IX

THERMAL RELAXATION AND DYNAMIC POLARIZATION IN SOLIDS

Hence you long-legg'd spinners, hence!
A MIDSUMMER-NIGHT'S DREAM.

In this chapter we extend the study of nuclear relaxation mechanisms to solids. The problem here is essentially the same as that for liquids and gases, namely to calculate the probability of a flip of a nuclear spin caused by its coupling with the thermal motion of a 'lattice'. In the same way as for liquid samples, this flip can always be visualized as resulting from a fluctuating magnetic field or a fluctuating electric-field gradient 'seen' by the nuclear spin under consideration. For some internal motions such as translational diffusion of atoms or hindered rotation of molecules, that take place in solids, the description used for liquids can be taken over with very little change.

There are, however, some significant differences. The internal motions in solids will often have much smaller amplitudes and/or much longer correlation times than in liquids. This has important consequences for the values of the relaxation times.

It is sometimes possible in solids to obtain relatively simple quantum mechanical models of the 'lattice' and to perform a realistic calculation of the relaxation times, using the quantum mechanical approach, which in liquids had a rather formal character. This approach becomes a necessity at very low temperatures when few degrees of freedom of the 'lattice' are excited.

For nuclei with spins larger than $\frac{1}{2}$ the existence of quadrupole interactions in nuclear environments with lower than cubic symmetry (due to crystal structure or to crystal imperfections) modifies the spacings between the spin energy levels and creates new situations, not met with in liquids.

Finally, in solids the tight coupling that exists between nuclear spins has important consequences. In liquids we were able to give a similar treatment both to the calculation of T_1, which measures the time required for the diagonal matrix elements of the density matrix of the spin system (populations) to reach their thermal equilibrium values,

and also to that of T_2, which is the decay time for the off-diagonal matrix elements.

In solids, the establishment of a thermal equilibrium between the spin system and the lattice, under certain conditions outlined in Chapter V, can be broken into two steps; first, the spin system reaches an internal thermal equilibrium with a spin temperature T_S in a time T_2, for which only a qualitative definition can be given since the approach of the spin system to equilibrium has no reason to be and in fact is not exponential; secondly, the spin temperature T_S tends towards the lattice temperature T with a time constant $T_1 \gg T_2$ which can be defined much less ambiguously than T_2, since the decay of a single parameter, the spin temperature (or rather its reciprocal, as will appear shortly), is involved.

A general expression for T_1 under the assumption of the existence of a spin temperature will be derived in the next section in connexion with the problem of nuclear relaxation in metals, which we shall consider first, as possibly the best example of a situation where the quantum mechanical features of the 'lattice' play an important role.

I. CONDUCTION ELECTRONS AND SPIN-LATTICE RELAXATION IN METALS

We saw in Chapter VI that in metals the hyperfine coupling between electronic and nuclear spins produced a modification of the energy levels of the nuclear spin system, expressed by a change in the nuclear Larmor frequency (Knight shift) and by the appearance of the so-called indirect couplings between the nuclear spins. We consider now a dynamical effect of this hyperfine coupling which is a powerful mechanism for nuclear spin-lattice relaxation. We shall assume in its evaluation that the hyperfine coupling is the scalar contact interaction

$$\hbar\mathscr{H} = -\frac{8\pi}{3}\gamma_e\gamma_n\hbar^2\delta(r_I)(\mathbf{I}.\mathbf{S}), \tag{1}$$

disregarding the usually much smaller dipolar coupling of the nuclear spins with the spins of the electrons, as well as their coupling with the orbital moments of the electrons.

In connexion with the contributions of the neglected hyperfine interactions the following point should, however, be made. As explained in Chapter VI, the existence of a dipolar hyperfine coupling could manifest itself through an anisotropy of the Knight shift, and the incomplete quenching of the orbital electronic momentum, responsible for the orbital hyperfine coupling, through a departure of the electronic g-factor from the spin-only value. The absence of these effects in the Knight shift and the g-factor does *not* permit us to conclude that the dipolar and orbital hyperfine couplings are ineffective for nuclear relaxation. The Knight shift has a tensor dependence on the orientation of the applied d.c. field H_0, and any nuclear environment with at least cubic symmetry will necessarily lead to an isotropic Knight shift whatever the character of the individual electronic wave functions.

For the probabilities of relaxation transitions it is the squares of the off-diagonal matrix elements of the dipolar hyperfine interaction that count and those may well be different from zero even if the anisotropic Knight shift vanishes. An analogous argument holds for the orbital coupling.

In that connexion, we saw many examples in Chapter VI of situations where, in spite of the absence of first-order effects, the dipolar and orbital hyperfine couplings were, through the squares of their off-diagonal elements, responsible for effects such as indirect spin-spin couplings and chemical shifts. A value of T_1 calculated on the basis of a purely scalar coupling, the magnitude of which is deduced from the isotropic Knight shift, could then be longer than the real one.

Nuclear relaxation by conduction electrons is not restricted to metals and exists in semiconductors also. However, in the latter it competes with another type of relaxation, that by fixed paramagnetic impurities to be described in Section II of this chapter, and we shall postpone the discussion of semiconductors till then.

A. An elementary calculation of the relaxation time

The relaxation mechanism originating in the scalar interaction (1) works as follows: this interaction can induce a simultaneous flip of the electron and nuclear spins in opposite directions, the energy $\hbar(\omega_e-\omega_n)$ (where $\omega_e = -\gamma_e H_0$ and $\omega_n = -\gamma_n H_0$ are the electronic and nuclear Larmor frequencies) required for such a flip being provided by an equal change in the kinetic energy of the electron. Two consequences, both important for the nuclear relaxation mechanism, follow from the Fermi statistics obeyed by the conduction electrons in a metal. First, the average kinetic energy of the electrons is much larger than the thermal energy kT and is of the same order of magnitude as the Fermi energy E_F; secondly, because of the Pauli principle most conduction electrons cannot take or give up the small energy $\hbar(\omega_e-\omega_n)$, and only the fraction (kT/E_F) on top of the Fermi distribution contributes to the nuclear relaxation process. The order of magnitude of the probability of a nuclear spin flip can be evaluated as follows. The electronic field produced by the conduction electron at a nucleus can be considered as a fluctuating local field with a correlation time τ_c. If we assume on the average one conduction electron per atomic volume, the order of magnitude of τ_c, which is roughly the duration for which a conduction electron can be localized on a given atom, is by a well-known quantum mechanical argument $\sim\hbar/E_F$, where E_F is the Fermi energy.

Since for a random perturbation $\hbar\mathscr{H}_1(t)$, with a very short correlation time τ_c, the transition probability is of the order of $|\overline{\mathscr{H}_1^2}|\tau_c$, we find

$$\frac{1}{T_1} \sim |\overline{\mathscr{H}_1^2}|\frac{\hbar}{E_F}\frac{kT}{E_F} \sim \left(\frac{8\pi}{3}\right)^2 \gamma_e^2\gamma_n^2\hbar^3|\psi(0)|^4\frac{kT}{E_F^2}, \tag{2}$$

which is the correct formula to within a dimensionless numerical factor of order unity. In (2), $\psi(r)$ is the electronic wave function normalized to unity in an atomic volume, and the factor kT/E_F takes account of the reduction through the Pauli principle in the number of conduction electrons that participate in the relaxation process. A more accurate calculation will be presented now.

We assume that nuclear spins are $I = \frac{1}{2}$ and that the applied field is sufficiently high for the nuclear spin-spin energy to be negligible in comparison with the nuclear Zeeman energy. Then the decay or growth of the nuclear magnetization, proportional to the difference p_+-p_- of the populations of the states $I_z = \pm\frac{1}{2}$, is clearly describable by a single exponential, and a single relaxation time can be defined for the nuclear spin system. For the electrons we assume that their own relaxation time is sufficiently short for us to consider their spins as being constantly in equilibrium with the lattice, and that the temperature is sufficiently high for the electronic Zeeman energy $-\gamma_e\hbar H_0$ to be much smaller than kT. Under those assumptions, electrons with spins up or down have approximately the same Fermi distribution function

$$f(E) = \frac{1}{1+\exp\{(E-E_F)/kT\}}. \tag{2'}$$

The probability of an electron making a transition from a state of kinetic energy E to a state of energy E' must be weighted by the factor $f(E)[1-f(E')]$, which is the simultaneous probability for the initial state to be occupied and for the final state to be empty prior to the transition. If the transition is that which involves a simultaneous electron-nuclear spin flip, the change in kinetic energy being very small, the assumption $E' \simeq E$ is legitimate and $f(E)[1-f(E')]$ may be safely replaced by

$$f(E)[1-f(E')] = \frac{\exp\{(E-E_F)/kT\}}{[1+\exp\{(E-E_F)/kT\}]^2} = -kT\frac{df}{dE} \simeq kT\,\delta(E-E_F). \tag{3}$$

The last approximate equality in (3) results from the fact that, since E_F is much larger than kT, $f(E)$ is practically the Heaviside unit-step function (with a minus sign) and its derivative is thus a δ function.

The probability $w_{(+-)\to(-+)}$ of a simultaneous electron-nuclear spin flip can be written

$$\frac{2\pi}{\hbar}|(i\,|\,\hbar\mathscr{H}\,|f)|^2\delta(E_i-E_f), \tag{4}$$

with

$$\begin{aligned} |i) &= U_{\mathbf{k}}(\mathbf{r})e^{i\mathbf{kr}}|+,-),\\ |f) &= U_{\mathbf{k}'}(\mathbf{r})e^{i\mathbf{k}'\mathbf{r}}|-,+),\\ E_i-E_f &= E_{\mathbf{k}}-E_{\mathbf{k}'}+\hbar(\omega_e-\omega_n) \cong E_{\mathbf{k}}-E_{\mathbf{k}'}, \qquad (5)\\ \hbar\mathscr{H}_1 &= -\frac{8\pi}{3}\gamma_e\gamma_n\hbar^2\delta(\mathbf{r}_I)\{I_z s_z+\tfrac{1}{2}(I_+s_-+I_-s_+)\}. \end{aligned}$$

k and **k**′ are the wave vectors of the Bloch wave functions

$$\phi_{\mathbf{k}} = U_k(\mathbf{r})e^{i\mathbf{kr}}$$

describing the initial and the final electronic orbits and are normalized to unity in the volume V of the sample. The symbol $|+,-)$ describes the state $s_z = +\frac{1}{2}$, $I_z = -\frac{1}{2}$. We get

$$w_{(+-)\to(-+)} \cong \frac{2\pi}{\hbar}\left\{\frac{8\pi}{3}\gamma_e\gamma_n\hbar^2\right\}^2|(\mathbf{k}\,|\,\delta(\mathbf{r}_I)\,|\,\mathbf{k}')|^2\tfrac{1}{4}\delta(E_{\mathbf{k}}-E_{\mathbf{k}'}). \tag{6}$$

To get the total probability $W_{(+-)\to(-+)}$ of a simultaneous flip, we must multiply (6) by

$$Z(\mathbf{k})Z(\mathbf{k}')f(E)[1-f(E')],$$

where $Z(\mathbf{k})$ is the density of states in the **k** space, and integrate over $d^3k\,.\,d^3k'$. We assume for simplicity that the Fermi surface has spherical symmetry in the **k** space, $\rho(E)\,dE$ being the number of states (of a given spin) in the interval dE, in the neighbourhood of $E = E_F$. Taking into account (3) we get

$$\begin{aligned} \left(\frac{1}{T_1}\right)_0 = 2W_{(+-)\to(-+)} &= 2\times\frac{2\pi}{\hbar}\left(\frac{8\pi}{3}\gamma_e\gamma_n\hbar^2\right)^2\tfrac{1}{4}|\phi_F(0)|^4kT\{\rho(E_F)\}^2\\ &= \frac{64\pi^3}{9}\gamma_e^2\gamma_n^2\hbar^3|\phi_F(0)|^4\{\rho(E_F)\}^2kT. \qquad (7) \end{aligned}$$

We write $(1/T_1)_0$ rather than $1/T_1$ to recall the restrictive assumptions

used to derive (7) (nuclear spins $\frac{1}{2}$ and high applied field). If the assumption of spherical symmetry of the Fermi surface is not valid, $|\phi_F(0)|^4$ must be replaced by an average of $|\phi_{\mathbf{k}}(0)|^2.|\phi_{\mathbf{k}'}(0)|^2$ over the Fermi surface.

The resemblance between the crude estimate (2) and the more careful one (7) can be seen if one remembers that, if $\psi_F(\mathbf{r})$ are normalized in the atomic volume $\Omega = V/N$, $|\psi_F(0)|^2 = N|\phi_F(0)|^2$, and that $\rho(E_F) \cong N/E_F$. For free electrons, where $\rho(E_F) = 3N/4E_F$, (7) can be rewritten

$$\left(\frac{1}{T_1}\right)_0 = 4\pi^3\gamma_e^2\gamma_n^2\hbar^3|\psi_F(0)|^4\frac{T}{T_F}\frac{1}{kT_F},$$

where $T_F = E_F/k$ is called the Fermi temperature.

The most remarkable feature of (7) is the proportionality of $1/T_1$ to the temperature T, which is to be contrasted with the much faster increase at low temperatures of relaxation times connected with lattice motions, such as thermal vibrations, diffusion, molecular rotation, etc.

Before comparing the theory with experiment we shall free ourselves from the two assumptions of nuclear spins $\frac{1}{2}$ and high applied fields.

B. Nuclear relaxation time and spin temperature

As recalled in the introduction to this chapter, a statistical description of a system of interacting nuclear spins by a spin temperature T_S, possibly different from that of the lattice, that is, by a density matrix $\rho \propto \exp(-\beta\mathscr{H}_0)$ with $\beta = 1/kT_S$ is, under certain conditions, a good approximation. Since the state of the spin system is then described by a single constant β it is reasonable to assume that the spin-lattice relaxation, that is, the trend of the spin temperature towards the lattice temperature, should be described by a single constant T_1 according to the relation

$$\frac{d\beta}{dt} = -\frac{1}{T_1}(\beta-\beta_0), \tag{8}$$

where $\beta_0 = 1/kT$ and T is the temperature of the lattice. It is clear that because of the Curie law, (8) coincides in high fields with the usual definition of T_1 through

$$\frac{dM_z}{dt} = -\frac{1}{T_1}(M_z-M_0).$$

With the assumption of spin temperature it will be possible to calculate the spin-lattice relaxation times for arbitrary nuclear spins and in arbitrary applied fields. This is done by calculating in two different ways the rate of change $d\bar{E}/dt$ of the average energy $\bar{E} = \mathrm{tr}\{\rho\mathscr{H}_0\}$ of the nuclear spin system.

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With the approximation, valid in practically all experimental situations, of high spin and lattice temperature

$$\bar{E} = \mathrm{tr}\{\rho\mathscr{H}_0\} = \frac{\mathrm{tr}\{\mathscr{H}_0 e^{-\beta\mathscr{H}_0}\}}{\mathrm{tr}\{e^{-\beta\mathscr{H}_0}\}} \cong -\frac{\beta\langle\mathscr{H}_0^2\rangle}{\langle 1\rangle}, \tag{9}$$

where $\langle\mathscr{H}_0^2\rangle = \mathrm{tr}\{\mathscr{H}_0^2\}$, $\langle 1\rangle$ is the trace of the unit operator, and use has been made of $\langle\mathscr{H}_0\rangle = 0$. Thus

$$\frac{d\bar{E}}{dt} = -\frac{d\beta}{dt}\frac{\langle\mathscr{H}_0^2\rangle}{\langle 1\rangle}. \tag{10}$$

The second evaluation of $d\bar{E}/dt$ is as follows (1). Let p_m be the populations (and p_m^0 the equilibrium populations) of the eigenstates $|m)$ of the nuclear spin system (unknown in low fields). With the assumption of a high spin temperature

$$p_m = \frac{1-\beta E_m}{\langle 1\rangle}.$$

The diagonal part of the master equation, which gives the rate of change of the populations, can be written

$$\frac{dp_m}{dt} = \sum_n W_{mn}\{(p_n-p_n^0)-(p_m-p_m^0)\}, \tag{11}$$

where $W_{mn} = W_{nm}$ is the transition probability from the state $|m)$ to the state $|n)$, induced by the hyperfine coupling (1) summed over all electron and nuclear spins. Equation (11) can be rewritten as

$$\frac{dp_m}{dt} = \frac{1}{\langle 1\rangle}(\beta_0-\beta)\sum_n W_{mn}(E_n-E_m). \tag{11'}$$

Multiplying both sides of (11′) by E_m and summing over m, we get

$$\frac{d\bar{E}}{dt} = \frac{1}{\langle 1\rangle}(\beta_0-\beta)\sum_{n,m} W_{mn}E_m(E_n-E_m)$$

or, from the relation $W_{mn} = W_{nm}$,

$$\frac{d\bar{E}}{dt} = -\frac{1}{2}\frac{1}{\langle 1\rangle}(\beta_0-\beta)\sum_{n,m} W_{mn}(E_n-E_m)^2. \tag{12}$$

A comparison of (8), (10), and (12) gives

$$\frac{1}{T_1} = \frac{1}{2}\frac{\sum_{n,m} W_{mn}(E_n-E_m)^2}{\langle\mathscr{H}_0^2\rangle}. \tag{13}$$

Equation (13) is quite general and its validity is by no means restricted to nuclear spins relaxed by conduction electrons.

It will be shown now that although each individual transition probability W_{mn} cannot be computed in general since the states $|m)$ of the nuclear spin system are not known, the expression (13) can be made to appear as a trace and calculated explicitly.

The elementary probability w_{mn} of a conduction electron passing from a state $|\mathbf{k})|s)$ to a state $|\mathbf{k}')|s')$, $|s)$ and $|s')$ being electron spin states, is given by

$$w_{mn} = \frac{2\pi}{\hbar}\left(\frac{8\pi}{3}\gamma_e\gamma_n\hbar^2\right)^2 \sum_{p,q}(\mathbf{k}\,|\,\delta(\mathbf{r}_p)\,|\,\mathbf{k}')(\mathbf{k}'\,|\,\delta(\mathbf{r}_q)\,|\,\mathbf{k})\times$$
$$\times\{(m\,|\,\mathbf{I}_p\,|\,n).(s\,|\,\mathbf{s}\,|\,s')\}\{(s'\,|\,\mathbf{s}\,|\,s).(n\,|\,\mathbf{I}_q\,|\,m)\}\delta(E_i-E_f), \tag{14}$$

where $\mathbf{I}_p$ and $\mathbf{I}_q$ are two nuclear spins separated from the electron by $\mathbf{r}_p$ and $\mathbf{r}_q$. Multiplying (14) by $Z(\mathbf{k}).Z(\mathbf{k}')f(E_i)\{1-f(E_f)\}$, integrating over d^3k and d^3k', and summing over the spin states $|s)$ and $|s')$, we get with the same simplifying assumptions as in Section A, namely high lattice temperature and spherical Fermi surface, the total probability W_{mn}:

$$W_{mn} = \sum_{p,q} a_{pq}(m\,|\,\mathbf{I}_p\,|\,n).(n\,|\,\mathbf{I}_q\,|\,m) \tag{15}$$

with

$$a_{pq} = \frac{64}{9}\pi^3\hbar^3\gamma_e^2\gamma_n^2|\phi(0)|^4\frac{\sin^2(k_F R_{pq})}{(k_F R_{pq})^2}kT[\rho(E_F)]^2, \tag{15'}$$

where k_F, the wave number at the Fermi surface, is defined by

$$\hbar^2k_F^2/2m = E_F.$$

To prove (15) use has been made of

$$\sum_{s,s'}(s\,|\,s_\alpha\,|\,s')(s'\,|\,s_\beta\,|\,s) = \mathrm{tr}\{s_\alpha s_\beta\} = \tfrac{1}{2}\delta_{\alpha\beta},$$

where s_α and s_β are components of the spin $\mathbf{s}$. From the expression (13) for $1/T_1$ and (15) for W_{mn} we get immediately

$$\frac{1}{T_1} = -\frac{1}{2}\sum_{p,q} a_{pq}\frac{\langle[\mathscr{H}_0,\mathbf{I}_p].[\mathscr{H}_0,\mathbf{I}_q]\rangle}{\langle\mathscr{H}_0^2\rangle}. \tag{16}$$

The relation (16) could be obtained immediately from the general master equation (66) of Chapter VIII:

$$\frac{d\sigma^*}{dt} = -\frac{1}{2}\int_{-\infty}^{\infty}\overline{[\mathscr{H}_1^*(t),[\mathscr{H}_1^*(t-\tau),\sigma^*-\sigma_0]]}\,d\tau$$

which, if there is a spin temperature, reads

$$\mathscr{H}_0\frac{d\beta}{dt} = \tfrac{1}{2}(\beta_0-\beta)\int_{-\infty}^{\infty}\overline{[\mathscr{H}_1^*(t),[\mathscr{H}_1^*(t-\tau),\mathscr{H}_0]]}\,d\tau.$$

Multiplying both sides by $\mathscr{H}_0$ and taking the trace with respect to the nuclear spin variables, we get

$$\frac{d\beta}{dt} = -\frac{1}{2}\frac{(\beta_0-\beta)}{\langle\mathscr{H}_0^2\rangle}\int\limits_{-\infty}^{\infty}\overline{\langle[\mathscr{H}_1^*(t),\mathscr{H}_0][\mathscr{H}_1^*(t-\tau),\mathscr{H}_0]\rangle}\,d\tau, \tag{17}$$

which from the assumed form of the scalar hyperfine Hamiltonian $\hbar\mathscr{H}_1$, shows immediately that $1/T_1$ should be given by a relation of the form of (16), if the correlation time of $\mathscr{H}_1(t)$ is very short.

Among the coefficients a_{pq} given by (15′), which can be rewritten as $a_k = a_{(p-q)}$ since they depend only on the distance R_{pq}, the coefficient a_0 is the largest and, unless the wavelength $\lambda_F = 2\pi/k_F$ is abnormally long, all the other coefficients a_k can be neglected for a first approximation. In the description which uses the concept of the local field produced at the nuclei by the electrons, the neglect of the a_k for $k \neq 0$ corresponds to the assumption that the local electronic fields at two different nuclei are incoherent. From (15′) we see that $a_0 = (1/T_1)_0$, as given by (7), whence from (16)

$$\frac{1}{T_1} = \left(\frac{1}{T_1}\right)_0 \frac{\left\langle-\sum\limits_p[\mathscr{H}_0,\mathbf{I}_p]^2\right\rangle}{2\langle\mathscr{H}_0^2\rangle}. \tag{18}$$

If we write $\mathscr{H}_0 = Z+\mathscr{H}_{SS}$, where Z is the Zeeman energy and

$$\mathscr{H}_{SS} = \mathscr{H}_d+\mathscr{H}_{\text{ex}}$$

is the sum of the dipolar spin-spin coupling and of an indirect scalar spin-spin coupling (if it exists), it is easily found from (18) that

$$\frac{1}{T_1} = \left(\frac{1}{T_1}\right)_0 \frac{\langle Z^2+2\mathscr{H}_{SS}^2\rangle}{\langle Z^2+\mathscr{H}_{SS}^2\rangle}. \tag{19}$$

This leads to a rather interesting conclusion (based solely on the assumption of incoherence between local fields 'seen' by two different nuclear spins): in high fields where $\langle Z^2\rangle \gg \langle\mathscr{H}_{SS}^2\rangle$ we have

$$(1/T_1) = (1/T_1)_0,$$

whilst in fields much smaller than the local field

$$(1/T_1) = 2(1/T_1)_0.$$

The opposite and less usual extreme of a complete correlation between the local fields 'seen' by neighbouring spins, that is, of a Fermi wavelength much larger than a lattice spacing, is expressed by the equality of all coefficients a_{pq} in (16) and yields

$$\frac{1}{T_1} \propto -\sum_{p,q}\frac{\langle[\mathscr{H}_0,\mathbf{I}_p].[\mathscr{H}_0,\mathbf{I}_q]\rangle}{\langle\mathscr{H}_0^2\rangle} \propto \frac{\langle Z^2+3\mathscr{H}_d^2\rangle}{\langle Z^2+\mathscr{H}_d^2+\mathscr{H}_{\text{ex}}^2\rangle}. \tag{20}$$

It is easy to verify that for a dipolar coupling $\mathscr{H}_d$ between like spins, the expectation value $\langle\mathscr{H}_d^2\rangle$ is $5\langle\tilde{\mathscr{H}}_d^2\rangle$, where $\tilde{\mathscr{H}}_d$ is the truncated dipolar Hamiltonian used for the calculation of the second moment of the nuclear resonance line in Chapter IV. It follows that if scalar spin-spin coupling is absent and a single spin species is present in the sample, the equations (19) and (20) can be replaced by

$$TT_1 \propto [H^2+\tfrac{5}{3}\Delta H^2]/[H^2+\tfrac{5}{3}\beta\,\Delta H^2], \tag{20′}$$

where β is 2 for uncorrelated and 3 for strongly correlated electronic fields at the nuclei, and ΔH^2 is the second moment of the resonance line.

An essential feature of the above calculations is the neglect of correlations between the individual conduction electrons. This approach is inadequate for an evaluation of the relaxation time in the superconducting state of the metal, where according to the present status of the theory, strong correlations exist between electrons.

It is not possible to give an account of the calculation of T_1 in the superconducting state without going into details of the theory of superconductivity that are outside the scope of this book. This calculation, which can be found in reference (**1**), predicts for the relaxation rate $1/T_1$ in zero field, a steep rise below the critical temperature T_c, followed by a decrease as the temperature goes down.

Finally, an important relation can be established between the relaxation time T_1 as given by (7) and the Knight shift given by eqn. (77) of Chapter VI:

$$T_1\left(\frac{\Delta H}{H_0}\right)^2 = \frac{1}{\pi(kT)}\frac{\chi_p'^2N^2}{\gamma_e^2\gamma_n^2\hbar^3[\rho(E_F)]^2}, \tag{21}$$

where χ_p' is the paramagnetic susceptibility per conduction electron. If the model of independent electrons is used then, as is well known (and will be shown in the next section), we have

$$\chi_p' = \frac{(\gamma_e\hbar)^2}{2N}\rho(E_F), \tag{21′}$$

whence the so-called Korringa relation:

$$T_1\left(\frac{\Delta H}{H_0}\right)^2 = \frac{\hbar}{4\pi kT}\left(\frac{\gamma_e}{\gamma_n}\right)^2. \tag{22}$$

The independent electron approximation is known to give incorrect results for the electronic paramagnetic susceptibility in contrast with the so-called collective theory (**2**). It would therefore seem advisable to use in (21) those values χ_s and ρ_s for the susceptibility and the density of states, taken from this theory. Eqn. (22) must then be replaced by

$$T_1\left(\frac{\Delta H}{H_0}\right)^2 = \frac{\hbar}{4\pi kT}\left(\frac{\gamma_e}{\gamma_n}\right)^2\left(\frac{\chi_s}{\chi_0}\right)^2\left[\frac{\rho_0(E_F)}{\rho_s(E_F)}\right]^2 \tag{22'}$$

where ρ_0 and χ_0 refer to the independent electron approximation.

C. Dynamic nuclear polarization in metals (the Overhauser effect)

(a) *Fermi statistics and non-equilibrium electron spin distribution*

In the calculations above it was assumed that the electronic spins were in thermal equilibrium with the lattice and that the fluctuating fields they produced at the nuclei could be considered as a part of the 'lattice' (as explained in Section II F (*b*) (3) of Chapter VIII). There are, however, situations where the electronic spins are not in equilibrium with the lattice, as for instance in dynamic polarization experiments when they are being driven by an r.f. field at the electronic Larmor frequency. Such situations have already been examined in Chapter VIII where, using the semi-classical model of random functions, it was shown that, in a liquid, for a nuclear spin **I** coupled to an electronic spin **S** by a bilinear coupling $\mathbf{I}.\mathscr{A}(t).\mathbf{S}$, the rate of change of

$$\langle i_z\rangle = \langle I_z\rangle/I(I+1)$$

is given by the formula

$$\frac{d\langle i_z\rangle}{dt} = -\frac{1}{T_1}\{\langle i_z\rangle - i_0 + \xi(\langle s_z\rangle - s_0)\}, \tag{23}$$

where $\langle s_z\rangle = \langle S_z\rangle/S(S+1)$.

For a scalar coupling and a very short correlation time, it was shown that $\xi = -1$.

At first sight we should expect equation (23) to hold, with the same value of ξ, for nuclear spins in a metal, where these conditions are realized for their coupling with conduction electrons. That this is actually not so, as will appear shortly, is due to the fact that, because of the exclusion principle, the conduction electrons in metals follow Fermi statistics. It is sometimes argued that this complication can be removed if instead of considering statistics of individual electrons the Gibbs statistical approach is taken, as explained in Chapter V. The macroscopic system made of all the electrons of a sample, when in thermal equilibrium, obeys Boltzmann statistics and is described by a statistical operator $\rho \propto \exp\{-\hbar\mathscr{F}/kT\}$, where $\hbar\mathscr{F}$ is the total Hamiltonian of the electrons including their interactions.

Although this statement is undoubtedly correct, it should be used with some circumspection as exemplified by the following erroneous calculation.

If in order to calculate the electron spin susceptibility we repeat a reasoning used in Chapter III, and write the electron Hamiltonian in the presence of a magnetic field H_0 as $\hbar\mathscr{H} = \hbar\mathscr{F} - H_0 M_z$, we get

$$\langle M_z\rangle = \frac{\operatorname{tr}\{\exp(-\hbar\mathscr{H}/kT).M_z\}}{\operatorname{tr}\{\exp(-\hbar\mathscr{H}/kT)\}}. \tag{24}$$

If we assume that $\mathscr{F}$ is independent of the spins and thus commutes with M_z and that $|M_z H_0| \ll kT$, both legitimate assumptions, we get

$$\langle M_z\rangle \cong \frac{\operatorname{tr}\{M_z^2\}}{\operatorname{tr}\{1\}}.\frac{H_0}{kT}, \tag{24'}$$

that is, the Curie law, well known to be invalid for the paramagnetism of conduction electrons. The error is due to the fact that the sum over states expressed by the traces (24) or (24′) should be restricted according to the Pauli principle to eigenstates of $\mathscr{H}$ that are completely antisymmetrical with respect to the orbital and spin coordinates of all electrons, whereas the trace technique takes in all eigenstates of $\mathscr{H}$, antisymmetrical or not. If the trace technique is to be retained the operation $\operatorname{tr}\{\rho M_z\}$ should be replaced by $\operatorname{tr}\{P\rho M_z P\}$, where P is the projection operator over antisymmetrical states only. This operator clearly contains spin variables, thus making it possible for the result (24′) to be wrong. For that reason, whilst keeping the general Gibbs approach in mind, and using it with caution for general arguments, we shall return for practical calculations to the one-electron description.

In the presence of a magnetic field $H_z = H_0$, the Fermi distribution function $f = [1+\exp\{(E-E_F)/kT\}]^{-1}$ describing electrons in thermal equilibrium has to be replaced by two functions $f_{\pm}$, one for each sign of S_z,

$$f_{\pm} = \left[1+\exp\left(\frac{E\pm\frac{1}{2}\hbar\omega_e - E_F}{kT}\right)\right]^{-1}, \tag{25}$$

where E represents the kinetic energy of the electron and $\omega_e = -\gamma_e H_0$. If $|\hbar\omega_e| \ll kT$, $f_{\pm} \cong f \pm \frac{1}{2}\hbar\omega_e(df/dE)$, where f is given by (2′), and df/dE by (3),

$$f_{\pm} = f \mp (\tfrac{1}{2}\hbar\omega_e)\delta(E-E_F).$$

The total magnetization of the N electrons of the sample will be

$$M = \tfrac{1}{2}\gamma_e\hbar\int \rho(E)[f_+ - f_-]\,dE = H_0(\tfrac{1}{2}\gamma_e^2\hbar^2)\rho(E_F) \tag{25'}$$

in accordance with (21′).

The distribution (25) describes electronic spins in thermal equilibrium. The electronic spin relaxation times, being of the order of 10^{-10} second or longer, are much longer than the relaxation times τ relative to the electronic kinetic energy, which are of the order of 10^{-13} sec. It is therefore a reasonable approximation to assume that electrons of either spin are in equilibrium among themselves and are described by two distributions:

$$f_\pm(E) = \left\{1+\exp\left(\frac{E\pm\frac{1}{2}\hbar\omega_e-E_F^\pm}{kT}\right)\right\}^{-1} \tag{26}$$

with values $E_F^\pm$ for their Fermi energies, which are usually different and become equal when the spins are in equilibrium with the other degrees of freedom.

The disappearance of electron paramagnetism caused by the saturation of the electron resonance corresponds to $f_+ = f_-$, or

$$\tfrac{1}{2}\hbar\omega_e-E_F^+ = -\tfrac{1}{2}\hbar\omega_e-E_F^-, \qquad E_F^+-E_F^- = \hbar\omega_e. \tag{26'}$$

If the departure of $E_F^\pm$ from the equilibrium value E_F is small compared with kT, the conservation of the total number of the electrons leads to $E_F^+ + E_F^- = 2E_F$, whence, writing $E_F^\pm = E_F\pm\frac{1}{2}\epsilon$, we get

$$\begin{aligned} f_\pm(E) &= f\{E\pm\tfrac{1}{2}(\hbar\omega_e-\epsilon)\} \cong f(E)\pm(\tfrac{1}{2}\hbar\omega_e-\tfrac{1}{2}\epsilon)\frac{df}{dE} \\ &\cong f\mp\tfrac{1}{2}(\hbar\omega_e-\epsilon)\delta(E-E_F). \end{aligned} \tag{27}$$

The expectation value $\langle S_z\rangle$ for one electron is obtained from (27):

$$\langle S_z\rangle = \frac{1}{2N}\int (f_+-f_-)\rho(E)\,dE = \frac{1}{2N}(\epsilon-\hbar\omega_e)\rho(E_F), \tag{28}$$

whence

$$\epsilon = E_F^+-E_F^- = \frac{2N}{\rho(E_F)}\langle S_z\rangle+\hbar\omega_e = \frac{2N}{\rho(E_F)}\{\langle S_z\rangle-S_0\}, \tag{28'}$$

where the equilibrium electron polarization S_0 is given by

$$S_0 = \frac{-\hbar\omega_e\rho(E_F)}{2N} = \frac{\gamma_e\hbar H_0\rho(E_F)}{2N}. \tag{28''}$$

Equation (28′) can then be rewritten as

$$E_F^+-E_F^- = \hbar\omega_e\frac{[S_0-\langle S_z\rangle]}{S_0}. \tag{28'''}$$

We shall define the saturation parameter s by the relation

$$E_F^+-E_F^- = s\hbar\omega_e. \tag{28$^{\text{iv}}$}$$

If the temperature is sufficiently high for the expansion (27) to be valid, according to (28‴),

$$s = \frac{S_0-\langle S_z\rangle}{S_0}.$$

On the other hand, whatever the temperature, we can still define s by the relation (28^{iv}). Thermal equilibrium corresponds to $E_F^+ = E_F^-$, or $s = 0$, equality of the populations of the two spins levels to $s = 1$, intermediate situations to $0 < s < 1$.

(b) *Dynamic polarization*

To demonstrate the possibility of dynamic polarization in metals (Overhauser effect) the assumption of high temperature is not necessary, as will be shown below.

Suppose for simplicity that the nuclear spins are $\frac{1}{2}$. The extension to nuclear spins $I > \frac{1}{2}$ is straightforward if spin-spin interactions maintain among them a spin-temperature as explained previously. The equation for the rate of change of n_+, the population of nuclei with spins up, normalized to $n_+ + n_- = 1$, can be written

$$\begin{aligned} \frac{dn_+}{dt} = \frac{2\pi}{\hbar}\int dE\{|(i\,|\,\hbar\mathscr{H}_1\,|\,f)|^2\}\rho(E)\rho(E-\hbar(\omega_e-\omega_n))\times \\ \times\{n_-f_+(E-\hbar(\omega_e-\omega_n))[1-f_-(E)]-n_+f_-(E)[1-f_+(E-\hbar(\omega_e-\omega_n))]\}. \end{aligned} \tag{29}$$

From the definitions (26) of f_+ and f_-, writing that the curly bracket in (29) vanishes, we obtain for the steady-state value of n_+/n_-

$$\left(\frac{n_+}{n_-}\right)_{\text{st}} = \exp\left\{\frac{E_F^+-E_F^--\hbar\omega_n}{kT}\right\}. \tag{30}$$

If the electron spins are in thermal equilibrium $E_F^+ = E_F^-$, and n_+/n_- is given by the nuclear Boltzmann factor, $\exp(-\hbar\omega_n/kT)$, as it should be. If, on the other hand, the electron spin polarization is made to vanish by a saturating r.f. field at the electron frequency ω_e, according to (26′), $E_F^+-E_F^- = \hbar\omega_e$ and the nuclear polarization is greatly enhanced since $|\omega_e| \gg |\omega_n|$:

$$\left(\frac{n_+}{n_-}\right) = \exp\left\{\frac{\hbar(\omega_e-\omega_n)}{kT}\right\}. \tag{31}$$

For incomplete saturation represented by the saturation parameter s $(0 < s < 1)$

$$\left(\frac{n_+}{n_-}\right) = \exp\left\{\frac{\hbar(s\omega_e-\omega_n)}{kT}\right\}. \tag{31'}$$

This is the Overhauser effect (3).