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Spin-Lattice Relaxation of Nuclei Due to Conduction Electrons at Very Low Temperatures

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Formulas for the spin-lattice relaxation time of nuclei in metals at very low temperatures have been derived. The formulas show that the law $\tau_1 \propto T^{-1}$ holds only when $kT \gg \gamma_n \hbar B$, whereas the relaxation becomes nonexponential (except in the case of $I=\frac{1}{2}$) and temperature-independent at lower temperatures.

In calculations concerning the spin-lattice relaxation of nuclei by conduction electrons it has usually been assumed that the nuclear Zeeman energy $\gamma_n \hbar B \ll kT$. However, this condition is not valid, e.g., in nuclear demagnetization and equilibrium nuclear orientation experiments. Cameron *et al.*[1] have noted that because of Fermi-Dirac statistics the spin-lattice relaxation time τ_1 of nuclei approaches a constant value when the temperature is lowered below $T_Z = \gamma_n \hbar B/k$. Brewer *et al.*[2] have observed this phenomenon experimentally. In this paper, we present results of calculations which lead to quantitative predictions for the temperature dependence of the spin-lattice relaxation time at very low temperatures.

For the sake of simplicity the case of a monoisotopic sample in a homogenous magnetic field will be considered. The direction of the magnetic field $\mathbf{B}$ is chosen as the z axis.

The coupling between the nuclei and the conduction electrons can be expressed in the form

$$H^{\text{int}} = \sum_i \mathbf{A}_i \cdot \mathbf{I}_i , \tag{1}$$

where $\mathbf{I}_i$ is the spin of the ith nucleus and $\mathbf{A}_i$ is a function of the spatial coordinates of the electrons and the nuclei and of the spins of the electrons; e.g., the contact interaction and the dipole-dipole coupling are of form (1). We assume that the coupling between the electrons is so weak that it is sufficient to consider only processes in which one electron scatters from the nuclear system. The probability for the transition of the nuclear spin system from the eigenstate $|I\rangle$ of total nuclear spin to the state $|I'\rangle$ is then

$$\begin{aligned} w(I \rightarrow I') = \frac{2\pi}{\hbar} \sum_{ss'} (2\pi)^{-6} \int d\mathbf{k}\, d\mathbf{k}'\, & f(E(\mathbf{k}) - \gamma_e \hbar \mathbf{s} \cdot \mathbf{B}) \\ & \times [1 - f(E(\mathbf{k}') - \gamma_e \hbar \mathbf{s}' \cdot \mathbf{B})] \\ & \times |\langle \mathbf{k}' s' I' | H^{\text{int}} | \mathbf{k} s I \rangle|^2 \delta(E_f - E_i) , \end{aligned} \tag{2}$$

where $|\mathbf{k}s\rangle$ and $|\mathbf{k}'s'\rangle$ are the states of the electron before and after the scattering, and E_i and E_f are the initial and final energies of the whole system. $\gamma_e \hbar \mathbf{s} \cdot \mathbf{B}$ and $\gamma_e \hbar \mathbf{s}' \cdot \mathbf{B}$ are the Zeeman energies of the electron before and after the scattering; $f(E) = \{1 + \exp[(E - E_F)/kT]\}^{-1}$ is the Fermi function. In metals at temperatures of interest $E_F \gg kT$ and $E_F \gg \gamma_e \hbar \mathbf{s} \cdot \mathbf{B} \gg \gamma_n \hbar \mathbf{I}_i \cdot \mathbf{B}$. Thus the integrand is different from zero only in the relatively narrow energy region, where

$$|E(\mathbf{k}) - E_F| \lesssim k(T + T_Z) ,$$
$$|E(\mathbf{k}') - E_F| \lesssim k(T + T_Z) .$$

Therefore, we can substitute in formula (2)

$$\begin{aligned} & f(E(\mathbf{k}) - \gamma_e \hbar \mathbf{s} \cdot \mathbf{B})[1 - f(E(\mathbf{k}') - \gamma_e \hbar \mathbf{s}' \cdot \mathbf{B})]\delta(E_f - E_i) \\ & \approx \frac{\gamma_n \hbar \mathbf{B} \cdot (\mathbf{I}' - \mathbf{I})}{1 - e^{-\gamma_n \hbar \mathbf{B} \cdot (\mathbf{I}' - \mathbf{I})/kT}} \delta(E(\mathbf{k}) - E_F) \delta(E(\mathbf{k}') - E_F) , \end{aligned} \tag{3}$$

where

$$\mathbf{I} = \sum_i \mathbf{I}_i .$$

In the derivation of the formula (3) we have used the equation

$$\int_{-\infty}^{\infty} f(E)(1 - f(E + \Delta E))\, dE = \Delta E / (1 - e^{-\Delta E/kT}) .$$

Summing (2) over all states with

$$I_z' = \sum_i I_{iz}' = I_z + 1 ,$$

and using formulas (1) and (3) we get

$$\begin{aligned} w(I+) \equiv & \sum_{I_z' = I_z + 1} w(I \rightarrow I') \\ & = (1 - e^{-T_z/T})^{-1} \sum_{ij} K_{ij} \langle I | I_{i-} I_{j+} | I \rangle , \end{aligned} \tag{4}$$

where

$$\begin{aligned} K_{ij} = \frac{\gamma_\eta{}^B}{32\pi^5} \int d\mathbf{k}\, d\mathbf{k}'\, & \delta(E(\mathbf{k}) - E_F) \delta(E(\mathbf{k}') - E_F) \\ & \times \mathrm{Tr}_s \langle \mathbf{k} | A_{i+} | \mathbf{k}' \rangle \langle \mathbf{k}' | A_{j-} | \mathbf{k} \rangle , \end{aligned} \tag{5}$$

$A_{i\pm} = A_{ix} \pm i A_{iy}$, and Tr_s means trace in the electron-spin space. The rate of change of the ensemble average

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[1] J. A. Cameron, I. A. Campbell, J. P. Compton, and R. A. G. Lines, Phys. Letters **10**, 24 (1964).

[2] W. D. Brewer, D. A. Shirley, and J. E. Templeton, Phys. Letters **27A**, 81 (1968).

TABLE I. Equlibrium value of the nuclear polarization and the momentary spin-lattice relaxation time as function of the temperature for $I \leq 5$.

I	T/T_Z	f_{10}	τ_1'/K^{-1}			
			$f_1=0$	$f_1=0.5$	$f_1=1$	$f_1=f_{10}$
$\frac{1}{2}$	0	1.0000	1.0000	1.0000	1.0000	1.0000
	0.3	0.9311	0.9311	0.9311	0.9311	0.9311
	1	0.4621	0.4621	0.4621	0.4621	0.4621
	3	0.1651	0.1651	0.1615	0.1651	0.1651
	10	0.0500	0.0500	0.0500	0.0500	0.0500
	30	0.0167	0.0167	0.0167	0.0167	0.0167
1	0	1.0000	0.7500	0.6514	0.5000	0.5000
	0.3	0.9631	0.7224	0.6339	0.4982	0.5136
	1	0.5752	0.4314	0.4052	0.3650	0.4007
	3	0.2182	0.1636	0.1601	0.1546	0.1622
	10	0.0666	0.0499	0.0496	0.0491	0.0499
	30	0.0222	0.0167	0.0166	0.0166	0.0167
$\frac{3}{2}$	0	1.0000	0.6000	0.4810	0.3333	0.3333
	0.3	0.9753	0.5852	0.4742	0.3333	0.3415
	1	0.6618	0.3971	0.3536	0.2906	0.3373
	3	0.2694	0.1616	0.1550	0.1445	0.1582
	10	0.0831	0.0499	0.0492	0.0482	0.0498
	30	0.0278	0.0167	0.0166	0.0165	0.0167
2	0	1.0000	0.5000	0.3807	0.2500	0.2500
	0.3	0.9815	0.4908	0.3772	0.2500	0.2547
	1	0.7260	0.3630	0.3089	0.2354	0.2805
	3	0.3183	0.1591	0.1496	0.1348	0.1533
	10	0.0996	0.0498	0.0489	0.0474	0.0496
	30	0.0333	0.0167	0.0166	0.0164	0.0167
$\frac{5}{2}$	0	1.0000	0.4286	0.3147	0.2000	0.2000
	0.3	0.9852	0.4222	0.3127	0.2000	0.2030
	1	0.7732	0.3314	0.2714	0.1949	0.2335
	3	0.3646	0.1562	0.1442	0.1257	0.1477
	10	0.1160	0.0497	0.0485	0.0465	0.0494
	30	0.0389	0.0167	0.0165	0.0163	0.0166
3	0	1.0000	0.3750	0.2682	0.1667	0.1667
	0.3	0.9877	0.3704	0.2668	0.1667	0.1687
	1	0.8081	0.3031	0.2402	0.1648	0.1962
	3	0.4080	0.1530	0.1388	0.1171	0.1416
	10	0.1322	0.0496	0.0481	0.0456	0.0492
	30	0.0444	0.0167	0.0165	0.0162	0.0166
$\frac{7}{2}$	0	1.0000	0.3333	0.2335	0.1429	0.1429
	0.3	0.9894	0.3298	0.2326	0.1429	0.1444
	1	0.8345	0.2782	0.2145	0.1422	0.1672
	3	0.4485	0.1495	0.1333	0.1091	0.1351
	10	0.1484	0.0495	0.0477	0.0448	0.0490
	30	0.0499	0.0166	0.0164	0.0161	0.0166
4	0	1.0000	0.3000	0.2068	0.1250	0.1250
	0.3	0.9908	0.2972	0.2061	0.1250	0.1262
	1	0.8548	0.2564	0.1932	0.1248	0.1446
	3	0.4860	0.1458	0.1278	0.1017	0.1284
	10	0.1644	0.0493	0.0473	0.0439	0.0487
	30	0.0555	0.0166	0.0164	0.0160	0.0166
$\frac{9}{2}$	0	1.0000	0.2727	0.1855	0.1111	0.1111
	0.3	0.9918	0.2705	0.1850	0.1111	0.1120
	1	0.8708	0.2375	0.1755	0.1110	0.1270
	3	0.5205	0.1420	0.1225	0.0948	0.1216
	10	0.1803	0.0492	0.0469	0.0431	0.0484
	30	0.0610	0.0166	0.0164	0.0159	0.0166
5	0	1.0000	0.2500	0.1682	0.1000	0.1000
	0.3	0.9926	0.2482	0.1678	0.1000	0.1007
	1	0.8836	0.2209	0.1605	0.1000	0.1129
	3	0.5522	0.1380	0.1173	0.0886	0.1149
	10	0.1960	0.0490	0.0465	0.0423	0.0481
	30	0.0665	0.0166	0.0163	0.0158	0.0166

$\langle I_z\rangle$ is

$$\frac{d}{dt}\langle I_z\rangle=\sum\nolimits_I p(I)[w(I+)-w(I-)], \tag{6}$$

where $p(I)$ is the probability that the system is in state $|I\rangle$.

Using (4) and a similar formula for

$$w(I-)=\sum_{I'} w(I\rightarrow I'),$$

where the sum extends over states with $I_z'=I_z-1$, we get

$$\frac{d}{dt}\langle I_z\rangle=\sum_{ij} K_{ij}(\langle \mathbf{I}_i\cdot\mathbf{I}_j\rangle-\langle I_{iz}I_{jz}\rangle) -\sum_i K_{ii}\langle I_{iz}\rangle \coth\frac{T_Z}{2T}. \tag{7}$$

Assuming further (see below) that the interference terms $i\neq j$ can be neglected in the first sum of formula (7) and noting that K_{ii} does not depend on i, we can write

$$\frac{d}{dt}f_1=K\left[\tfrac{2}{3}(I+1)-If_2-f_1\coth\frac{T_Z}{2T}\right], \tag{8}$$

where $K=K_{ii}$, $f_1=\langle I_{zi}\rangle/I=\langle I_z\rangle/NI$ is the polarization of the nuclei, and $f_2=\langle I_{zi}^2\rangle/I^2-(I+1)/3I$ is the alignment.

In the case $I=\frac{1}{2}$, f_2 is identically zero and the relaxation is thus exponential with a time constant

$$\tau_1=(1/K)\tanh(T_Z/2T), \tag{9}$$

and the saturation value of polarization is

$$f_{10}=\tanh(T_Z/2T). \tag{10}$$

In the high-temperature limit $T\gg IT_Z$, the term If_2 can usually be ignored because either $f_2\lesssim f_1$ or $f_2\ll 1$. In this case, we get

$$\frac{d}{dt}f_1=K\left(\tfrac{2}{3}(I+1)-f_1\frac{2T}{T_Z}\right), \tag{11}$$

and for $\tau_1 T$ we get the constant value

$$(\tau_1 T)_\infty=T_Z/2K, \tag{12}$$

which is the conventional result for the relaxation time, often called the Korringa law. Formula (12) can be used to the experimental determination of K.

As the spin-spin coupling energy corresponds to a temperature of a few μdeg only, we can still in the millidegree region consider states corresponding to the same value of I_z as degenerate. On the other hand, the spin-spin relaxation time τ_2 in metals at low temperatures is much shorter than τ_1 so that all states with the

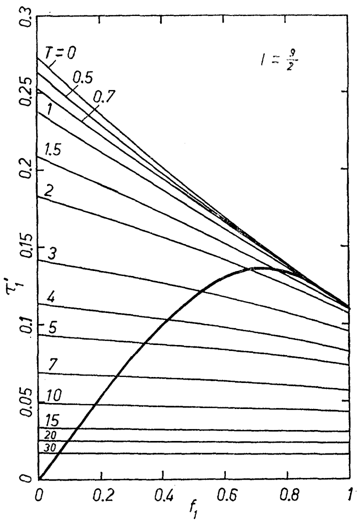

FIG. 1. Apparent spin-lattice relaxation time τ_1' of nuclei ($I=\frac{9}{2}$) as function of nuclear polarization f_1 and temperature T. τ_1' is given in units of K^{-1} and T given in units of T_Z. The heavy line starting from the origin gives the saturation value of polarization and corresponding relaxation time as function of T.

same value of I_z will also be equally probable during the relaxation process provided that the splitting caused by spin-spin coupling can be neglected. As N is a large number, we can characterize the subspace in which $I_z=M$ by $f_1 I=\langle I_{zi}\rangle=M/N$. This substitution is similar to the transition from a microcanonical to a canonical ensemble in statistical mechanics. From the previous considerations we see that we can use the density operator

$$\rho_{i,m}=(1/Z)e^{\alpha m} \tag{13}$$

for individual nuclear spins, where m is an eigenvalue of I_{zi}, Z is the sum of states, and $\alpha=T_Z/T_s$ with T_s as the spin temperature. Using (13) to calculate the expectation values of I_z and I_{zi}^2, we get

$$f_1=[(2I+1)/2I]\coth[\tfrac{1}{2}(2I+1)\alpha] -(1/2I)\coth\tfrac{1}{2}\alpha \tag{14}$$

and

$$f_2=\tfrac{2}{3}(I+1)/I-(1/I)f_1\coth\tfrac{1}{2}\alpha, \tag{15}$$

so that (8) becomes

$$\frac{d}{dt}f_1=Kf_1(x-A), \tag{16}$$

where $A=\coth(T_Z/2T)$ and $x=\coth\frac{1}{2}\alpha$. Formula (14) can now be written in the form

$$f_1=\frac{2I+1}{2I}\,\frac{(x+1)^{2I+1}+(x-1)^{2I+1}}{(x+1)^{2I+1}-(x-1)^{2I+1}}-\frac{1}{2I}x. \tag{17}$$

From Eqs. (16) and (17), it is easy to calculate numerically the time derivative of f_1 at any value of f_1 and T. As f_1 determines the density operator through formulas (13) and (14), it is further possible to calculate the time development of any observable depending on nuclear spin. Although the relaxation is not exponential, we can define an apparent momentary relaxation time

$$\tau_1'=(f_{10}-f_1)\bigg/\left(\frac{d}{dt}f_1\right),$$

where the equilibrium value of the polarization f_{10} can be calculated from formula (14) for $T_s=T$.

Numerical calculations show that for $I>\frac{1}{2}$, τ_1' decreases with increasing f_1 so that the maximum value of τ_1' for fixed temperature is

$$\tau_1'(f_1=0)=3f_{10}/2(I+1)K \tag{18}$$

and the minimum value is

$$\tau_1'(f_1=1)=(1-f_{10})/(A-1)K. \tag{19}$$

Regardless of which side the equilibrium is approached from, the relaxation ends with the time constant

$$\tau_1'(f_1=f_{10})=\frac{1}{2IKf_{10}}\times\left(1-\frac{4(2I+1)^2(A^2-1)^{2I}}{[(A+1)^{2I+1}-(A-1)^{2I+1}]^2}\right). \tag{20}$$

Although the relaxation is not exponential, it is often convenient to fit an exponential decay to the experimentally observed deviations from equilibrium. In this way, one gets an experimental relaxation time, which is dependent on the way in which the fit is done. For most ways measurements should, however, give a result which is between $\tau_1'(f_1=0)$ and $\tau_1'(f_1=f_{10})$ if $f_1<f_{10}$ or between $\tau_1'(f_1=f_{10})$ and $\tau_1'(f_1=1)$ if $f_1>f_{10}$. In Table I, τ_1' is presented as a function of temperature for $f_1=0$, 0.5, 1, and f_{10} when $I\leq 5$. The temperature is given in units of T_Z and τ_1' in units of K^{-1}.

In order to give a more detailed picture of the influence of the temperature on the relaxation in Fig. 1, we present τ_1' as function of f_1 at various temperatures for $I=\frac{9}{2}$ (units are the same as in Table I).

Brewer *et al.*[2] have measured the spin-lattice relaxation time of Co^{60} nuclei in iron using NMR/ON technique (resonant destruction of nuclear orientation) at temperatures between 7 and 75m°K. Because the γ-ray anisotropy, which is detected in NMR/ON measurements, does not depend on f_1 but on f_2 (and higher-order orientation parameters), a fair comparison of theory with experiments requires further calculation. The most satisfactory way would be to compare the measured and theoretical curves giving the γ-ray anisotropy or the nuclear-spin temperature as function of time. However, we have only compared the relaxation times measured by Brewer *et al.* with those calculated from formulas (18) and (20). The agreement appeared to be satisfactory, when we use parameters $T_Z = 7.9$m°K and $(\tau_1 T)_\infty = 1.5$ sec °K.[3]

The present theory suggests that some recent measurements of $\tau_1 T$ for nuclei in ferromagnetic materials should be reexamined in the light of the saturation effects.[4]

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[3] The value of T_Z is calculated from experimentally measured value of hyperfine field given by D. A. Shirley, in *Hyperfine Structure and Nuclear Radiations*, edited by E. Matthias and D. A. Shirley (North-Holland Publishing Co., Amsterdam, 1968), Appendix B. The value of $(\tau_1 T)_\infty$ is an approximate fit to the measurements.

[4] See, e.g., P. G. E. Reid, M. Scott, and N. J. Stone, in Ref. 3, p. 799. For the nuclei Ir^{192}, Au^{198}, and Sb^{125}, I has the values 4, 2, and $\frac{7}{2}$ and T_Z has the values 17, 14, and 6°mK.

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Knight Shift and Nuclear Spin-Lattice Relaxation Rate in Solid and Liquid Copper*

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Measurements of the Knight shift K of Cu^{63} and the nuclear spin-lattice relaxation rate T_1^{-1} of Cu^{63} and Cu^{65} are reported for solid and liquid copper. The temperature T range covered for the solid is 300°K to the melting point (1356°K). Measurements of K in the liquid extend from 1200°K (supercooled) to 1450°K; measurements of T_1^{-1} cover the range 1200–1370°K. In the solid, the Knight shift shows a slight increase with temperature and, up to about 1000°K, the product T_1TK^2 is constant. Above 1000°K, an additional contribution to T_1^{-1} is observed which is attributed to a quadrupolar interaction with diffusing imperfections. There is a sudden increase of about 3.7% in K and 20% in the inferred magnetic contribution to T_1^{-1} on going from the solid to the liquid state at 1356°K. In the liquid state, both K and T_1T are independent of T. The values of T_1^{-1} in the liquid are consistent with a lack of quadrupolar contribution to T_1^{-1}.

I. INTRODUCTION

RECENT pulsed nuclear-magnetic-resonance investigations of the polyvalent liquid metals gallium,[1] mercury,[1] indium,[2,3] antimony,[2] and indium antimonide[2] have yielded useful information about the electronic structure and local atomic order of these systems. Some characteristics of the static and dynamic magnetic fields experienced by a nucleus in a liquid metal can be obtained from measurements of the Knight shift K and the contribution of magnetic hyperfine interactions to the nuclear spin-lattice relaxation rate T_1^{-1}. Such measurements permit inference of the changes of electronic structure and changes in electron-electron correlation and exchange effects that accompany fusion. Unfortunately, interpretation of the experiments in the above polyvalent metals is rendered difficult by the fact that most of them exhibit noncubic structures in the solid state. The resulting large static electric quadrupolar interactions complicate measurement of K and T_1 in the solids and make accurate determinations of their melting-point changes difficult. (Although indium antimonide exhibits cubic symmetry in the solid state, it transforms from a liquid metal to a semiconductor on solidification, and is thus not typical of a normal metal.) Investigations of T_1 and K in the solid and liquid states of cubic metals are therefore particularly valuable, since in these metals the melting-point changes may be rather precisely determined.

In addition to the magnetic interactions, some characteristics of the dynamic electric field gradients in the liquid may also be obtained for nuclei which possess electric quadrupole moments, since the quadrupolar interaction may make an observable contribution to spin-lattice relaxation. The experiments cited above show that these effects are quite important in the polyvalent liquid metals. They have not, however, appeared in the monovalent alkali metals.[4] This is presumably due to the smaller ionic charge and low degree of p character of the conduction-electron wave functions in the alkali metals. However, for reasons given below, a direct experimental determination of the quadrupolar spin-lattice relaxation contribution is possible in only one alkali metal (rubidium). It is thus of interest to

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