

Laboratori Nazionali di Frascati

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AND LATTICE TEMPERATURE.

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V. MONTELATICI  
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## Thermodynamical Approach to Spin and Lattice Temperature.

V. MONTELATICI

*Laboratori Nazionali di Frascati del CNEN - Frascati*

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**Summary.** — In a previous article we studied the dynamic polarization of a system with spins  $S = I = \frac{1}{2}$  using a thermodynamic treatment. In this article the lattice and spin temperatures are deduced. Also, in the case where the temperatures of the two kinds of spin are equal, the conditions on the relaxation times and on the energy levels have been worked out.

### 1. — Introduction.

In a previous paper (hereafter referred to as I) <sup>(1)</sup>, we studied the dynamic polarization of two different types of magnetic moments, namely those associated with the spin angular momentum of electrons and nuclei.

The system was considered as an ideal gas and the Boltzmann distribution was assumed. The general relation for the internal entropy production rate

$$(1) \quad \left(\frac{dS}{dt}\right)_{\text{int}} = -\frac{1}{T} \sum_i \mu_i \frac{dn_i}{dt}$$

was applied, where  $\mu_i$  and  $n_i$  stand for the chemical potentials and the mean occupation number of the  $i$ -th energy level respectively;  $T$  is the temperature of the heat bath.

Imposing that the quantity (1) be zero, in thermal equilibrium at temperature  $T$  and with the right conditions of saturation between certain levels, it was possible to obtain an expression for the polarization for one type of magnetic moment (that of the nuclei).

<sup>(1)</sup> V. MONTELATICI: *Nuovo Cimento*, **32**, 1613 (1964).

Only the expressions for the polarization were given in paper I, but in a pumping radiofrequency field the two types of magnetic moment are at different temperatures.

The purpose of this paper is to deduce, using a statistical approach, the temperatures of the two types of magnetic moments; also the conditions on the relaxation times for the two types of spins which would yield the same temperatures for all the spins are investigated.

## 2. - Spin temperature and chemical potential.

In the study of dynamic polarization, as in other phenomena involving transitions between energy levels, the usual way is to consider the system as composed of subsystems at different temperatures.

The possibility of defining these temperatures implies an interaction mechanism <sup>(2)</sup> which conserves the energy among the spins (*i.e.* as a result of this interaction among the spins the number of transitions per unit time in one direction equals that in the reverse direction).

After a characteristic time the spins are at the same equilibrium temperature.

In the electronic and nuclear spin double resonance an electromagnetic field and a heat bath can change the temperatures of the two types of spin and of the lattice.

When the electromagnetic field is applied, the system reaches a new equilibrium state in which the population ratios of the subsystems change.

Generally the two spin temperatures are different from that of the lattice, and from one another.

Another view point is possible <sup>(3)</sup>: the subsystems (of the two types mentioned: electronic and nuclear) are divided into groups according to the spin energy state in which they lie. To each group a chemical potential is assigned, which becomes the parameter describing the population distribution. In this case the temperature is fixed by the initial conditions which the chemical potentials satisfy in the absence of an electromagnetic field.

The heat bath fixes the lattice and spin temperature in the initial state.

Clearly, these two viewpoints must lead to the same populations ratios for the various possible equilibrium states when an electromagnetic field is applied to the system. That is, the distribution may be represented by spin temperatures, or by chemical potentials.

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<sup>(2)</sup> N. RAMSEY: *Phys. Rev.*, **103**, 20 (1956).

<sup>(3)</sup> Subdivision of electrons and nuclei into groups is implicit in the article by P. BROVETTO and G. CINI: *Nuovo Cimento*, **11**, 618 (1954).

### 3. - Spin and lattice temperatures in the double effect.

We consider a system composed of two subsystems of magnetic moments associated with the spin angular momentum of electrons and nuclei with  $S = I = \frac{1}{2}$ . Hereafter the notation shall be as in paper I.

Let a system of magnetic moments in a constant magnetic field have a temperature  $T$ .

The population ratios are, according to the Boltzmann distribution,

$$(2) \quad \left(\frac{n_+}{n_-}\right)_{\text{e.m.}} = \exp\left[\frac{-\Delta E}{KT^*}\right],$$

when they interact with an electromagnetic field of right frequency, where  $T^*$  is the new temperature.

When the electromagnetic field is switched off the system reaches a new equilibrium state at the temperature  $T$  of the heat bath. Now the population ratio is

$$(3) \quad \left(\frac{n_+}{n_-}\right)_{\text{bth.}} = \exp\left[\frac{-\Delta E}{KT}\right].$$

The temperature  $T^*$  is the parameter defining the population ratio and takes all the values between  $T^* = +0$  and  $T^* = +\infty$ .  $T$  is related to the electromagnetic field power  $P$  by

$$(4) \quad T^* = T\left(1 + \frac{W}{w}\right),$$

where  $W \propto P$  is the induced transition probability due to the alternating field and  $w$  is that of the thermal relaxation.

The distribution (2) using chemical potentials is written

$$(5) \quad \left(\frac{n_+}{n_-}\right) = \exp\left[\frac{\Delta\mu - \Delta E}{KT}\right] = \exp\left[\frac{(\mu_+ - \mu_-) - (E_+ - E_-)}{KT}\right].$$

Since the equilibrium state must give the same population ratios, one obtains from (5) and (2)

$$(6) \quad \Delta\mu = \Delta E\left(1 - \frac{T}{T^*}\right).$$

The behaviour of (6) is represented in Fig. 1, which shows some properties of a system with the gyromagnetic ratio  $\gamma_s < 0$  (solid line) and  $\gamma_s > 0$  (dotted line); hereafter the symbols ( $S$ ) and ( $I$ ) are introduced,  $S$  refers to electrons,

$I$  to nuclei; when an energy  $\Delta E$  is given to the system, the populations of the two levels are equal.

Negative temperatures  $r$  correspond to the higher energy level having a larger population than the lower.

Total occupation of the higher level corresponds to a temperature  $T = -0$ ; while the temperature  $T = +0$  corresponds to the total filling of the lower level.

The difference  $\Delta\mu$  in the chemical potential of a subsystem is related to the power  $P \propto W$  of the radiation on field by

$$(7) \quad \Delta\mu = \frac{\Delta E}{1 + w/W}.$$

The radiation field in the double effect equalizes the populations of the levels between which the energy differences are

$$(8) \quad h\nu = \hbar(\nu_s \mp \nu_I).$$

The saturation conditions give relations between the difference of chemical potentials and the energies of the levels.

Moreover (1) gives relations between differences of chemical potentials and transition probabilities:

$$(9) \quad \begin{cases} \Delta\mu^{(I)} = \pm \Delta\mu^{(S)} \frac{w_S + w_{x,y}}{w_I + w_{x,y}}, \\ \Delta\mu^{(S)} \pm \Delta\mu^{(I)} = \Delta E^{(S)} \pm \Delta E^{(I)}. \end{cases}$$

The upper sign is for  $N_+n_+ = N_-n_-$ , the lower one for  $N_+n_- = N_-n_+$ .

When  $1/\omega_I \gg 1/\omega_{x,y} \gg 1/\omega_S$  one obtains, by solving for  $\Delta\mu^{(S)}$  and  $\Delta\mu^{(I)}$ ,

$$(10) \quad \Delta\mu^{(I)} \neq 0, \quad \Delta\mu^{(S)} = 0.$$

From Fig. 1 it is clear that the spin temperatures are different for the two subsystems ( $S$ ) and ( $I$ ).

Writing the population ratio for the subsystem ( $I$ ) in the two representations

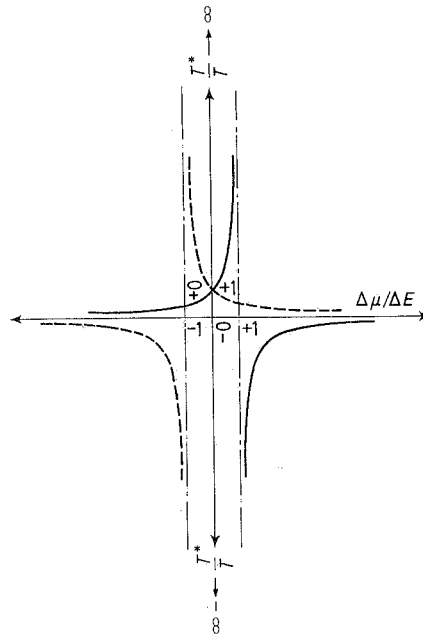


Fig. 1. - Schematic dependence of  $(T^*/T)$  vs.  $(\Delta\mu/\Delta E)$  for two subsystems. Dashed line  $\gamma_I > 0$ , solid line,  $\gamma_S < 0$ .

one obtains

$$(11) \quad T_I^* = \pm T_S^* \frac{\gamma_I}{|\gamma_S|} = \pm T \frac{\gamma_I}{|\gamma_S|}.$$

The temperature of the subsystem ( $I$ ) is lowered when the transition corresponding to the upper sign in (8) is saturated; while it is raised when the transition corresponding to the lower sign is saturated, that is, one has a nuclear maser effect.

#### 4. - Equal spin temperatures for two different spin systems.

A dynamical equilibrium is reached in the double effect in which  $T_S^* \neq T_I^*$  under either of the two possible saturation conditions:

$$(12) \quad N_+ n_+ = N_- n_-, \quad N_+ n_- = N_- n_+,$$

and for a relaxation time  $\tau_s \ll \tau_I$ . An electromagnetic field with sufficient power in fact satisfies one of the relations (12).

Now one asks how must the energy levels intervals be modified and what relations may be found between the relaxation times for subsystems ( $S$ ) and ( $I$ ) when all these three conditions apply:

- a) one of the two relations (12) holds,
- b) the two subsystems have the same temperature  $T_S^* = T_I^*$ ,
- c) the electromagnetic field is absent.

A system composed of two subsystems ( $S$ ) and ( $I$ ) is considered and it is assumed to be irradiated with an electromagnetic field of small enough intensity to keep the population ratios well away from saturation conditions.

In this case one can write expression (1) explicitly. Moreover one must write the expression for the partition function  $Z_i$  in a way which accounts for the interaction mechanism, which bring the two subsystems to the same temperature.

This interaction among all the spins may be represented by a fictitious mean field.

Now the system shall be a set of particles under the action of an effective field which is the sum of the external field and the fictitious field.

The way to determine such a mean field is given in the Appendix.

The potential energy shall be indicated by

$$(13) \quad \varphi_i = \varphi(\mathbf{r}_i, \mathbf{p}_i),$$

where the suffix  $i$  stands for the potential energy of the particles in the  $i$ -th level.

Now the Boltzmann distribution is applicable to the spin system, and the energy of the  $i$ -th level is

$$(14) \quad E_i^{\text{tot}} = E_i + \varphi_i,$$

where  $E_i$  is the energy due to the external field. The expression for the free energy is

$$(15) \quad F_i = -KT \log Z_i = -KT \log \left[ \frac{1}{n_i!} \exp \left[ \frac{-(E_i + \varphi_i)}{KT} \right] \right]^{n_i},$$

from which one obtains  $n_i$  as a function of the total energy of a level. From (1) one obtains as in I:

$$(16) \quad (\mu_1 - \mu_2) = \mp (\mu_3 - \mu_1) \frac{w_s + w_{xy}}{w_I + w_{xy}},$$

under the conditions (12), the upper sign is valid for the first, the lower for the second of conditions (12).

If one requires  $T = T_s^* = T_I^*$ , then it follows that

$$(17) \quad \mu_1 - \mu_2 = \mu_3 - \mu_1 = 0.$$

From (16) the condition (17) holds only for <sup>(4)</sup>

$$(18) \quad \begin{cases} a) & w_s = w_I & \text{or} & \tau_s = \tau_I, \\ b) & w_{xy} \gg w_s, w_I & \text{or} & \tau_{xy} \ll \tau_s, \tau_I. \end{cases}$$

From (12), bearing in mind that  $\mu_i = \partial F_i / \partial n_i$ , one obtains

$$(19) \quad (\mu_3 - \mu_1) - (E_3^{\text{tot}} - E_1^{\text{tot}}) = \pm (\mu_1 - \mu_2) - (E_1^{\text{tot}} - E_2^{\text{tot}}).$$

For  $\gamma_s < 0$  and  $\gamma_I > 0$ , (19) gives

$$(20) \quad \hbar H |\gamma_s| + (\varphi_3 - \varphi_1) \pm \hbar H \gamma_I + (\varphi_2 - \varphi_1) = 0.$$

<sup>(4)</sup> These conditions on relaxation time are worked out in a density matrix representation by R. T. SCHUMACHER: *Phys Rev.*, **112**, 837 (1958). The relaxation times due to the transition probability  $w_{x,y}$  is a cross-relaxation or thermal mixing time which characterizes the energy transfer between the two subsystems, as shown by N. BLOEMBERGEN, S. SHAPIRO, P. S. PERSHAN and J. O. ARTMAN: *Phys. Rev.*, **114**, 445 (1959).

The relation (20), with the lower sign, gives the energy balance between the Zeeman energies and the potential energy due to the fictitious field, which is always small compared to the Zeeman energy.

Therefore the energy is conserved in those transitions in which

$$\Delta m_s = \Delta m_I = \pm 1.$$

In this case the energy due to the fictitious field supplies  $(\varphi_3 - \varphi_1) - (\varphi_2 - \varphi_1) = \Delta\varphi$  to permit energy conservation according to  $\hbar\nu_s - \hbar\nu_I = \Delta\varphi$ .

These transitions are not radiative, in the sense that no energy is transferred to the lattice.

Naturally one of the conditions (18) must hold, and moreover one infers from (20) that the gyromagnetic ratios must be nearly equal.

In the transitions in which  $\Delta m_s = -\Delta m_I = \pm 1$ , corresponding to the upper sign in (20), the spin energy is not conserved and energy is exchanged with the lattice.

To obey the energy conservation requirements a term giving the total energy, due to  $\mathcal{N}/t$  transitions in unit time, must be subtracted:

$$(21) \quad \hbar H |\gamma_s| + \hbar H \gamma_I - \frac{t}{\mathcal{N}} \frac{E_{\text{tot}}}{t} = 0.$$

This energy is supplied to the lattice as rotational energy to maintain  $T = T_s^* = T_I^*$ .

The Hamiltonian  $\mathcal{H}$  of the system depends on the external field  $H$  and its derivative is the magnetic moment, which is proportional to angular momentum.

Bearing in mind that

$$\left(\frac{\partial \mathcal{H}}{\partial H}\right)_{|+\rightarrow} - \left(\frac{\partial \mathcal{H}}{\partial H}\right)_{|-\rightarrow} = \left(\frac{\partial \Delta E}{\partial H}\right)_{\Delta m_s = -\Delta m_I},$$

where the states  $|+\rightarrow\rangle$  and  $|-\rightarrow\rangle$  represent respectively the states characterized by  $(S = +\frac{1}{2}, I = -\frac{1}{2})$  and  $(S = -\frac{1}{2}, I = -\frac{1}{2})$ , one obtains

$$(22) \quad P = \text{total angular momentum} = 2\mathcal{N}\hbar$$

for  $|\gamma_s| \simeq \gamma_I$ .

Since the transitions appear in a time of the order of  $\tau =$  relaxation time,  $P = 2\mathcal{N}\hbar/\tau$ . When the gyromagnetic ratios have the same sign, energy and angular momentum are conserved for transitions with  $\Delta m_s = -\Delta m_I \pm 1$ .

The angular momentum and energy are conserved, in the transitions  $\Delta m_s = \Delta m_I = \pm 1$ , only if rotational energy is transferred to the lattice.



An experiment to detect the mechanical effect related to paramagnetic resonance has been performed with positive result by ALZETTA and GOZZINI<sup>(5)</sup> on a sample of DPPH.

#### APPENDIX

Assume the energy of the system is quadratic in the occupation number, and the suffixes  $\xi, \eta$  represent the two different types of magnetic moments:

$$(A.1) \quad E^{\text{tot}} = \sum_{\xi} \sum_i n_i^{\xi} E_i^{\xi} + \sum_{\xi\eta} \sum_i \sum_j \Phi_{ij}^{\xi\eta} n_i^{\xi} n_j^{\eta},$$

where  $E_i^{\xi}$  is energy of  $i$ -th level of the type  $\xi$  magnetic moment due to external field,  $\Phi_{ij}^{\xi\eta}$  some quantities to be determined.

If the interaction among spins is described by the sum over all possible pairs  $i^{(\xi)}$  and  $j^{(\eta)}$  of the interaction between two spins  $i^{(\xi)}$  and  $j^{(\eta)}$ , the total energy is

$$(A.2) \quad E^{\text{tot}} = \sum_{\xi} \sum_i n_i^{\xi} E_i^{\xi} + \frac{1}{2} \sum_{\xi\eta} \sum_i \sum_j n_i^{\xi} n_j^{\eta} \chi(\mathbf{r}_i^{\xi}, \mathbf{P}_i^{\xi} | \mathbf{r}_j^{\eta}, \mathbf{P}_j^{\eta}),$$

where

$$\chi_{ij}^{\xi\eta} = \chi(\mathbf{r}_i^{\xi}, \mathbf{P}_i^{\xi} | \mathbf{r}_j^{\eta}, \mathbf{P}_j^{\eta})$$

is the interaction which depends on the radius vector  $\mathbf{r}$  and the momentum vector  $\mathbf{P}$ .

The term  $\sum_j n_j^{\eta} \chi_{ij}^{\xi\eta}$  represents the statistical mean of the function  $\chi_{ij}^{\xi\eta}$  on the suffix  $j$  and it depends on the suffix  $i$  and the particular distribution  $(n_1^{\eta} \dots n_j^{\eta} \dots n_n^{\eta})$ .

By comparing (A.1) and (A.2) the total energy becomes

$$(A.3) \quad E^{\text{tot}} = \sum_{\xi} \sum_i n_i^{\xi} E_i^{\xi} + \frac{1}{2} \sum_{\xi\eta} \sum_i n_i^{\xi} \varphi_i^{\xi\eta},$$

where

$$(A.4) \quad \varphi_i^{\xi\eta}[\mathbf{r}_i^{\xi}, \mathbf{P}_i^{\xi} | \dots n_j^{\eta} \dots] = \sum_j n_j^{\eta} \chi_{ij}^{\xi\eta} = 2 \sum_j n_j^{\eta} \Phi_{ij}^{\xi\eta},$$

the  $i$ -th energy level is

$$(A.5) \quad E_i^{\text{tot}} = \frac{\partial E^{\text{tot}}}{\partial n_i} = \sum_{\xi} E_i^{\xi} + \sum_{\xi\eta} \sum_i n_i^{\xi} (\Phi_{ij}^{\xi\eta} + \Phi_{ji}^{\eta\xi}) = \sum_{\xi} E_i^{\xi} + 2 \sum_{\xi\eta} \sum_{ij} n_i^{\xi} \Phi_{ij}^{\xi\eta},$$

<sup>(5)</sup> A. GOZZINI: *Proceedings of the XII Colloque Ampere* (Amsterdam, 1963), p. 82;  
A. GOZZINI and G. ALZETTA: *Proceedings of XII Colloque Ampere* (Amsterdam, 1963), p. 209.

with  $\Phi_{ij}^{\xi\eta} = \Phi_{ji}^{\eta\xi}$  and putting

$$\sum_{\xi} E_i^{\xi} = E_i, \quad \sum_{\xi\eta} \varphi_i^{\xi\eta} = \varphi_i,$$

one obtains (14).

The mean occupation number of a type of magnetic moment is

$$(A.6) \quad n_i^{\xi} = N^{\xi} \frac{\exp[(1/KT)(-E_i^{\xi} - \sum_{\eta} \varphi_i^{\xi\eta})]}{\sum_i \exp[(1/KT)(-E_i^{\xi} - \sum_{\eta} \varphi_i^{\xi\eta})]},$$

with the normalization  $\sum_i n_i^{\xi} = N^{\xi}$ .

From (A.4) and (A.6) one obtains

$$(A.7) \quad \sum_{\xi\eta} \varphi_i^{\xi\eta} = \sum_{\xi\eta} \sum_j n_j^{\eta} \chi_{ij}^{\xi\eta} = \sum_{\xi\eta} N^{\xi} \frac{\sum_j \chi_{ij}^{\xi\eta} \exp[(1/KT)(-E_j^{\xi} - \sum_{\eta} \varphi_j^{\xi\eta})]}{\sum_j \exp[(1/KT)(-E_j^{\xi} - \sum_{\eta} \varphi_j^{\xi\eta})]}.$$

For further insight into this self-consistent field problem, see ref. (6).

(6) C. A. BARLOW jr.: *Am. Jour. Phy.*, **31**, 247 (1963).

#### RIASSUNTO

In un articolo precedente fu studiata la polarizzazione dinamica di un sistema di spin con  $S = I = \frac{1}{2}$  applicando un procedimento termodinamico. In questo articolo si deducono le temperature di spin e di reticolo. Inoltre, si ricavano, per il caso che le temperature delle due specie di spin siano uguali, le condizioni per i tempi di rilassamento e per i livelli di energia.

#### Термодинамическое приближение для температур спина и решетки.

**Резюме (\*).** — В предыдущей статье мы изучили динамическую поляризацию системы со спинами  $S = I = \frac{1}{2}$ , используя термодинамическую интерпретацию. В этой статье выводятся температуры для спина и решетки. Также, в том случае, когда температуры двух типов спина равны, выведены условия на времена релаксации и уровни энергии.

(\*) Переведено редакцией.