{cm}^{-1}$) are

$$\begin{aligned} E\{^6S\}-E\{^4G\}&=33\,377\ , \\ E\{^4P\}-E\{^4G\}&=3044\ , \\ E\{^4F\}-E\{^4G\}&=19\,773\ . \end{aligned} \tag{28}$$

The cubic field term can be estimated to be 1600 $\mathrm{cm}^{-1}$. The $\mathcal{H}_c$ Hamiltonian is given in Table I.

The diagonalization of $\mathcal{H}_c$ gives the eigenvalues of energy $\Delta_1=19\,666\ \mathrm{cm}^{-1}$, $\Delta_2=46\,356\ \mathrm{cm}^{-1}$, and $\Delta_3=56\,926\ \mathrm{cm}^{-1}$. The eigenstates are linear combinations as seen in Eq. (24). The values of $\delta_i$, $\theta_i$, $\nu_i$ coefficients are listed in Table II.

The spin-orbit interaction mixes the different $_i^4\Gamma_4$ states with the $^6S$ ground state, which is written

$$|S,M_S\rangle'=|^6S,M_S\rangle-\sum_1^3\frac{\delta_i}{\Delta_i}\zeta[a(M_S)|_i^4\Gamma_4 1,M_S-1\rangle+b(M_S)|_i^4\Gamma_4-1,M_S+1\rangle+c(M_S)|_i^4\Gamma_4 0,M_S\rangle]\ .$$

The $a(M_S)$, $b(M_S)$, $c(M_S)$ coefficients have been tabulated by Sharma *et al.*[52] So we find $M^2\sim100$ and $\mu'\sim18$.

We have computed $H_{\mathrm{dip}}$ from Eq. (20). Adopting for $\mathrm{Fe}^{3+}$ alum $g\sim2$ and $\zeta=2.15\times10^{21}$ centers/$\mathrm{cm}^3$, we obtain $H_{\mathrm{dip}}=270$ Oe. It can be also estimated from thermodynamic parameters. The remark concerning chromium alum remains valid because $S>\frac{1}{2}$ and one must use the expression[34] $H_{\mathrm{dip}}=(14.4)^{1/2}g\mu_B\zeta[S(S+1)]^{1/2}$, which gives $H_{\mathrm{dip}}=450$ Oe.

To determine $T_{10}^{-1}$ at 77 K, Eq. (5) cannot be used with an $S$ state. In this case, it is necessary to mix the excited states in the ground state. So we obtain

$$T_{10}^{-1}=\frac{9\hbar^2 I_8}{\pi^3\rho^2 v^{10}\Delta^4}\left(\sum_{nm,n'm'}\langle^6S'M_S|V_n^m|_i^4\Gamma,M_S\rangle\langle_i^4\Gamma_4M_S|V_{n'}^{m'}|^6S'M_S+1\rangle\right)^2\ . \tag{29}$$

$T_{10}^{-1}$ is calculated using $\rho=1.7\ \mathrm{g/cm}^3$ and $v=2.3\times10^3$ m/s. $I_8$ is obtained from Eq. (8). Adopting $\Theta_D=330$ K as for chromium alum, we find $I_8=1.3\times10^{20}\ \mathrm{s}^{-9}$ and $T_{10}^{-1}=7\times10^5\ \mathrm{s}^{-1}$.

## IV. EXPERIMENTAL TECHNIQUES

To test the validity of the Orbach-Huang equations and their extension to the iron group, experimental data were necessary. Some found by nonresonant methods can be seen in the literature. But, they are difficult to use for the following reasons:

(i) The measurements at 77 and 90 K, performed by Gorter and Smits[13] with chromium alum, only concern two values of magnetic field (0 and 4 kOe). So a precise determination of $\mu_1'$ is not possible.

(ii) Concerning copper potassium double sulfate, the measurements given by the same authors[13] are restricted to three $H$ values (400, 800, and 2400 Oe). Here again, the precise determination of $\mu_1'$ is difficult.

(iii) Gorter[13] has given a detailed field dependence in iron potassium alum at 77 and 90 K. But the values of $T_1$ are very short and the nonresonant determinations are then inaccurate.

In particular, with $H=100$ Oe, he found $T_1=4\times10^{-8}$ s at 77 K and $6.4\times10^{-9}$ s at 90 K, which indicates $T_1^{-1}\sim T^{12}$, a very doubtful temperature dependence. Thus, these data could not be used for a precise determination of $\mu'$. We shall only use them for comparison with our experimental results. For all these reasons, we have tried to find a more precise experimental verification, using a technique adequate for short $T_1$ measurements.

### *1. Principle of the modulation method (Refs. 27, 28, and 53)*

Two orthogonal fields are applied to the sample, a magnetic field $\vec{\mathrm{H}}$ with the direction $Oz$ and a microwave field $\vec{\mathrm{H}}_1$ the amplitude of which is modulated with the circular frequency $\Omega$. Then the magnetization is modulated and a coil, close to the sample and axis along the magnetic field, picks up an efm hereafter called $S$ and proportional to $dM_z/dt$.

### *2. Calculation of signal S*

If we suppose the coil is tuned on the frequency $\Omega/2\pi$ and the sample is little as compared to the mean diameter of a turn, we can write $S=(nQ_b\mu_0/2R)(dM_z/dt)$, where $n$ is the number of turns of the coil, $R$ is the radius, and $Q_b$ is the factor of quality. From the Bloch equations[54] we find at resonance

$$S(X)=S_0X\left[\frac{1+p^2X^2/4}{(1+X^2)(1+p^2X^2)}\right]^{1/2} , \qquad (30)$$

where $X=\Omega T_1$, $p=T_2/T_1$,

$$S_0=(\mu_0 n Q_b \tau a M_0)/[RT_1(1+\tau^2)] ,$$

$\tau$ is the modulation ratio, $M_0$ is the equilibrium magnetization, $\mu_0$ is the free space magnetic permeability, and $a=\mu_0 H_1^2\gamma^2T_1T_2$ is the saturation factor. Equation (30) is written assuming $a << 1$. Three curves $S(X)$ are shown on Fig. 1 and the graphical determination of $T_1$ is also indicated. The spin system easily "follows" the modulation for low $\Omega$ values. In contrast, relaxation "slows down spins" for high $\Omega$ values. So, a "skeleton" of the curve $S(\Omega)$ can be imagnined as constituted by the tangent for $X=0$ and the asymptote. It shows the two opposite behaviors of the spin system submitted to either slow or rapid modulation. $T_1$ can be found from the change of behavior.

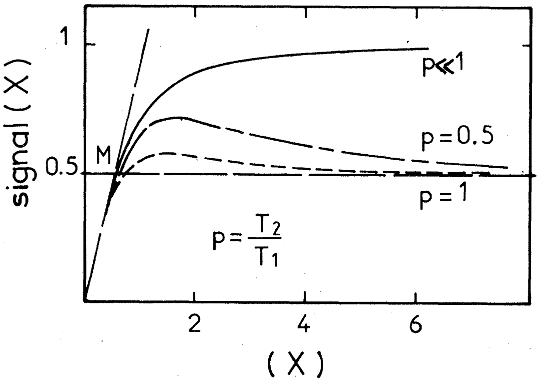

FIG. 1. Theoretical plots of modulation signal $S\propto dM_z/dt$ vs $X(=\Omega T_1)$ for three values of $p=T_1/T_2$. The tangent for $X=0$ and the asymptote cross at point $M$ with abcissa $X=\frac{1}{2}$. This allows to determine $T_1$ from an experimental curve. The saturation is assumed to be negligible.

### *3. The range of $T_1$ measurements*

A typical value for $\Omega/2\pi$ is 1 MHz which makes easy modulation and detection. In our graphical determination, it corresponds to $1/\Omega^*=T_1=10^{-7}$ s. For a precise determination of $T_1$ a sufficient range of $\Omega$ values must be used typically from $1/3\Omega^*$ to $3\Omega^*$. For an easy radio-frequency detection, the condition $0.3(\Omega/2\pi) > 10$ kHz has to be obeyed. On the other hand, a reasonable upper limit for the frequency of the modulation is $3(\Omega/2\pi) < 50$ MHz. So, the range of measurements is $10^{-6} > T_1 > 10^{-8}$ s.

### *4. Determination of $T_1 < 10^{-8}$ s*

The aforesaid techniques cannot be used because a modulation at very high frequency is hard to obtain. In effect, the cavity constitutes a selective filter; at frequencies above 50 MHz, the effective modulation ratio becomes very low within the cavity, so reducing the signal and the sensitivity. To overcome the difficulty, we have imagined the following variant to the method. The signal $S(\Omega)$, detected by the pickup coil, has an amplitude which depends on term $\Omega T_1$. Now, let us consider the "classical signal" $\bar{S}$, found in the same spectrometer using a crystal detector which receives the reflected wave of the cavity, following the techniques of usual ESR spectrometers. It is independent of $\Omega T_1$, i.e., shows the same behavior as $S$ when $\Omega T_1 >> 1$. Consequently, the beginning of the $S(\Omega)$ curves is easily obtained using a low modulation frequency and the asymptote is found from the ratio between $S$ and $\bar{S}$. This is evaluated by means of a test sample with a long $T_1$ (free radical).

### *5. The case of saturation*

The aforesaid results suppose a negligible saturation, i.e., $a=\mu_0\gamma^2H_1^2T_1T_2 << 1$. (We mean by $\gamma$ the gyromagnetic ratio of the sample.) If the condition is not obeyed two cases have to be considered.

*a. The ESR line is homogeneously broadened.* Then $S(X)$ becomes

$$S=S_0\frac{a}{1+a}\times\frac{X(1+p^2X^2/4)^{1/2}}{[a^2+2a(1-pX^2)+(1+X^2)(1+p^2X^2)]^{1/2}} . \qquad (31)$$

The tangent for $X=0$ and the asymptote are crossing at a point with the abcissa $X=\frac{1}{2}(1+a)$. Several curves, corresponding to different $a$ values, have to be plotted and $T_1$ is found by extrapolating to $a = 0$.

*b. The ESR line is inhomogeneously broadened (Refs. 28 and 55).* We suppose many spin packets are present, each one giving a Lorentzian line very much narrower than the whole line. Then $S(X)$ for one packet can be expressed as

$$S(X,\delta)=\frac{2\tau M_0 a}{T_1}\frac{1+jpX/2}{1+a+\delta^2p^2T_1^2}\left[jX\left(1+\frac{\delta^2p^2T_1^2}{1+jpX}\right)\Big/a+(1+jX)\left(1+jpX+\frac{\delta^2p^2T_1^2}{1+jpX}\right)\right], \tag{32}$$

where $j^2=-1$ and $\delta=\omega-\omega_0$ is the difference between the resonance frequency of one packet and that of the whole line. For all the packets

$$S(x)=\int_{-\infty}^{+\infty}S(X,\delta)f(\omega)\,d\omega=\frac{aX(1+jpX/2)(-a+jpX)}{a(1+jpX)+(1+jX)(2jpX-a-p^2X^2)(1+a)}+\frac{a-pX^2+jpX}{a(1+jX)/(1+jpX)+(1+jX)^2}, \tag{33}$$

$f(\omega)$ being the shape function of a spin packet. The aforesaid graphical determination gives the value $X=\Omega T_1=(1+a)(1+\sqrt{1+a})/(2+a)$ to be extrapolated to $a=0$.

### *6. Limiting sensitivity*

The question arises how to know the minimum number of paramagnetic centers necessary for $T_1$ measurements. More generally, we have to know the minimum number of centers to observe an ESR line, one oersted wide, with a signal-to-noise ratio equal to 1. The experimental sensitivities obtained at 77 K with the different spectrometers are listed in Table III. We note a correct $T_1$ measurement requires a center number about twenty higher than the detection of the ESR line.

### *7. Precision in $T_1$ determination*

The precision is about 4% on the range $10^{-8} < T_1 < 10^{-6}$ s. Using the method modified for very short $T_1$, it becomes about 15% on the range $10^{-8} > T_1 > 10^{-10}$ s.

TABLE III. The necessary sensitivities to detect the ESR line at 77 K with the four spectrometers used. For $T_1$ measurements, the minimum number of centers is about twenty times higher.

| | | | | |
|---|---|---|---|---|
| Operating frequency (GHz) | 0.2 | 0.7 | 4 | 8.2 to 12.4 |
| Mean value of sensitivity (centers per Oe and signal-to-noise ratio equal to 1) | $5\times10^{15}$ | $10^{14}$ | $5\times10^{13}$ | $10^{12}$ |

### *8. Apparatus (Figs. 2 and 3)*

Our purpose was to measure $T_1$ for different $H$ values. So, four spectrometers have been built, using the principle described above. They operated at 0.2, 0.7, 4, and from 8.2 to 12.4 GHz, respectively. The various temperatures were obtained from an ESR 9 Oxford Instruments device. The sample was placed in a chamber manufactured from ultrahigh-purity signal-free quartz. A continuous flow of He gas flushed the sample. The gas temperature was locked in by a heater and a temperature controller. It gave the temperature range 3.7 to 300 K and the temperature stability in the gas phase of ±0.02 K.

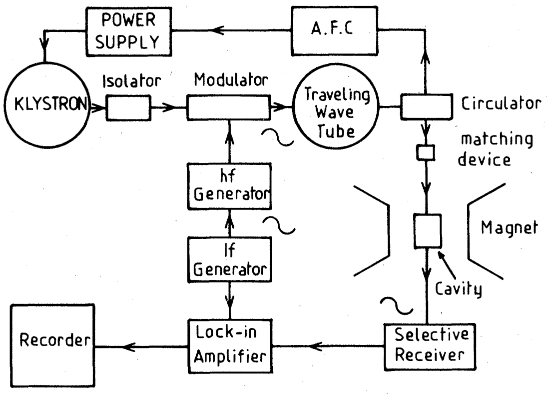

FIG. 2. Block diagram of a typical modulation spectrometer used for $T_1$ measurements. The microwave resonator is a reflection cavity when operating at $X$ or $L$ band. It is replaced by a strip line at 0.7 GHz and a helix at 0.2 GHz. The hf generator modulates the microwaves at the frequency $\Omega/2\pi$. This generator is amplitude modulated at 1 kHz by the lf one which permits the lock in detection of the signal $S$.

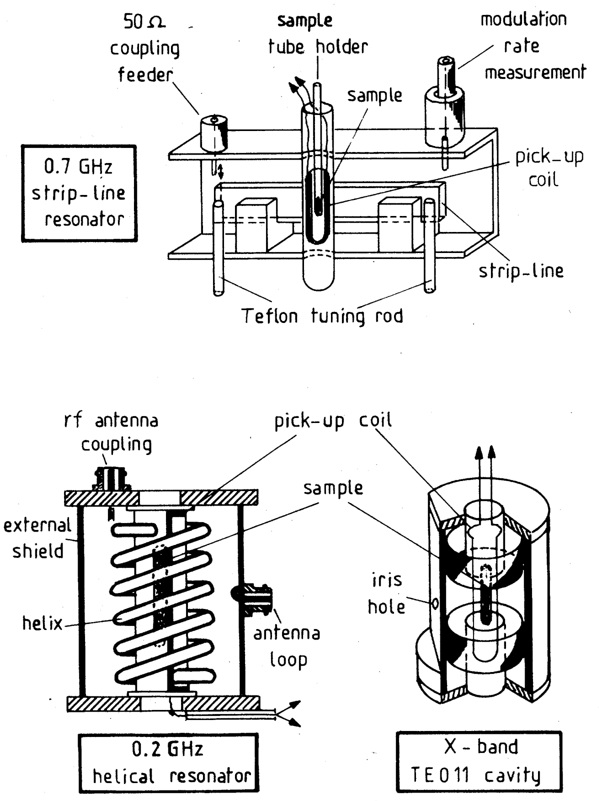

FIG. 3. The cavity for $X$-band spectrometer. The "saddle-shaped" pickup coil, is wound around the sample holder tube within the cavity. The coil is tuned at the frequency $\Omega/2\pi$ by a variable capacitance. It is connected to a selective receiver through a low noise impedance-matching circuit.

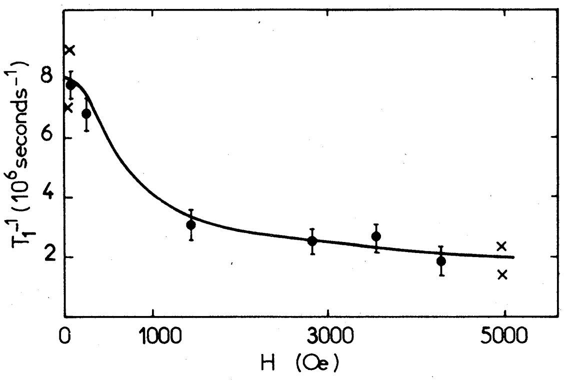

FIG. 4. Relaxation rate vs magnetic field in chromium potassium alum at 77 K. (●) our measurements; (×) Gorter measurements. The solid curve corresponds to the best fit with our data. It is well described by the equation $T_1^{-1} = 2\times10^6(H^2+2.6\times10^6)/(H^2+6.5\times10^5)$ from which we obtain $\mu'=4$, $H_{\text{dip}}=1140$ Oe.

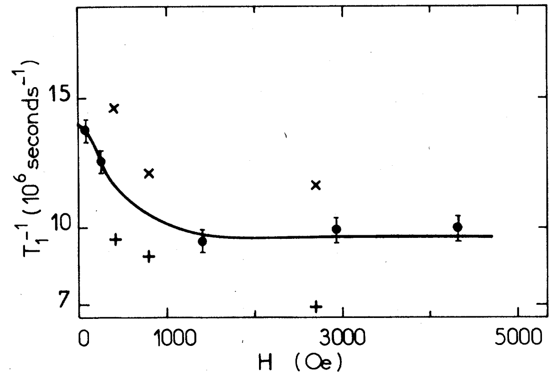

FIG. 5. Relaxation rate vs magnetic field in copper potassium double sulfate. (●) our measurements at 77 K; (+) Gorter measurements at 77 K; (×) Gorter measurements at 90 K. The solid curve corresponds to the best fit with our data. It is well described by the equation $T_1^{-1} = 10^5(H^2+2.6\times10^5)/(H^2+1.8\times10^5)$ from which we obtain $\mu_1'=1.45$, $H_{\text{exch}}=600$ Oe.

## V. EXPERIMENTAL RESULTS

We have performed preliminary experiments to compare $T_1$ values for powdered and monocrystalline samples. With the three investigated salts an the used temperatures range, the same $T_1$ values have been encountered in the two cases. So, our definitive measurements have been developed with powders. They make possible the use of a "big" sample resulting in a high signal-to-noise ratio and a satisfactory precision on $T_1^{-1}$ determination, especially in low magnetic field. The samples were cylindrical with a diameter of 0.4 cm, a length of 2 cm, and a mass of

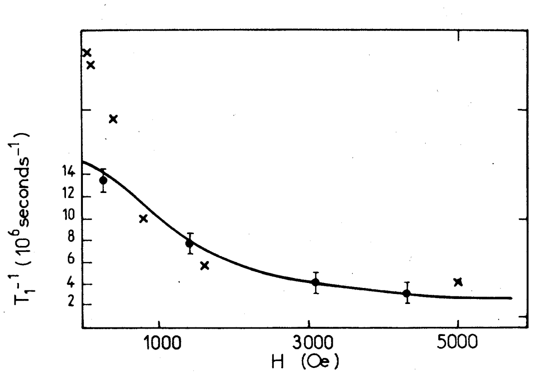

FIG. 6. Relaxation rate vs magnetic field in iron potassium alum at 77 K. (●) our measurements; (×) Gorter measurements. The solid cuve corresponds to the best fit with our data. It is well described by the equation $T_1^{-1} = 10^6(H^2+1.6\times10^7)/(H^2+1.1\times10^6)$ from which we obtain $\mu'=14$, $H_{\text{dip}}=2300$ Oe.

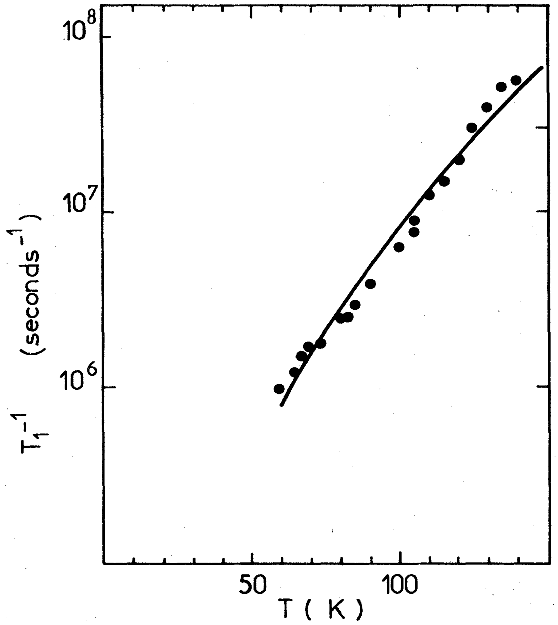

FIG. 7. Relaxation rate vs temperature in chromium potassium alum at 9.3 GHz. The solid curve fits the law $T_1^{-1}=1.53\times10^{-3}T^{4.8}$.

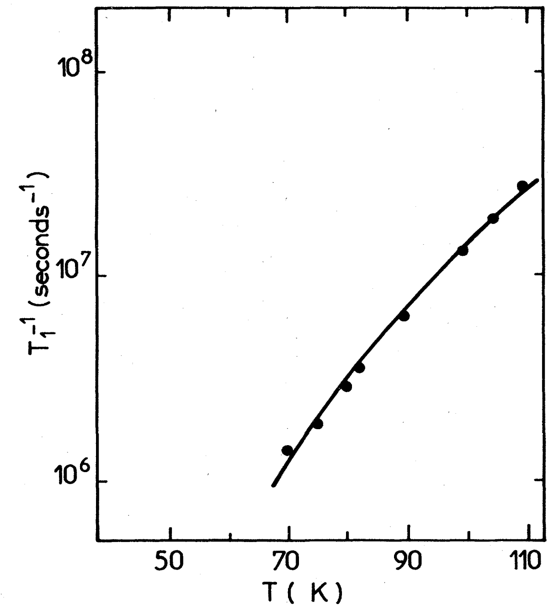

FIG. 9. Relaxation rate vs temperature in iron potassium alum at 9.3 GHz. The solid curve fits the law $T_1^{-1}=1.11\times10^{-6}T^{6.5}$.

about 0.5 g. We have determined the $T_1^{-1}(H)$ dependences at 77 K for the two alums and the double sulfate.[30,56] They are shown on Figs. 4–6. The values, found by other authors using nonresonant techniques, are also given. Furthermore, we have determined the temperature dependences of the relaxation rate in these salts (Figs. 7–9). The temperature ranges are centered at 77 K. The dependences fit the following laws:

CrK alum $T_1^{-1}=1.53\times10^{-3}T^{4.8}$ ,

CuK double sulfate $T_1^{-1}=2.32\times T^{3.4}$ ,

FeK alum $T_1^{-1}=1.11\times10^{-6}T^{6.5}$ .

Entering these data in Eq. (8), we obtain, respectively, $\Theta_D=400$, 330, and 600 K.

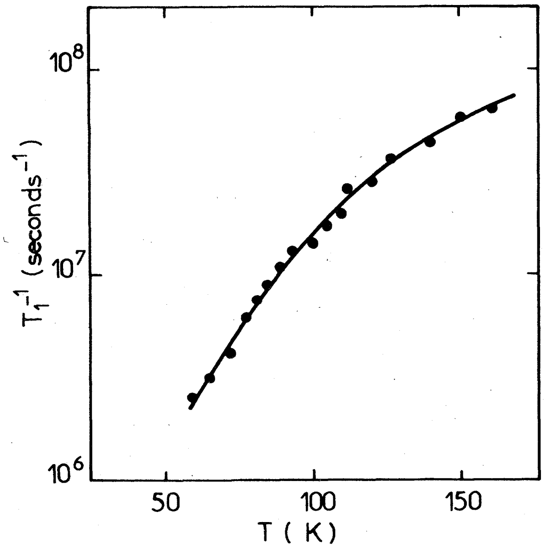

FIG. 8. Relaxation vs temperature in copper potassium double sulfate at 9.3 GHz. The solid curve fits the law $T_1^{-1}6=2.32T^{3.4}$.

## VI. DISCUSSION

### A. Comparison with other results

Noticeable differences are clearly seen between Gorter measurements and ours (Figs. 4–6). But nonresonant data, obtained several decades ago, were not precise and chiefly concerning $T_1$ shorter than $10^{-7}$ s. the absolute error in the Gorter measurements with chromium alum is higher than ours by a factor of 4.5. However, the errors are averaged when determining $\mu'$ or $\mu_1'$ from the plots $T_1(H)$. So, the values of $\mu'$ and $\mu_1'$ obtained by Gorter and us for chromium alum and copper potassium double sulfate are very close to each other. In contrast, they differ by a factor of 2 for iron alum. But, as seen in Sec. III, the Gorter data concerning this salt are very doubtful.

Our data concerning $H_{\mathrm{dip}}$ or $H_{\mathrm{exch}}$ are in good agreement with the Gorter measurements for chromium alum and copper potassium double sulfate. The agreement is rather poor for iron alum. But, the Gorter determination was not obtained from the curves $T_1(H)$ which might explain the discrepancy. The agreement concerning $T_{10}^{-1}$ values is good for chromium alum, moderate for copper potassium double sulfate, and poor for iron alum. The explanations given for $\mu'$ and $\mu_1'$ remain valid here.

### B. Comparison between our calculations and experiments

The agreement concerning $\mu'$ and $\mu_1'$ is excellent for CuK double sulfate. (See Table II.) It is good for FeK alum and rather moderate for CrK alum. So, we have to discuss the assumptions used in calculation. They were the following: (i) The crystal-field model can be used here; (ii) the matrix elements of the dynamical crystalline potential can be replaced by those of the static potential; (iii) $L$ and $S$ are separately conserved; (iv) the internal field is essentially due to dipolar interaction in alums and exchange interaction in CuK double sulfate.

The first assumption, which is fundamental for the Orbach theory, is well justified with the three investigated salts.[34,40,58] It has also permitted determinations of energy levels in good fit with experiment.[39,52] The second assumption has been used because the matrix elements of the dynamcial crystalline potential are hard to estimate. The agreement between the computed and measured values is sufficient to justify the assumption. It is perhaps responsible for the small disagreement encountered in chromium alum. The validity of the third assumption is bound to the value of the spin-orbit coupling constant. For the iron group it reaches its maximum value with $\mathrm{Cu}^{++}$ $\lambda \sim 800\ \mathrm{cm}^{-1}$. But, in double sulfate[39] $V_{\mathrm{cryst}} \sim 15\,000\ \mathrm{cm}^{-1}$. So the inequality $V_{\mathrm{cryst}} \gg \lambda$ is obeyed, making this assumption valid.

Concerning the fourth assumption, the hyperfine field is negligible in these salts, as compared with dipolar or exchange fields. This arises from the weakness of nuclear magnetic moments.[59] On the other hand, the Néel temperature in chromium alum[60] is $10^{-3}$ K and the ESR line is strictly Gaussian which indicates $H_{\mathrm{dip}} \gg H_{\mathrm{exch}}$ in this salt. The conclusion remains valid for iron alum which presents the same crystalline lattice. In copper potassium double sulfate[40] $H_{\mathrm{dip}}/H_{\mathrm{exch}} \sim 0.1$. We have calculated $\mu_1'$ supposing $H_{\mathrm{dip}} \ll H_{\mathrm{exch}}$. The computed and measured values are equal which confirms the validity of the assumption. However, in the alums, the difference between the computed and experimental values of $H_{\mathrm{dip}}$ might indicate that the linewidth is due to several interactions. In this case, Eq. (11) should in-

TABLE IV. Measured and computed values of $T_{10}^{-1}$, $\mu'$, $\mu_1'$, $H_{\mathrm{dip}}$, and $H_{\mathrm{exch}}$ for CrK alum, CuK double sulfate, and FeK alum. (1) Using the $\Theta_D$ value obtained from literature (the references are given in Sec. III). (2) Using the $\Theta_D$ value obtained from our experimental dependence $T_1^{-1}(T)$.

| | $T_{10}^{-1}$ ($10^{-6}$ $\mathrm{s}^{-1}$) | | | | $\mu'$ or $\mu_1'$ | | | $H_{\mathrm{dip}}$ or $H_{\mathrm{exch}}$ ($10^{-3}$ Oe) | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Calc. (1) | Calc. (2) | Meas. | Other[a] Meas. | Calc. | Meas. | Other Meas. | Calc. | Meas. | Other Meas. |
| $\mathrm{KCr(SO_4)_2{\cdot}12H_2O}$ | 1 | 1.5 | 2 ± 0.2 | 1.9 ± 0.35 | 6 | 4 ± 0.3 | 4.5 ± 1.4 | 0.30 | 1.14 ± 0.05 | 1.14 |
| $\mathrm{K_2Cu(SO_4){\cdot}6H_2O}$[b] | $1.8 \times 10^{-3}$ | 10 | 9.6 ± 0.4 | 7 | 1.6 | 1.45 ± 0.1 | 1.5 | 0.43 | 0.6 ± 0.2 | 0.49 |
| $\mathrm{KFe(SO_4)_2{\cdot}12H_2O}$ | 0.7 | 1.8 | 1 ± 0.1 | 3 | 18 | 14 ± 1 | 8 | 0.45 | 1.5 ± 0.3 | 0.75 |

[a] References 13 and 57.

[b] The influence of the adopted $\Theta_D$ values in the calculation of $T_{10}^{-1}$ is relevant here since difference by three orders of magnitude is clearly seen.

clude supplementary terms such as $\frac{1}{2}\mu''H^2$ . . . . We have not taken them into account which can explain the differences between the computed and measured $\mu'$ values. Also, it has to be remembered that the purpose of the theory, outlined in Sec. II, was essentially to give an order of magnitude for the relaxation parameters. Thus, the difference between the computed and measured values of $\mu'$ in chromium alum can be considered as acceptable. Moreover, the same type of disagreement has been reported for both DyES[24] and NdES.[18] For calculating $T_{10}^{-1}$, we have used the dependence $T_1(T)$. In chromiuim alum, the theoretical dependence fits well wtih the experimental data adopting $\Theta_D = 400$ K. This value is in marked disagreement with the result of sound-velocity measurements $\Theta_D = 147$ K, performed by Fedorov[61] in aluminium potassium alum. But, in Ref. 23, at the end of the paper, Van Vleck announces $\Theta_D = 330$ K. In iron potassium alum, the experimental dependence $T_1(T)$ shows that $\Theta_D = 600$ K. But, the value of 330 K, suggested by Van Vleck for chromium alum, should be convenient here since both alums present almost the same lattice. Here, the discrepancy is significant but unexplained. At last, concerning copper potassium double sulfate, the value $\Theta_D = 350$ K is found from the dependence $T_1^{-1}(T)$. Here again, the value of $\Theta_D$ is different from that obtained from specific-heat measurements (105 K), even adopting the De Vries[45] determination (220 K). In fact, for the investigated complex lattices, the $\Theta_D$ parameter is poorly defined. It has to be considered rather as an adjustable parameter, as clearly suggested by Marchand and Stapleton.[19]

We have also developed calculations for CrK alum and CuK double sulfate, using the Scott and Jeffries (SJ) assumptions about the dynamic crystalline potential [Eq. (4)]. The obtained $T_{10}^{-1}$ values are noticeably too high, which confirms the inadequacy of the model for $3d$ salts. We find again the conclusion drawn by Singh and Sapp[18] and by Huang.[62] The SJ model is adequate for relaxation in rare-earth salts, because it influences chiefly the 6th-order terms of the crystalline potential. These terms disappear in $3d$ salts.

## VII. SUMMARY OF RESULTS AND CONCLUSION

We have proposed an extension of the Orbach-Huang theory to the iron group. It has been used to compute the parameters of the relaxation field dependence in three salts chosen as making possible calculations and showing various physical situations. We have measured the parameters using the modulation method, a resonant technique well suited to short $T_1$ measurements. The agreement between the calculated and measured parameters is excellent for copper potassium double sulfate and good for iron potassium alum, in spite of the complex computation in an $S$-state salt. The agreement is less satisfactory for chromium slum. So, we have carefully examined the assumptions used in calculation but none can be considered as unreasonable. Furthermore, the theory used is very complex and only adequate to give an order of magnitude. In determining parameter $T_{10}^{-1}$, we have considered the dependence of relaxation with temperatures ranging from 50 to 150 K. The experimental dependence leads to a value of the upper limit for the $I_8$ for the Van Vleck integral, generally higher than the Debye temperature as found from specific-heat or sound-velocity measurements. The difference is small for chromium alum, more important for CuK double sulfate, and large for iron alum. The calculations and experiments presented here show the Orbach-Huang theory and its extension to the iron group to be a very useful and general tool adequate for explaining experimental data. Furthermore, it is based upon assumptions which can be considered as well justified throughout the investigated salts.

## ACKNOWLEDGMENTS

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