RELAXATION OF LOCALIZED MOMENTS IN *Gd* PURE METAL, ABOVE THE CURIE TEMPERATURE DETERMINATION OF T_{fl}, T_{fs} AND T_{sf}

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ABSTRACT

The use of an amplitude modulated microwave field, allows the quantity $d\,(M_f + M_s)_z/dt$ to be detected, from which direct measurement of $T_{1\,eff} = 1/T(^{-1}_{fs} + T^{-1}_{fl})$ can be drawn. The method is adequate for very short values of $T_{1\,eff}$, and, applied to *Gd* metal at 353 K (paramagnetic region), it yields $T_{1\,eff} = 1.,5 \cdot 10^{-10}s$. This value is in good agreement with that which can be obtained from the linewidth. By comparing with BURZO and DOMŞA's results and the relation giving the relaxation rate T^{-1}_{fs}, T_{fl}, T_{fs}, T_{sf} can be deduced, if an assumption on the temperature dependence of T_{fl} is accepted.

INTRODUCTION

The mechanism of *f l*-coupling in rare earth metals is as yet unknown, in spite of many approaches. So, direct measurement of T_{fl} would be very useful. We have tried to obtain results in this way by determining the rate of return of $(M_f + M_s)_z$ to the thermal equilibrium. For that, we have utilized a modulation method primitively carried out for very short T_1 measurements in insulators. First we recall the principle of this method.

I. MEASUREMENT OF VERY SHORT SPIN LATTICE RELAXATION TIMES IN PARAMAGNETIC SALTS

The microwave field H_1 is amplitude modulated with the frequency $\Omega/2\Pi$. Then a signal s proportional to dM_z/dt is induced into a pick-up coil close to the sample, and with axis parallel to H_0, the Zeeman field. When Ω is varied, keeping constant all the other parameters, T_1 may be found from the variation of s with Ω. The method is adequate for very short times, less than $10^{-6}s$ and free of H_1 and

T_2 measurement [1, 2]. The calculation of s, by means of Bloch's equations is readily obtained, assuming the modulation ratio very low. It gives:

$$s \propto |dM_z/dt| \propto \left\{ X^2 \cdot \left(\frac{1+P^2X^2}{4} \right) / (1+X^2) \cdot (1+P^2X^2) \{ \tfrac{1}{2} \} \right.$$

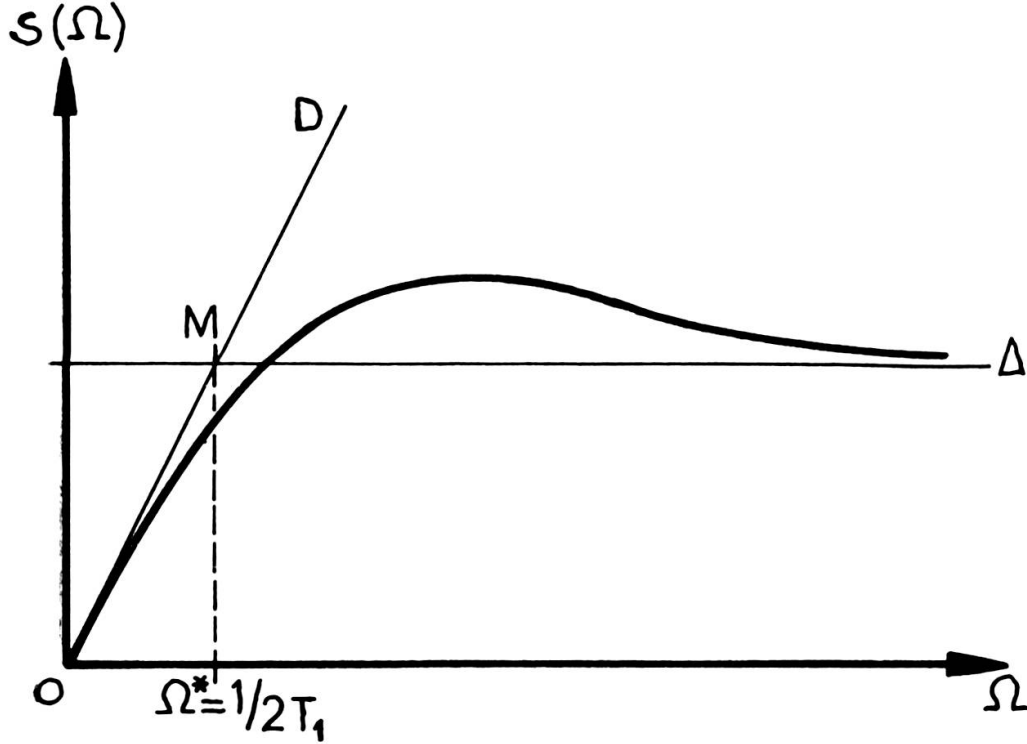where $X = \Omega T_1$ and $P = T_2/T_1$.

FIG. 1. — Determination of T_1 from the curve s (Ω) in the modulation method. The curve s (Ω) is plotted by means of the experimental datas. The straight lines D and Δ are deduced of it. The abcissa of M, the point were D and Δ are crossing, yields $1/2$ T_1.
For very short T_1, the beginning of the curve is only traced and gives D. We find indirectly Δ by comparing the signal s with the transmitted signal v.

The determination of T_1, from the curve s (Ω) is clearly seen on figure 1. The resonance is supposed unsaturated. The block-diagram of the apparatus is given in figure 2.

When T_1 is less than $10^{-8}s$, a high value is required for $\Omega/2\Pi$. But technological difficulties prevent the apparatus from producing $\Omega/2\Pi$ values higher than about 30 MHz. Therefore the asymptote Δ can no more be outlined from the curve s (Ω). In this case Δ will be so obtained [2, 3]:

The signal s, given by the pick-up coil, is again measured, but also the signal v yielded by the same spectrometer, working in transmission (fig. 3). The signal v is obviously independent of the modulation and it is readily seen, from a simple calculation [3], that a constant ratio K exists between v and the plateau-value of s. Hence a very short T_1 will be found:

s is measured for some values of Ω obtainable with the apparatus. Thus, D can be drawn (fig. 1). Then v is measured and, if K has been calculated, the asumptote Δ can be determined and also T_1.
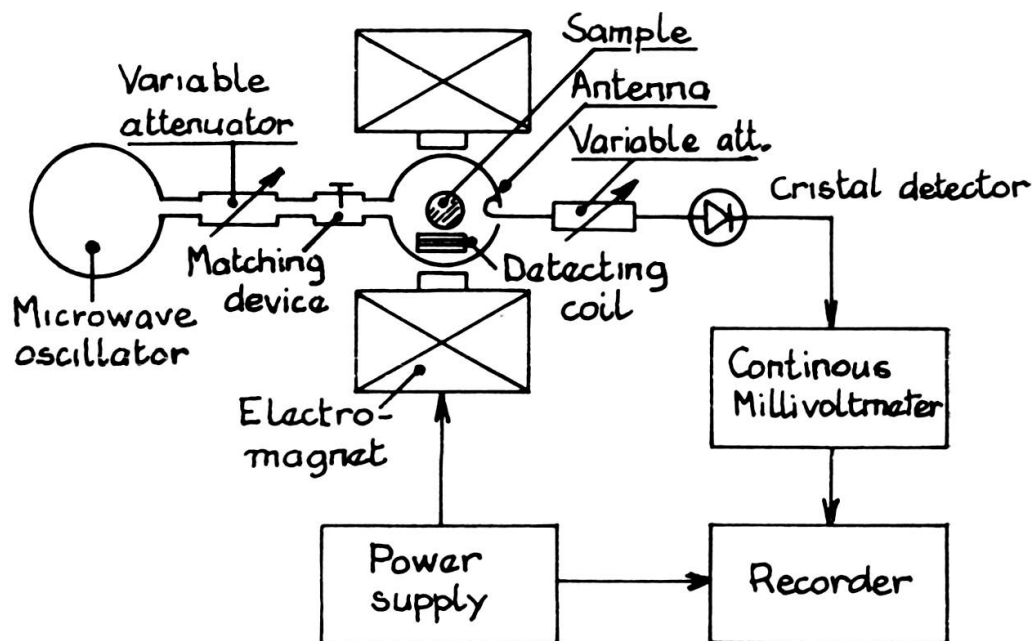

FIG. II. — Block diagram of the apparatus.
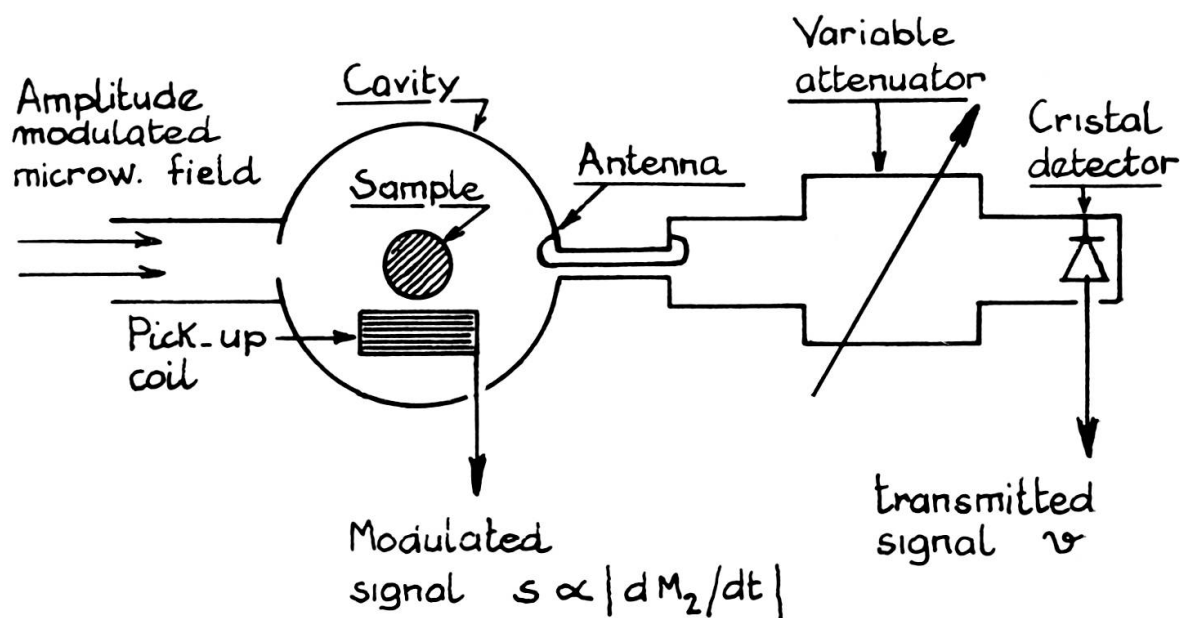

FIG. III. — Arrangement for short T_1 measurements.
A constant ratio K between the plateau-value of s and v, exists.

II. MEASUREMENT OF VERY SHORT RELAXATION TIMES IN METALS

The equations written for paramagnetic salts are inadequate for metals and a new complete calculation must be carried out for them. For this calculation, we have adopted the phenomenological equations of Langreth et al. [4, 5, 6], neglecting the diffusion term for conduction electrons, not essential here:

$$d\vec{M}_s/dt = \gamma \vec{M}_s \times (\vec{H} + \alpha \vec{M}_f) - (T_{sf+}^{-1} T_{sl}^{-1})(\vec{M}_s - \chi_s^\circ(\vec{H} + \alpha \vec{M}_f))$$
$$+ T_{fs}^{-1}(\vec{M}_f - \chi_f^\circ(\vec{H} + \alpha \vec{M}_s))$$
$$d\vec{M}_f/dt = \gamma \vec{M}_f \times (\vec{H} + \alpha \vec{M}_s) - (T_{fs+}^{-1} T_{fl}^{-1})(\vec{M}_f - \chi_f^\circ(\vec{H} + \alpha \vec{M}_s))$$
$$+ T_{fs}^{-1}(\vec{M}_s - \chi_s^\circ(\vec{H} + \alpha \vec{M}_f))$$

They had to be solved with:

$$\vec{H} = \vec{H}_0 + \vec{H}_1 = \vec{H}_0 + \hat{H}_1(1 + me^{i\Omega t}).\vec{u}, \text{ assuming } m \ll 1.$$

Being respectively $M_{u,v,z}$ and $m_{u,v,z}$ the components of $\vec{M}_f$ and $\vec{M}_s$ in the rotating frame, the following solutions were to be expected:

$$M_{u,v,z} = M_{u,v,z}^\circ + D_{u,v,z} \cdot e^{i\Omega t}$$
$$m_{u,v,z} = m_{u,v,z}^\circ + d_{u,v,z} \cdot e^{i\Omega t}$$

and the signal s was expressed as:

$$s \propto \left| \frac{d}{dt}(M_z + m_z) \right| \propto \left| \Omega(D_z + d_z)e^{i\Omega t} \right|$$

The calculation has been made by means of linear algebra methods. In order to simplify equations, several assumptions were used:

the resonance is unsaturated

the substance investigated is *Gd* pure metal, above the Curie point, for which $\Delta g = -0,020$ [7]. This means the absence of bottleneck and therefore:

$$T_{sl}^{-1} > T_{sf}^{-1}$$

For pure *Gd*, $\chi_r^\circ \gg 1$ and $T_{sl}^{-1} > T_{sf}^{-1} \gg T_{fs}^{-1}, \alpha \chi_s^\circ \ll 1$ and $\alpha^2 \chi_s^\circ \chi_f^\circ \ll 1$

Then, we have obtained:

$$s \propto \left| m\gamma^2 \hat{H}_1^2 H_0 \Omega \chi_f \cdot \frac{1}{T_{fs}^{-1} + T_{fl}^{-1} + i\Omega} \cdot \left(\frac{1}{T_{fs}^{-1} + T_{fl}^{-1}} + \frac{1}{T_{fs}^{-1} + T_{fl}^{-1} + i\Omega} \right) \right|$$

This suggests that localized moments relax with a characteristic time T_{1eff} defined as:

$T_1^{-1}{}_{eff} = T_{fs}^{-1} + T_{fl}^{-1}$ which gives:

$$s \propto \frac{2ma\,M_f}{T_{1\,eff}} \cdot \frac{X\,(1+X^4/4)^{1/2}}{1+X^2} \qquad \text{where } \begin{array}{l} X = \Omega\,T_{1eff} \\ a = \gamma^2\,H_1^2\,T_{1eff}^2 \end{array}$$

The expression obtained in section I, but with $P = T_2/T_1 = 1$, is found again. It follows that the method is adequate for Gd pure metal and allows the measurement of T_{1eff}, as defined above.

III. EXPERIMENTAL RESULTS

The method has been applied to Gd pure metal. The powered sample was prepared by filing an ingot with 99,9 % purity. The grains were calibrated with a sieve and mixed with powered suprasil quartz. The maximum size of the grains was less than 20μ.

The Curie temperature of Gd, yielded by extrapolating the Curie-Weiss law, is 302 K [8].

We have measured T_{1eff} at 353 K, which gives:

$$T_{1eff} = (1,50 \pm 0,10) \cdot 10^{-10}s.$$

We have also measured T_{2eff}, from the line-width. This was very easy because $|dM_z/dt|$ gives a simple absorption line, in contrast with classical spectrometers which give the Dyson line. The value found was:

$$T_{2eff} = (1,46 \pm 0,10) \cdot 10^{-10}s.$$

To within the experimental accuracy, a good agreement with Burzo and Domşa (hereafter referred to as BD) results appears. Furthermore, we notice the equality:

$$T_{1eff} = T_{2eff}$$

As a result of our experiments and calculations we have probably given the first verification of this equality in metals. It could be due to the ability of our method to measure short relaxation times.

The equality shows the line-width dependence on T_{fs} and T_{fl}, via the definition of T_{1eff}. It justifies the calculations of section II and the assumptions used in it.

We have also performed some preliminary experiments over the temperature range from 283 to 353 K. Close to the Curie temperature, the above equality breaks down and T_{2eff} becomes less than T_{1eff}. This could be due to magnetization fluctuations and perhaps the appearance of some spinwaves, with a very complicated processus of relaxation.

IV. INTERPRETATION

The rate of loss of magnetisation from the local spins to the conduction electrons ($f \rightarrow s$) is [5, 6]:

$$T_{fs}^{-1} = (\Pi/\hbar)(J/\eta)^2 \, \eta(E_f)^2 \, k(T - \theta)$$

Taking for J and $\eta(E_f)$ the value drawn from the band structure of Gd [7]:

$$J = 0,011 \, eV \quad ; \quad \eta(E_f) = 1,80 \, eV^{-1}, \quad \text{we find } T_{fs} = 1,21 \cdot 10^{-10} s$$

which is less than T_{1eff}. These two results are inconsistent because T_{1eff} must be shorter than both T_{fs} and T_{fl}. It can be reasonably thought that this so calculated T_{fs} value is wrong. In effect, J and $\eta(E_f)$ utilized values do not account for interactions between f-electrons which should be strong in pure metals.

So, we calculate T_{fs} by another way. The half line-width of Gd, which at 353 K presents a rather gaussian line shape, can be expressed as [9]:

$$\frac{(\Pi \, Ln2)^{1/2}}{\gamma \, T_{2eff}} = \frac{(\pi \, Ln2)^{1/2}}{\gamma \, T_{1eff}} = \zeta(T_{fs}^{-1} + T_{fl}^{-1})$$

with $\zeta = (\pi \, Ln2)^{1/2}$

But BD give, for the same, the expression $a + bT$ where $a = -1125,6 \, G$ and $b = 4,8 \, G/K$ (in good fit with results of section III). The relaxation rate ($f \rightarrow s$) can be written again as:

$$T_{fs}^{-1} = \lambda(T - \theta), \text{ with: } \lambda = (\pi/\hbar)(J/n)^2 \, \eta(E_f)^2 \, k$$

From all these equations, we obtain:

$$T_{fl}^{-1} = a/\zeta + \lambda \theta + (b/\zeta - \lambda) \, T \quad \text{or:} \quad T_{fl}^{-1} = c \, T + d$$

Now, to progress without further measurements, an assumption becomes necessary. Firstly, we assume T_{fl} temperature independent. This implies $c = 0$, that is to say $\lambda = b/\zeta$, and, it is readily found:

$$T_{fl} \simeq 2,6 \cdot 10^{-10} s$$
$$T_{fs} \simeq 3,4 \cdot 10^{-10} s \qquad \text{(at 353 } K)$$

Taking $\chi_r^\circ = 3965$ (value calculated for pure Gd at 353 K) we have:

$$T_{sf} \simeq 8,6 \cdot 10^{-14} s$$

In contrast with our first theoretical estimate of T_{fs}, we obtain nearly equal contribution of fs and fl-couplings to the relaxation of localized spins.

Now, it is useful to consider the inverse situation, in which T_{fl} would be temperature dependent. This case corresponds to c different of zero and we have:

$$T_{fl}^{-1} = cT + d$$

for simplicity we assume $d = 0$. Then the equations give:

$$T_{fl} \simeq 2,2 \cdot 10^{-10} s$$
$$T_{fs} \simeq 4,4 \cdot 10^{-10} s$$
$$T_{sf} \simeq 1,1 \cdot 10^{-13} s$$

These values are not very different of the preceeding, in spite of a processus probably quite different.

The essential question is to choose between the two contradictory assumptions. The first assumption seems to indicate that phonons play no role in the relaxation. It would be opposite to Monod and Schultz results [10], from which a phonon influence would appear above $20\,K$; but they are concerned with iron group dilute alloys, which can be very different to our case.

The second assumption leads to a temperature dependence similar to that encountered with direct process in paramagnetic salts. A priori, it would imply phonons in the mechanism of relaxation.

At last, it must be remembered that we are concerned with pure Gd, in which interactions between f-electrons themselves are probably strong. This could play an essential role in the relaxation mechanism. But it is obvious that further experiments and calculations will be necessary to attain a better understanding of the phenomenon.

CONCLUSION

The measurement of $d(M_f + M_s)_z/dt$, with an amplitude modulated microwave field allows the determination of the parameter:

$$T_{1eff} = \frac{1}{T_{fl}^{-1} + T_{fs}^{-1}}$$

in Gd pure metal. The equality $T_{1eff} = T_{2eff}$ (being T_{2eff} drawn from the linewidth) has been verified at 353 K. It breaks down when approaching the Curie temperature.

By comparing these results with BD's and the relaxation rate ($f \to s$) relation, T_{fl}, T_{fs} and T_{sf} can be determined, if an assumption on the temperature dependence of T_{fl} is accepted. fl and fs-couplings seem to bring equal contributions to the relaxation of localized moments.

We are trying to extend the method to other metals and dilute alloys at low temperature.

A future publication shall give complete analysis of the calculation outlined in section II, and detailed information about experiments on *Gd* when temperature is varied.

ACKNOWLEDGEMENTS

REFERENCES

[1]   J. PESCIA, Ann. Phys. *10*, 389 (1965).
[2]   B. VIGOUROUX, thesis, University of Toulouse III (1973).
[3]   J. C. GOURDON, B. VIGOUROUX and J. PESCIA, Physics Letters, *45A*, 69 (1973).
[4]   D. C. LANGRETH, D. L. COWAN and J. W. WILKINS, sol. state com. *6*, 131 (1968).
[5]   D. C. LANGRETH and J. W. WILKINS, Phys. Rev. B *6*, 9, 3189 (1972).
[6]   J. H. PIFER and R. T. LONGO, Phys. Rev. B *4*, 3797 (1971).
[7]   E. BURZO and F. DOMSA, Rev. Roum. Phys. *17*, 893 (1972).
[8]   "AMERICAN INSTITUTE OF PHYSICS HANDBOOK" MC GRAWHILL BOOK COMPANY, Second edition, p. 5—220 (1963).
[9]   R. S. ALGER, "ELECTRON PARAMAGNETIC RESONANCE" INTERSCIENCE PUBLISHERS, p. 45 (1968).
[10] P. MONOD and S. SCHULTZ, Phys. Rev. *173*, 645 (1968).